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THE CHEMICAL NEWS.

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LANDOLT'S EXPERIMENTS ON CHANGE OF WEIGHT IN CHEMICAL TRANSFORMATION.

By T. H. LABY.

Prof. Landolt has recently published (*Sits. d. K. Akad. d. Wissen.*, 1906, viii., 266, and Chemical News, xciii. p. 271 *et seq.*) the results of his further experiments on this subject. It will be sufficient to quote the following passage to indicate his experimental methods :—"The substances were introduced separately into the two limbs of a glass vessel shaped thus ∩; the open ends of the vessel were then fused up, two such pieces of apparatus (A and B), of almost equal weight and of the same external volume, being prepared and placed upon the two scale pans of the balance. The difference of weight of these two vessels was then determined—(1) in the original condition, (2) after the reaction had taken place in apparatus A, (3) after the reaction had taken place in B, by which each experiment was performed twice."

The results of these new experiments, omitting many details, are shown in the Tables (see next page).

It is proposed to show (1) that in the "blank" and "solution" experiments the change in weight is equally often a gain as it is a loss of weight, and so is accidental; (2) the change in the reaction experiments, except in one case, is always a loss, and to some extent is proportional to the reacting mass.

Landolt has given in Table IV. the results obtained when the contents of the vessels undergo *no* chemical change, and such alterations of weight as were observed would consequently be due to the weighing error and change of weight of the vessel itself due to handling, &c. From a consideration of Landolt's methods the observation of a loss or gain in these experiments appears equally likely, and so in a number of experiments these will tend to balance. This is fully borne out by combining these results, thus :—

Blank Experiments (*Table* IV.).

8 + experiments : total gain, +0·067 mgrm. ; average, +0·008 mgrm.

11 − experiments : total loss, −0·107 mgrm. ; average, −0·01 mgrm.

19 + and − experiments : total change, −0·040 mgrm. ; average, −0·002 mgrm.

(A + experiment is one in which there is a gain of weight ; a − experiment one in which there is a loss).

As these results afford a standard of comparison it is most important to notice that the conditions of the experiments from which they were obtained were exactly similar to those of the reaction experiments, except that the heat of reaction of the latter was absent. For in Experiments 8 to 19 of Table IV. "the apparatus in which a reaction had already taken place was used, and the previous operation was repeated with the then homogeneous mass contained in it. To replace the missing heat of reaction in several experiments (4, 5, 10, 11), the vessel was placed for some time in an air-bath heated to 30—40°." In Table IV. it is seen that the observed changes in these experiments were :—Experiment 4, +0·002 mgrm. ; Experiment 5, −0·007 mgrm. ; Experiment 10, +0·015 mgrm. ; Experiment 11, −0·010 mgrm. ; or the average change was ± 0·000 mgrm. The importance of these four results will be referred to shortly.

Combining the solution experiments of Table IX. we get :—

Solution Experiments (*Table* IX.).

6 + experiments : with total gain +0·136 mgrm. ; average, +0·023 mgrm.

7 − experiments : with total loss −0·119 mgrm. ; average, −0·017 mgrm.

13 + and − experiments : with total change +0·017 mgrm. ; average, +0·001 mgrm.

Thus, under the conditions of Experiments IX. (a fall of temperature in 1 to 9 when AmCl dissolved in water)—conditions which are, excepting in the sign of the temperature change, exactly similar to the conditions of the reaction experiments of Tables V., VI., VII., VIII.—Landolt obtained + and − changes which balanced better than in the blank experiments of Table IV. Or in 32 (19+13) of his experiments the total losses and gains of weight were very nearly equal as seen in this table.

Blank and Solution Experiments Tables IV. *and* IX. *combined.*

14 + experiments : total gain, +0·203 mgrm. ; average, +0·014 mgrm.

18 − experiments : total loss, −0·226 mgrm. ; average, −0·012 mgrm.

32 + and − experiments : total change, −0·023 mgrm. ; average, −0·0007 mgrm.

In thirty-two experiments, then, there is a complete absence of a systematic error of one sign ; such errors as exist are of purely chance nature, and the losses and gains of weight equalise.

If there be no change of weight in the reaction experiments, cannot similar results to the above be expected for them ? The only want of similarity between the two is the absence in the blank and solution observations of the rise of temperature occurring in the reaction ones.

Blank Experiments (*Table* IV.).

No.	Contents of vessel.	Observed alteration of weight. Mgrm.
1.	Water	−0·003
2.	„	+0·005
3.	„	+0·007
4.	„	+0·002
5.	Paraffin oil	−0·007
6.	Water	−0·008
7.	Mercury	−0·017
8.	I_2 and Na_2SO_4 solution	+0·014
9.	„ „	+0·012
10.	Cu and $FeSO_4$ solution	+0·015
11.	„ „	−0·010
12.	„ „	−0·023
13.	„ „	−0·024
14.	Ag and $Fe_2(SO_4)_3$ solution	−0·009
15.	„ „	+0·006
16.	„ „	−0·002
17.	„ „	−0·001
18.	$UO_2(NO_3)_2$ solution	+0·006
19.	„ „	−0·003

Reaction Experiments (*Tables* V., VI., VII., VIII.).

No.	Cu, Ag, or I_2 separated. Grms.	Observed alteration of weight. Mgrms.
	Table V.: $Ag_2SO_4 + 2FeSO_4 = 2Ag + Fe_2(SO_4)_3$ or $AgNO_3$ + &c.	
4.	31·2	−0·085
5.	24·2	−0·103
6.	24·2	−0·068
7.	24·2	−0·042
8.	24·2	−0·029
9.	63·5	−0·199
10.	63·5	−0·137
11.	63·5	−0·079
12.	16·5	+0·003
13.	16·5	−0·003
	Table VI.: $Fe + CuSO_4 = Cu + FeSO_4$.	
1.	17·0	−0·004
2.	17·0	−0·022
3.	17·0	−0·024
4.	17·0	−0·041
	Table VII.: $HIO_3 + 5HI = 6I + 3H_2O$.	
7.	43·3	−0·120
8.	43·3	−0·098
9.	64·9	−0·004
10.	64·9	−0·019
11.	64·9	−0·033
12.	54·0	−0·083
13.	54·0	−0·053
	Table VIII.: $2I + NaHSO_3 + H_2O = 2HI + NaHSO_4$.	
5.	50	−0·021
6.	80	−0·034

Solution Experiments (*Table* IX.).

No.	Salt. Grms.	Observed alteration of weight. Mgrms.
1.	37·5	−0·024
2.	37·5	−0·002
3.	23·7	+0·008
4.	23·7	+0·005
5.	44·0	+0·078 ?
6.	44·0	+0·017
7.	60·0	−0·008
8.	60·0	+0·019
9.	51·0	−0·033
1.	72·5	−0·038
1.	136·0	+0·009
2.	136·0	−0·010
3.	136·0	−0·004

The results, however, of the reaction experiments are quite unlike the ones so far considered. Thus:—

$Ag_2SO_4 + 2FeSO_4$ = &c. (*Table* V.).

1 + experiment: gain, +0·003 mgrm.; average, +0·003 mgrm.

9 − experiments: total loss, −0·745 mgrm.; average, −0·083 mgrm.

$Fe + CuSO_4$ = &c. (*Table* VI.).

4 − experiments: total loss, −0·091 mgrm.; average, −0·023 mgrm.

$HIO_3 + 5HI$ = &c. (*Table* VII.).

7 − experiments: total loss, −0·410 mgrm.; average, −0·059 mgrm.

$2I + NaHSO_4 + H_2O$ = &c. (*Table* VIII.).

2 − experiments: total loss, −0·055 mgrm.; average, −0·027 mgrm.

Tables V., VI., VII., VIII.

1 + experiment: gain, +0·003 mgrm.; average, +0·003 mgrm.

22 − experiments: loss, −1·301 mgrms.; average, −0·059 mgrm.

23 + and − experiments: change, −1·298 mgrms.; average, −0·056 mgrm.

How is it that the average change of weight in these "reaction" experiments, −0·056 mgrm., is eighty times as great as in the "solution" and "blank" experiments, where it is −0·0007 mgrm.? Only two kinds of explanations appear open to us, namely, (1) the vessels changed in weight to about the same extent as in the thirty-two "blank" and "solution" experiments (average, −0·0007 mgrm.), and a loss of weight occurred in the weight of the reacting substances, which accounts for the observed change; (2) no loss of weight accompanied the chemical changes, but the heat of reaction caused the glass vessels to change in weight, and so the observed alteration arose. The whole question turns, then, on the effect of the heat of reaction on the weight of the vessels. Where Landolt heated the reaction vessels (blank Experiments 4, 5, 10, 11, Table IV.) to 30° or 40° C., as mentioned above, the total of the observed changes was ± 0·000 mgrm. Heydweiller also tried heating his vessels, and found "practically no alteration of weight could be proved." The little experimental evidence there is on the matter, then, is directly against a uniform loss of weight being caused by the rise of temperature due to the chemical reactions. And so explanation (2) would appear to fit the evidence better than (1).

The greatest difficulty, however, in accepting the observed alterations in weight of the reacting substances is (as Prof. Poynting indicated to me) the want of proportionality between the mass of the substances reacting and the observed change of weight. This is seen most in Experiments 9 and 11 of Table V., both in Thuringian glass:—(9) 63·5 grms. Ag separated, loss −0·199 mgrm.; (11) 63·5 grms. Ag separated, loss −0·079 mgrm.; while the total error of weighing, &c., if the same as that of the blank experiments, was not more than 0·015 mgrm. This want of proportionality is shown again in Experiments 7 and 9, Table VIII.

In the experiments of Table V., in which a silver salt was reduced to silver, the total silver separated in Experiments 4 to 13 was 351·5 grms. with a loss of weight of −0·745 + 0·003 = 0·742 mgrm.; or, per 100 grms. of silver precipitated, of −0·211 mgrm. This gives, assuming the loss of weight to be proportional to the Ag precipitated, the loss in each experiment in thousandths (0·001) of a mgrm., as shown under "calculated" in the table below. The results of the thirteen solution experiments (Table IX.) may be justly taken as showing that no change occurred in the weight of the contents of the vessel in those experiments, and such change as was observed was due, on this

view, to the errors of weighing, handling, &c. In the thirteen experiments, disregarding sign, the total observed change was 0·255 mgrm., or an average of 0·02 mgrm. The calculated losses are subject to this error of ± 20 thousandths of a mgrm.

Experiment.	Loss of weight. Observed.	Calculated.
4.	−85	−65 ± 20
5.	−103	−51 ± 20
6.	−68	−51 ± 20
7.	−42	−51 ± 20
8.	−29	−51 ± 20
9.	−199	−134 ± 20
10.	−137	−134 ± 20
11.	−79	−134 ± 20
12.	+3	−35 ± 20
13.	−3	−35 ± 20

The want of proportionality in this reaction is not so great as it at first sight appears.

On the evidence of Landolt's experiments it may be said that it is probable that a loss of weight accompanies certain chemical reactions, and that the explanation which Landolt seems to favour of a loss through the walls of the vessel is supported by the irregularity in its amount.

THE DETERMINATION OF MANGANESE IN IN WATER.

By ROBERT SPURR WESTON.

THE need for a convenient method of determining manganese in water has been recognised by many analysts. In the ordinary practice of the water analyst either the determination is made gravimetrically or it is omitted.

Manganese together with iron occurs in many ground waters, and very often its presence complicates or vitiates the processes used for the removal of iron from water supplies. At Breslau, in 1904, the sudden presence of manganese in the ground water made the supply useless for a time, notwithstanding the fact that the water was treated by aeration and filtration for the purpose of removing the iron from it.

Extremely valuable data are missing because of the inconveniences of the present time-consuming methods for the determination of manganese. Such data will be collected only if the methods be as facile as other methods used in water analysis. Waters rarely contain more than 10 milligrms. of manganese in a litre. Gravimetric methods are often beyond consideration, and the only ones which seem generally practicable are those in which the manganese is oxidised to permanganic acid. Of these latter the lead oxide methods of Chatard and others (Sutton's "Volumetric Analysis") and the sodium bismuthate method seemed to be the most promising. The sodium bismuthate method was used because of the greater ease with which the solution could be freed from the precipitate. This method has been used for the determination of manganese in ores and steels and is described by Blair (*Journ. Am. Chem. Soc.*, xxvi., 793). It was proposed by Schneider (*Dingler's Poly. Journ.*, cclxix., 224) and modified first by Reddrop and Ramage (*Journ. Chem. Soc.*, 1895, 268) and then by Brearley and Ibbotson ("The Analysis of Steel Works Materials").

The method is based upon the fact that in the presence of an excess of nitric acid a manganous salt is oxidised to permanganic acid by bismuth tetroxide. Blair states that:—

"The permanganic acid formed is very stable in nitric acid of 1·135 sp. gr. when the solution is cold, but in hot solutions the excess of bismuth tetroxide is rapidly decomposed, and then the nitric acid reacts with the permanganic acid, and as soon as a small amount of manganous salt is formed the remainder of the permanganic acid is decomposed, manganous nitrate dissolves, and manganese dioxide precipitates."

Reddrop and Ramage showed that it was difficult to get bismuth tetroxide free from chlorides, the presence of which would vitiate results, so they proposed the use of sodium bismuthate.

The manganese in the permanganic acid produced by oxidation may be determined in two ways. After filtering off the excess of bismuthate Blair adds an excess of ferrous sulphate to the filtrate, and by titration with permanganate solution determines the amount necessary to deoxidise the permanganic acid. For waters containing less than 1 mgrm. of manganese, however, comparison of the filtrate colorimetrically with permanganate run from a burette into an equal volume of dilute sulphuric acid free from organic matter contained in a Nessler tube, proved to be simpler and more precise; for larger quantities, however, the titration method should be used.

Method.

Evaporate with about 25 cc. of nitric acid (sp. gr. 1·135) enough of the sample of water to give from 0·01 to 1 mgrm. of manganese. Gently ignite the residue or bake it for half-an-hour at 130°. Add 50 cc. of nitric acid (sp. gr. 1·135) and when the solution is cool add about 0·5 grm. of sodium bismuthate. Heat until the pink colour disappears.

At this point Blair, in his determination of manganese in iron, adds sulphurous acid, ferrous sulphate, or sodium thiosulphate, to clear the solution if manganese dioxide is precipitated, and heats it to dispel all oxides of nitrogen. With waters this step was usually unnecessary, but whenever so, thiosulphate was the reagent used.

To the cool solution add sodium bismuthate in excess, stir a few minutes, and filter through thoroughly washed asbestos in a Gooch filter. Wash with dilute nitric acid, transfer filtrate to a large Nessler tube, and make up to 100 cc. with dilute nitric acid.

In another tube put 100 cc. of dilute sulphuric acid and add standard potassium permanganate solution until the colour of the sample is matched. The volume of potassium permanganate in cc. × 0·0001 gives the weight of manganese in grms. Express results as parts per million, —mgrms. per litre.

Reagents.

Potassium Permanganate Solution.—Dissolve 0·288 grm. of potassium permanganate in water and make up to 1 litre. 1 cc. is equivalent to 0·1 mgrm. manganese.

Nitric Acid (sp. gr. 1·135).—A mixture of three parts of water and one part of strong nitric acid (sp. gr. 1·42) is used.

Dilute Nitric Acid.—30 cc. of strong nitric acid to the litre.

Sulphuric Acid.—25 cc. of pure concentrated sulphuric acid to the litre. Add enough permanganate to colour the solution slightly but perceptibly pink.

Asbestos.—Prepare asbestos in the usual way by washing with acid and igniting. It should be free from organic matter.

Notes and Precautions.

The first experiments with this method gave unsatisfactory, erroneous results. Each reagent was tested to ascertain the cause of the error. It was found that the "C.P." nitric acid used was impure; it contained oxides of nitrogen. Several methods of purification were tried. The most efficient process proved to be that of passing a current of air through the concentrated acid for about half an-hour.

The presence of organic matter also vitiates results; when in large amounts the colour of permanganic acid does not appear in the filtrate. This difficulty is overcome by ignition of the residue or by baking it for half an-hour at 130°. The asbestos must be free from organic matter; otherwise the permanganic acid will be reduced.

The presence of chlorides also interferes with the determination. Samples which contain large amounts of chlorine should be treated before evaporation with a slight excess of silver nitrate and then filtered.

Experiments were made in which the bismuthate was added but once, the excess filtered off immediately, and the permanganic acid determined. Satisfactory results, however, were not obtained by this shorter method. The oxidation is complete only after the second addition of bismuthate.

The method is very delicate. It will detect 0·00002 grm. of manganese.

Experiments.

The first experiments were made with distilled water and known solutions of manganese sulphate and potassium permanganate. The results were as follows :—

No.	Manganese added. Grm.	Manganese recovered. Grm.
	A. *With Manganese Sulphate.*	
1.	0·00010	0·00009
2.	0·00010	0·00010
3.	0·00010	0·00010
4.	0·00050	0·00050
	B. *With Potassium Permanganate.*	
1.	0·00010	0·000095
2.	0·00020	0·00020
3.	0·00050	0·00045

C. Effect of Organic Matter.—Experiments were made like the above, except with the addition of varying volumes of leaf infusion, this being considered typical of the organic matter contained in water. The results were as follows :—

No.	Manganese added. Grm.	Leaf infusion. Cc.	Manganese recovered. Grm.
	(a) *Without Ignition of Residue.*		
1.	0·00010	1	0·00010
2.	0·00010	2	0·00008
3.	0·00010	10	0·00007
4.	0·00010	25	Colour faded in five minutes.
	(b) *Residue Ignited.*		
1.	0·00010	25	0·00010
2.	0·00010	25	0·00010

D.—Two trials of the method were made, first with Boston water, a surface supply, and second with Reading water, a ground water supply containing about two parts per million of iron. The Boston water contains no appreciable amount of manganese, but manganese is present in the Reading water. Besides determining the manganese in the water, determinations were made with the water containing varying amounts of added manganese.

No.	Taken. Cc.	Manganese added. Grm.	Manganese recovered. Grm.
	(a) *Boston Water.*		
1.	100	—	—
2.	100	0·00010	0·00009
3.	100	0·00010	0·00010
4.	1000	0·00010	0·00009
	(b) *Reading Water.*		
1.	100	—	0·000065
2.	100	—	0·000070
3.	100	—	0·000075
4.	100	0·00010	0·000170
5.	100	0·00010	0·000170
6.	100	0·00010	0·000165

E.—The following experiment shows the effect upon the determination of large amounts of chlorine.

No.	Boston City water. Cc.	Chlorine added to a litre. Mgrms.	Manganese added. Grm.	Manganese recovered. Grm.
1.	1000	50	0·00010	0·000085
2.	1000	500	0·00010	0·000075
3.	100	50	0·00010	0·000079
4.	100	500	0·00010	0·000080
5.	100 (*a*)	500	0·00010	0·000080

(*a*) Boston water contains about 2·5 parts of chlorine per million.

The writer finds this method rapid, convenient, serviceable, and reasonably accurate. He recommends it to other analysts with the hope that more data regarding the manganese content of ground waters may be placed on record.

He also wishes to thank his friend, Professor Henry Fay, for fundamental suggestions, and to acknowledge the services of his assistant, Miss Grace Ide Fairchild, who has made most of the determinations.—*Journal of the American Chemical Society*, xxix., No. 7.

STUDIES ON CHARCOAL AND LIQUID AIR.*

By Prof. Sir JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S., Fullerian Professor of Chemistry, R.I.

THE object of the lecture was to demonstrate experimentally a few novel applications of liquid air observed in the course of laboratory experiments. Some of them may be said to take the character of lecture illustrations, while others deal with an extension of the scientific uses of charcoal at low temperatures, a subject which was first discussed in a Friday Evening Discourse delivered by the Professor in the year 1896.

Electrical Stimulation at Low Temperatures.

Bodies cooled to the temperature of liquid air have the surface film of water, which is more or less deposited on them, frozen exceptionally hard, and therefore not in a good condition for the dissipation of any electric charge that may be given to them. The result is that a substance like glass cooled in liquid air is exceedingly easily electrified by friction, and retains its charge for a long time. This property of glass was shown in the following manner :—

A glass tube shaped like a two-pronged fork was arranged so that a magnified image of it could be projected on a screen. (See Fig. 1). The prongs were

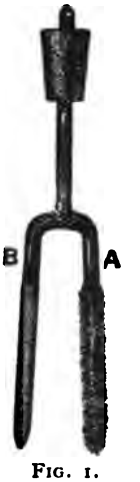


FIG. 1.

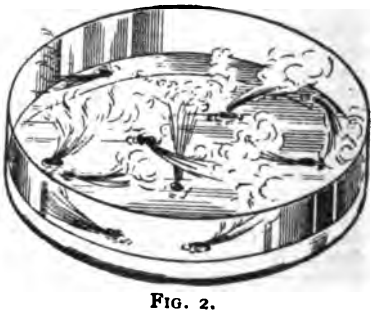


FIG. 2.

cooled in liquid air, and one prong, A, while it was being removed from the liquid air, was gently flicked with flannel

* A Discourse delivered at the Royal Institution, June 8, 1906.

or silk to electrify it. On being exposed to the air the moisture in the atmosphere was deposited as ice on both prongs, but the character of the deposit was different on the unelectrified and the electrified prong, crystals of ice beginning to form on the latter, speedily causing it to assume the appearance of a miniature forest of growing and moving crystals shown on A in Fig. 1, while B shows simply a dead coating of ice. The electrified prong by induction attracts the moisture in the air, and as fresh moisture is drawn in repulsion between like electricities causes the new crystals to be deposited as far out as possible, thus presenting the appearance in the diagram. With good projection one can see some of the crystals on A repelled and shot across to B. A similar experiment of another kind is the facility with which an electrified glass rod clears up ordinary opalescent liquid air by attaching the finely suspended impurities of ice crystals, solid carbonic acid, and organic matter to its surface when moved about in the liquid. The same thing may also be done by moving about a crystal of nitrate of uranium, which by cooling becomes highly electrified without the need of direct friction as when glass is used.

The Spheroidal State of Liquid Air on the Surface of Liquids.

As volatility depends on vapour pressure, of two liquids that having the higher vapour pressure at any given temperature is necessarily the more volatile. The difference in the facility of condensation of the vapours produced by different liquids may easily be demonstrated by the use of liquid air.

A series of liquids with different boiling-points, like tetrachloride of carbon, water, caustic potash solution, benzoic ether, and strong sulphuric acid, were selected, and each placed to the depth of about an inch in a number of shallow cylindrical cups, as shown in Fig. 2, the surfaces of which could in succession be projected on a screen by means of a horizontal lantern.

On allowing drops of liquid air to fall on the surfaces of these liquids, best by filtration through a small filter-paper funnel, they immediately assume the spheroidal state, and the projection through the liquid showed they were moving about with considerable rapidity, impinging on the sides of the vessel, and getting deflected like an elastic body, while followed by clouds of condensed vapour, the relative amount of which may be taken as roughly proportional to the volatility of the liquid. With water the cloud was very dense, being less so in the case of the alkali solution, more so for the tetrachloride of carbon, and least for sulphuric acid. On the sulphuric acid the drops moved about slowly owing to the high viscosity of the liquid, but with hardly any cloud, while on the surface of benzoic ester, a lively agitation accompanied by a light cloud was observed. In the case of the tetrachloride of carbon, the effect was most striking; dense clouds swayed to and fro over the surface, and the drops of liquid air shot to the walls of the vessel at all angles of incidence, and rebounded, followed by tails of vapour, making them look like miniature comets. In order to secure a good view of the movements, it is necessary occasionally to blow the fume away from the upper part of the vessel by a current of dry air. Care must be taken to avoid the fall of too much liquid air in one place, which would cause a rapid local cooling of the liquid attended with solidification, which inevitably arrests all spheroidal motion. This may be prevented to a great extent by having the liquids in the vessels used for projection slightly heated before the experiments are begun.

Thermal Conductivity.

Going to another subject, the well-known experiment of Ingenhousz on the relative conductivities of metals may be repeated at low temperatures by means of liquid air.

A vacuum-jacketed cup V (see Fig. 3) is filled with liquid air and covered with a sheet of mica (A B), having a set of small holes in it, through which a series of equal wires of different metals (copper, brass, bismuth, &c.) are fixed. After immersing their lower ends in the liquid air a coating of frozen moisture is deposited from the surrounding atmosphere, and is seen to collect round the lower parts of the wires above the mica screen, ultimately forming definite heights of an ice cap on each wire according to their conductivities. As in the Ingenhousz experiment, the relative conductivities are proportional to the squares of the heights to which the ice ultimately rises on the wires above the level of the mica sheet. In this manner it is possible to determine rapidly conductivities at low temperatures. The following table gives some rough measurements made in this way :—

	Height of ice in mm.	Conductivities (copper being taken as 1).
Bismuth	10	0·005
Fusible metal	27	0·035
Lead	38	0·069
German silver	40	0·076
Tin	54	0·139
Steel	57	0·155
Iron	62	0·183
Brass	65	0·201
Copper	145	1·000

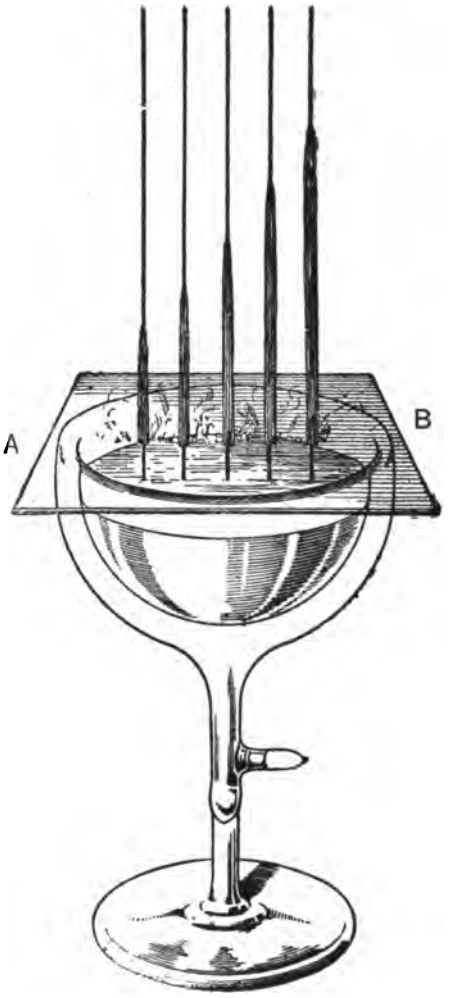


FIG. 3.

A similar method might be employed to determine conductivities at temperatures lower than the melting-point of

ice; for instance, the experiment might be made in a dry hydrogen atmosphere containing a small amount of sulphurous acid, continuously renewed, in which case the relative conductivities would be found from the melting-point of sulphurous acid instead of from that of ice.

Gas Absorption by Charcoal at Low Temperatures.

Some of the more important facts regarding the absorption of gases by charcoal at low temperatures were detailed in the Address given in 1905, entitled "New Low Temperature Phenomena," and to those a few additions were made due to further experience. Other porous materials are found to possess the power of absorption for gases at low temperatures to a less extent. Thus, dry aluminium oxide shows a remarkable power of absorbing air just like charcoal, 1 grm. condensing at atmospheric pressure some 70 cc., and the same property is possessed by meerschaum and silica. The retentive power of alumina is much inferior, however, to that of charcoal, and consequently is of no use in forming high vacua. All charcoals possess the property of gas absorption at low temperatures. Light charcoal, such as is used in the manufacture of gunpowder, or the variety got from animal substances like blood, both act, but experiments made at the Royal Institution show that charcoal prepared by careful carbonisation from cocoanut is one of the most convenient varieties to use. While using the same process of carbonisation, the absorptive effect is enhanced by making it take place slowly and with gradually increasing temperature. With the samples made a year ago, it was possible to get an absorption of about 150 cc. of air per grm. of charcoal at -185° C., but with care the amount can be raised to as much as 350 to 400 cc. per grm.

The amount absorbed at atmospheric pressure and at the temperature of liquid air can be quickly determined. A grm. of charcoal, previously heated to a red heat, is placed in a glass bulb connected by an indiarubber tube and stopcock to a graduated vessel containing air kept over strong sulphuric acid or a high boiling-point oil, so that on cooling the charcoal and opening the stopcock the absorption is measured. This absorptive power can be shown by means of the balance and the electro-magnet. From one arm of a balance was suspended a copper-wire gauze sphere containing charcoal which was carefully counterpoised. A flask partly filled with liquid air was now brought up below it, so that the vapour rising from the liquid air surrounded the charcoal. The absorption soon became visible through the beam of the balance descending as the charcoal became charged, and by adding weights the amount of gas absorbed per unit of time could be determined. If a rod of charcoal was hung up by a thread between the poles of an electro-magnet and sufficient torsion applied, so that its length was at right angles to the line joining the poles, when the magnetic field was produced, on bringing a vessel of liquid air close below it after a short time on turning on the electric current to "make" the magnet, the rod now set itself along the line joining the poles, proving that it had become magnetic. This action is dependent on the well-known magnetic property of oxygen, one of the constituents of the air, which surrounded the charcoal rod and which had condensed within its pores. On taking away the cool vapour of the liquid air the temperature soon rose, and the behaviour of the rod under magnetic action showed that it had lost the magnetic property.

Effect of Increased Pressure of Gas on the Absorption of Charcoal at Low Temperatures.

The absorption of hydrogen by charcoal at the temperature of liquid air and under atmospheric pressure is very considerable, and the question arises how much more could be got in by the use of higher pressure. The amounts absorbed by 6·7 grms. of charcoal, at the temperature -185° C. for various pressures, are given in the following table:—

Pressure in atmospheres.	Volume in cc.
1	620
5	925
10	1050
15	1000
20	975
25	925

The amount absorbed is seen to increase with the pressure to 10 atmospheres, after which the absorption in the pores of the charcoal seems to be independent of the pressure. At the temperature of liquid air this sample of charcoal would not absorb more than 1 litre of hydrogen, even when the pressure was raised from 10 to 25 atmospheres or the absorption had come to a limit. Increased absorption, which does not reach more than twice that at the ordinary atmospheric pressure, is the sole result of the use of higher pressures.

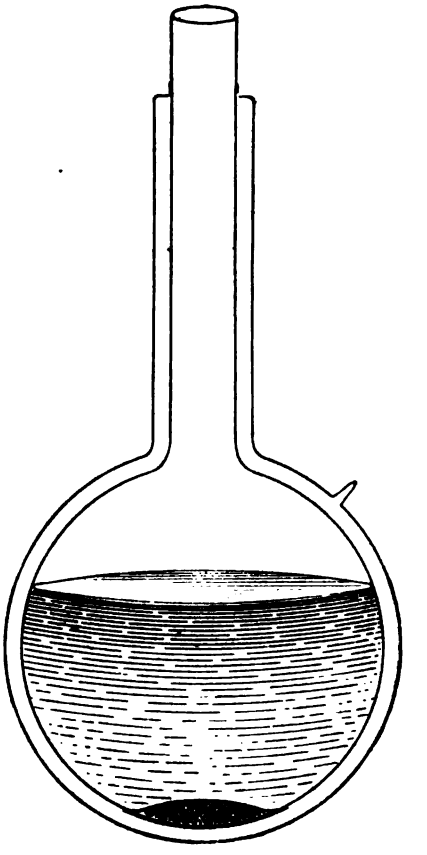


FIG. 4.

Vacua produced by Charcoal under different Circumstances.

The absorptive power of charcoal for air is very remarkable. On stopping the passage of a stream of air into a charcoal bulb immersed in liquid air, to which a small manometer was attached, hardly any gas pressure was shown. This was further exemplified by the action of a Röntgen tube, partially exhausted, connected to a charcoal bulb. On immersing the bulb in liquid air the characteristic phosphorescent glow of the Röntgen tube was soon reached, but disappeared when the liquid air was removed. When hydrogen was used instead of liquid air, the pressure was so much reduced that the glow was entirely stopped. A Crookes's radiometer, filled with hydrogen at atmospheric pressure, had a charcoal bulb attached. On immersing the

charcoal bulb in liquid air no rotation took place, even when the beam of an electric lamp was thrown upon it; but when liquid hydrogen replaced the liquid air the motion became exceedingly rapid. This shows that high vacua can be attained by the use of charcoal in an atmosphere of pure hydrogen, provided it is cooled in a liquid hydrogen bath instead of liquid air. A similar radiometer, filled with helium at atmospheric pressure, remains inactive even when liquid hydrogen is the cooling agent, thus proving that the absorption of the helium by charcoal at 20° abs. is relatively inefficient for the production of vacua as compared with hydrogen. This is only another mode of proving the much greater volatility of helium over hydrogen.

Laws of Absorption at Low Temperatures.

The general laws of the dependence of the absorptive power of charcoal upon the pressure, temperature, and volume of the gas absorbed are apparently complicated, but in average circumstances they can be stated approximately. For a supply of gas at constant pressure the volume and temperature are related by a curve of hyperbolic form. There must clearly be a lower limit of temperature for absorption, for the gas will eventually liquefy; on the other hand, however small the absorption may be, as the temperature rises it can never entirely vanish. If the temperature be kept constant we should expect an increased absorption with increasing pressure up to a certain limit. Experiment indicates that this is the case, and we have again a curve of hyperbolic form connecting pressure and volume, but differing from the previous case in having the convexity turned the opposite way. When the pressure is small the absorption will be a minimum, but any slight increase of pressure will be associated with the molecular attraction of the charcoal, and the absorption may be expected to increase much more rapidly in proportion to the pressure. Finally, when the volume absorbed is kept constant the relation between the pressure and the temperature is of a logarithmic form, like those of a saturated vapour or a dissociating body.

For the absorption of hydrogen in charcoal at the temperature of liquid air the expression $\log p = a + bV - c V^4$ holds, where p is pressure, V the volume of gas occluded, and a, b, and c constants. For small concentrations of gas the pressure grows in a linear relation to the volume.

Hypothetical Densities of Gases Occluded in Charcoal.

Mitscherlich's measurements made on the charcoals used by him showed that in a piece of charcoal the space occupied by charcoal-substance is to the pore-space nearly in the ratio of 13 to 20. The Professor's observations on the real and apparent densities of cocoanut charcoal lead to the conclusion that in 100 grms. the pore-space may be taken on the average as about 15 cc. This enables us to compare the average hypothetical density of any absorbed gas with the density of the same gas when liquefied. The following table shows some such comparisons, and it may be noted that the densities of the absorbed gases at their boiling-points are equal to or a little greater than the corresponding liquefied gases at the same temperatures, so far as they are known. Whether the density of the monadic gases will turn out as satisfactory is a matter for future inquiry.

Gas.	Temperature of absorption. Cent.	Abs.	Density of gas occluded in charcoal.	Density of gas liquefied
Carbonic acid .	+15°	288°	0·7	0·8
Oxygen	−183°	90°	1·33	1·12
Nitrogen ..	−193°	80°	1·00	0·84
Elecrolytic gas	—	—	0·58	?
Hydrogen ..	−193°	80°	0·06	0·07
„ ..	−210°	63°	0·08	—
„ ..	−252°	21°	0·11	—
Helium	−258°	15°	0·17	?

Metallic Vacuum Vessels.

With the aid of charcoal, it is easy to make useful vacuum vessels of metal instead of glass. The metallic vessels resemble the ordinary glass silvered vessels, and are of from 2 to 10 litres capacity (see Fig. 4). The envelopes may be made of brass, copper, nickel, or tinned iron, with necks made of a bad conducting alloy. The vacuum between the walls of these vessels was maintained by enclosing some charcoal in a small globular space, A, constituting part of the inner vessel that is filled with liquid air. The necks may be covered with silvered glass vacuum cylinders which act as stoppers, and at the same time utilise the cold of the slowly evaporating liquid. The efficiency of the best metallic flasks is equal to that of the chemically silvered glass vacuum vessels, now generally used in low temperature investigation. Vessels of this type will be of use in industrial cryogenic operations and for the storage and safe transit of liquid air.

Diffusion of Gases into Charcoal at Low Temperatures.

Although, as regards general absorption, charcoal under corresponding conditions behaves in a similar manner to all gases, nevertheless it possesses a certain selective power, when in presence of a mixture of gases. A quantity of charcoal which has been heated, exhausted, and then saturated with ordinary air at −185° C., must have gases occluded in its pores of the average composition of the air. Let, however, a stream of air at the same low temperature pass slowly and continuously over it for some hours, and it will be found that at first the issuing gas is almost pure nitrogen, while the occluded gas reaches a new and definite composition. If now the gas absorbed by the charcoal be expelled by heating it to the ordinary temperature, it will contain on the average some 60 per cent of oxygen. Fig. 5

FIG. 5.

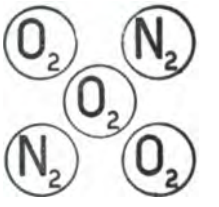


FIG. 6.

represents roughly the molecular composition of the air initially present in the pores of the charcoal, namely, about four molecules of nitrogen to one of oxygen. The final average molecular composition of the absorbed gas after the passing of the slow current of air, cooled to −185° C., over the charcoal is similarly represented in Fig. 6, where it can be seen that diffusion, or fractional distillation at constant temperature, has gone on until about two of the molecules of nitrogen have been replaced by two of oxygen. If the charcoal, in equilibrium with air gases in the condition specified in Fig. 6, has a current of hydrogen at the temperature of liquid air passed over it, the hydrogen will diffuse in, until about one molecule in five is present, as shown in Fig. 7. Again, if charcoal be

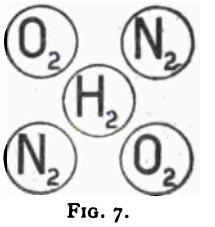


FIG. 7.

saturated with oxygen to begin with, and hydrogen be passed over it when cooled to −185° C., the hydrogen will

diffuse in, until it constitutes one-third of the gas present in the pores (Figs. 8 and 9). Similarly, if we employ

FIG. 8.

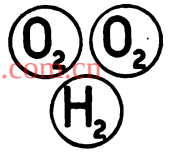


FIG. 9.

nitrogen in place of oxygen, the hydrogen will displace about two-thirds of the nitrogen (Figs. 10 and 11). On the

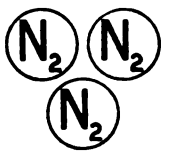


FIG. 10.

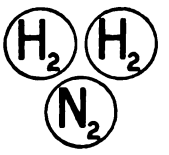


FIG. 11.

other hand, if the charcoal be initially saturated with hydrogen at -185° C. (Fig. 12), and air passed over it at that temperature, the whole of the hydrogen is practically displaced, and the gas remaining in the charcoal is represented by the composition shown in Fig. 13, which is the same as in Fig. 6.

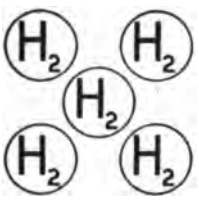


FIG. 12.

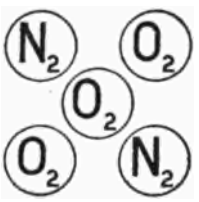


FIG. 13.

If, instead of analysing the whole of the occluded gas that is given off, samples are taken from the charcoal between definite temperatures, from the boiling-point of air up to the ordinary temperature, then a regular fractionation of the occluded gases takes place, resembling that of an ordinary mixed liquid, and the problem is an entirely different one. Further, even in the simpler mode of treatment as described above, the relative proportions of the absorbed gases depends at any time after the experiment has started upon the relation between the current of gas used at the constant temperature of -185° C. and the nature and condition of the charcoal. The simplification of the problem is due to making the time very long.

(To be continued).

Metacetaldehyde.—A. Hantzsch and J. Oechslin.—By determining the molecular weight of both freshly prepared and old specimens of pure metacetaldehyde, the authors have shown that this compound exists in only one form. It is quite stable when pure, and dissolves in phenol solutions without undergoing any change. It is not tri-molecular in phenol solution, but undoubtedly tetra-molecular, $(C_2H_4O)_4$; and in thymol solution it is most probably hexamolecular, $(C_2H_4O)_6$. It is undoubtedly not an isomer of paraldehyde, but a polymer of higher molecular weight. As its molecular weight varies from $(C_2H_4O)_6$ to $(C_2H_4O)_4$, according to the phenol used as solvent, it is probable that in the solid state it is a high polymer of diacetaldehyde, $(C_2H_4O)_{2n}$, which depolymerises more or less according to the nature of the medium. This agrees with the fact that metaldehyde is much more easily totally depolymerised than paraldehyde. —*Berichte*, xl., No. 15.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 19th, 1907.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

THE President referred to the death of Lord Kelvin, and stated that the Society would be represented at his funeral.

It was also announced that the Society had lost through death Mr. Samuel Hall, and Prof. B. J. Harrington, of McGill University, Montreal.

Messrs. P. V. Dupré, G. H. Martin, C. P. Matthews, W. S. Mills, M. Wechlser, E. Wheeler, and R. Whymper were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Guy Barr, B.A., B.Sc., 79, Fillebrook Road, Leytonstone, N.E.; Walter Brown, jun., Brookvale, Strathaven, N.B.; David Cowan Crichton, M.A., B.Sc., A.I.C., Backhill House, Musselburgh; Andrew L. Scott, F.I.C., Fir Lodge, Cheshunt, Herts; John Armstrong Smythe, 15, The Poplars, Gosforth, Newcastle-on-Tyne; Charles Sedgley Spiers, The Woodlands, Scalford Road, Melton Mowbray; John Watson, B.Sc., 5, Kendrew Street, Darlington; William Henry Withey, B.A., Stroud, Glos.; Joseph Yates, 18, Park Street, Haslingden, Lancs.

Certificates have been authorised by the Council under By-law I. (3) in favour of the following:—Puran Singh, Dehra Dun, India; Archibald Edgar Collens, Government Laboratory, Port of Spain, Trinidad.

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

*254. "*Attempted Synthesis of* β—N—β / β—CHβ *-Dinaphthacridine; Condensation of Methylene Dichloride and 1-Substituted-2-naphthylamines.*" By ALFRED SENIER and PERCY CORLETT AUSTIN.

In attempting to synthesise derivatives of the unknown β—N—β / β—CHβ -dinaphthacridine (compare Senier and Austin, *Trans.*, 1906, lxxxix., 1387) by condensing methylene dichloride with derivatives of β-naphthylamine in which the hydrogen of the α-position adjacent to the amino-group had been substituted, the authors have found that when the substituent was a halogen, either Reed's dinaphthacridine or a meso-derivative thereof was formed, thus completing the proof that this base has the constitution assigned to it. In the case of 1-nitro-2-naphthylamine, no acridine was obtained.

1-Chloro-2-naphthylamine reacts with methylene dichloride to form β—N—β / α—CHα -dinaphthacridine. 1-Bromo-2-naphthylamine and methylene dichloride yield *7-bromo-*β—N—β / α—CHα *-dinaphthacridine*, which crystallises from benzene in yellow needles, melting at 215·5° (corr.). Its solutions are fluorescent, and it differs from the halides of the dinaphthacridines (Senier and Austin, *Trans.*, 1904, lxxxv., 1196), as it may be boiled with potassium hydroxide solution, and even distilled under reduced pressure, without decomposition.

The *hydrochloride*, *aurichloride*, and *platinichloride* are yellow powders.

With glacial acetic acid, the base forms a deep yellow crystalline *compound*, melting at 273°. Reduction with stannous chloride leads to the production of bis-β—N—β / α—CHα dinaphthacridine dihydride.

*255. "*Cobaltamine Compounds.*" (Preliminary Note). By CHARLES EDWARD GROVES.

During the past few years, the author has investigated some of the cobaltamine compounds, and owing to the recent appearance of papers on the subject, he considers it advisable to publish a preliminary account of some of the results obtained.

Crimson Carbonate.—When freshly-precipitated cobalt carbonate, suspended in dilute ammonia, is agitated with air and then exposed to the air for three or four days, the solution becomes brownish red, and deposits bright crimson crystals. These can be purified by recrystallisation from water at about 45°, or, better, from a very dilute solution of ammonium bicarbonate. The carbonate is readily decomposed by acids with evolution of carbon dioxide, and formation of the corresponding salts. It is almost insoluble in cold water, but on heating gently (45°) the crystals dissolve; at a higher temperature, the solution becomes brown and turbid. The substance is practically insoluble in dilute ammonia in the cold, and very little dissolves even on heating. It is almost insoluble in dilute alcohol even on boiling. The author purposes, provisionally, calling this compound *carycinocobaltamine carbonate* (καρύκινος, blood-red).

Blue-black Compound.—This is formed when the crimson carbonate is treated with nitro-hydrochloric acid. On gradually adding the latter to the carbonate under water, it dissolves with effervescence, but on adding more of the acid a red crystalline precipitate is produced, which if left in the liquid for a day or more is converted into the "bluish black" crystals. This compound dissolves readily in concentrated ammonia, forming a rose-coloured liquid. When boiled with hydrochloric acid, it is, apparently, completely converted into the purpureo chloride. In an aqueous solution of ammonium bicarbonate, it dissolves to a purple liquid.

Bronze-green Chloride and the corresponding *Nitrate.*—Of these two salts, the nitrate is the more readily prepared, and it can be easily converted into the chloride, which is bronze-green, the colour of the nitrate being greyish-green. The nitrate is most easily prepared by gradually adding a solution of cobalt nitrate in dilute nitric acid, in the proper proportion, to a mixture of dilute ammonia with a solution of ammonium persulphate contained in a large flask, and, after it is thoroughly oxidised by shaking it with air, acidifying the mixture with dilute nitric acid.

This nitrate is almost insoluble in water, but dilute ammonia dissolves it readily, forming a pink solution, and it is also soluble in ammonium bicarbonate solution. It is neither altered nor dissolved by nitric acid, whether concentrated or dilute, and it is also insoluble in boiling acetic acid, but on adding concentrated hydrochloric acid to the mixture it dissolves at once.

The hydrochloride is easily obtained from the nitrate by heating the latter with dilute hydrochloric acid (1 : 2) at 70° for twenty to twenty-five minutes. It can easily be recrystallised from hot very dilute hydrochloric acid, when it separates in long, bronze-green needles. The purified hydrochloride dissolves in cold water, forming a deep blue liquid, but this soon decomposes, especially when warmed, depositing a brown powder, apparently cobaltous-cobaltic oxide.

Grass-green Compound.—If purpureo-cobaltic chloride (or nitrate) is heated for some hours with dilute ammonia, or, better, ammonium carbonate solution, it dissolves, and the dark red solution containing roseo-cobaltic salt, if kept for some time, deposits a crystalline mass consisting of minute pink needles. After these have been separated, concentrated nitric acid is added to the mother-liquor, the brick-red precipitate thus formed is removed by filtration, and a slow current of crude nitrosyl chloride passed into the purple-red filtrate. This after twenty-four hours deposits a mixture of red and green crystals. These can be separated by washing with water, which easily dissolves the red crystals, leaving the grass-green compound, which is comparatively insoluble in water.

This green salt is only sparingly soluble in water and in dilute ammonium bicarbonate solution, and is practically insoluble in alcohol and dilute acids. When boiled with dilute hydrochloric acid, it appears to be converted into the purpureo-chloride.

*256. "*The Direct Interaction of Aryl Halides and Magnesium.*" By JAMES FREDERICK SPENCER and ELEANOR MARGUERITE STOKES.

The authors find that cyclic halogen compounds react with magnesium powder without the use of ether when the two substances are heated together. The products, which are of the type R·MgX, are light grey solids, and are readily decomposed by water with considerable evolution of heat and production of the hydrocarbon: $R{\cdot}MgI + H_2O = R{\cdot}H + Mg(OH)I$.

Iodo- and bromo-benzene yielded benzene and diphenyl; *p*-iodo- and *o*-bromo-toluene gave toluene; *m*-bromo- and *o*-chloro-aniline gave aniline; *p*-bromo-phenol yielded phenol, and α-bromonaphthalene and bromoacenaphthene gave the respective hydrocarbons. The yields in all these cases were extremely good. Chloro-substitution products do not react generally in this way. In the case of aliphatic compounds, methyl iodide, methylene iodide, and *iso*propyl iodide were indifferent, but bromosuccinic acid gave succinic acid.

DISCUSSION.

Dr. MCKENZIE pointed out the interest of the observations of the authors in connection with Tschelinzeff's results with the "individual" magnesium compounds of the type R·MgX, obtained by the interaction of magnesium and halogen compounds in benzene solution with the use of dimethylaniline as catalyst.

In view of the results of Schroeter (*Ber.*, 1903, xxxvi., 3005) on the action of carbon dioxide on magnesium phenyl bromide, Dr. McKenzie asked if the formation either of triphenylcarbinol or benzophenone had been noted by the authors in the experiment on the formation of benzoic acid described by them.

Dr. SPENCER replied that, owing to the large yields obtained, triphenylcarbinol and benzophenone had not been looked for, and their formation could only take place to a small extent, if at all.

257. "*Derivatives of Tetramethyl Glucose.*" By JAMES COLQUHOUN IRVINE and AGNES MARION MOODIE.

Tetramethyl glucoseoxime, which was obtained as a mixture of α- and β-forms melting at 61—68°, shows in methyl-alcoholic solution a specific rotation of +25·9° without mutarotation. The constitution of the compound, deduced from its behaviour on alkylation and the hydrolysis of the product, shows that it does not possess the normal oxime structure, but is produced by the reaction of the sugar in its γ-oxidic forms. Similar arguments point to the fact that tetramethyl glucoseanilide also possesses the γ-oxidic linking, and is not derived from an alkyloxyaldehyde. The compound melted at 132—134°, and gave $[\alpha]_D$ 20 +229·5° in acetone solution.

Tetramethyl chloroglucose and *tetramethyl bromoglucose* were obtained as uncrystallisable syrups, which, in their reactions, closely resemble the corresponding tetra-acetyl compounds. As they were readily converted into a mixture of α- and β-tetramethyl methylglucosides when treated with methyl alcohol and silver oxide, the preparations doubtless consisted of mixtures of α- and β-forms.

Negative results were obtained in attempts to produce acetal derivatives of tetramethyl glucose, and the application of the Grignard reaction also led to no result.

With one doubtful exception, all the derivatives studied indicate that the alkylated sugar reacts invariably in the γ-oxidic form, but this characteristic linking appears to be absent in tetramethyl glucose-hydrazone.

In the course of the work, it was found that the silver oxide method of alkylation can be readily applied to the methylation of different types of oximes, thus furnishing a convenient method of determining the hydroxyl content of such compounds.

258. "*The Characterisation of Mercerised Cotton.*" (Preliminary Note). By JULIUS HÜBNER.

The author has studied the action of a number of reagents on cotton, both before and after mercerisation, and finds that the following methods afford a certain means of distinguishing between mercerised and non-mercerised cotton, and also enable the degree of mercerisation to be approximately ascertained.

The cotton to be examined is steeped in a saturated solution of potassium iodide containing iodine; after a few seconds' immersion, the sample is withdrawn and washed five or six times in a 2 per cent potassium iodide solution. After this treatment, mercerised cotton is found to have acquired a brownish-black colour, whilst unmercerised cotton remains white; on then treating the samples with water, the mercerised cotton turns bluish-black and the unmercerised sample remains quite white.

Another convenient method for distinguishing between mercerised and untreated cotton consists in steeping the samples in an aqueous solution, 100 cc. of which contain 93·3 grms. of zinc chloride and about 0·005 grm. of iodine; in this liquid, non-mercerised cotton remains practically white, whilst the mercerised material becomes of a dark navy-blue colour.

259. "*Note on the Action of Metallic Calcium on Alcohols.*" By FREDERICK MOLLWO PERKIN and LIONEL PRATT.

It has been stated that metallic calcium has no action on alcohol, and may therefore be employed as a dehydrating agent for alcohols. The authors find, however, that, when metallic calcium is allowed to remain in contact with ethyl or methyl alcohol for from thirty to sixty minutes, reaction ensues and may become very vigorous. Once started the reaction continues to completion, according to the equation $2CH_3.OH + Ca = (CH_3\cdot O)_2Ca + H_2$.

If the mixture is heated to the boiling point of the alcohol, the reaction proceeds much more rapidly. With propyl, *iso*butyl, amyl, and benzyl alcohols, the reaction takes place exceedingly slowly at the ordinary temperature, but completes itself in the course of a few hours at the boiling point of the alcohol. Analysis shows the white, amorphous powder obtained in all cases to be $(Alk\cdot O)_2Ca$.

260. "*Note on the Iodates and Periodates of the Alkalis and the Ammonium Radicle.*" By THOMAS VIPOND BARKER.

The author gave a description of rubidium periodate, together with an account of some specific gravity and solubility determinations of the iodates of rubidium and cæsium, and the periodates of sodium, potassium, rubidium, cæsium, and ammonium.

261. "*The Colour of Cupric Salts in Aqueous Solution.*" By NEVIL VINCENT SIDGWICK and HENRY THOMAS TIZARD.

The authors have measured the depth of colour of aqueous solutions of cupric salts from the point where they become blue, and the influence on it of the anion and the concentration, using the Donnan tintometer. The main results are:—

1. All the salts examined (propionate, acetate, formate, monochloroacetate, chloride, bromide, sulphate, nitrate) showed the same tint at dilutions greater than about N/4, but the depth of colour varied with the anion and the dilution. This shows that they contain at least two substances of the same tint, but of different depths of colour.

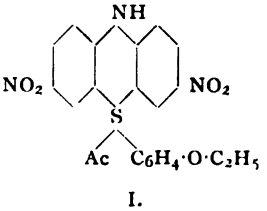
2. The weak acid salts are deeply coloured at high concentrations, and the more so the weaker the acid. On dilution, the colour diminishes, tending to a value from two to four times that for copper sulphate, according to the acid, and hence greater than that of the cupric ion. It is therefore suggested that the change is due to the dissociation of CuA_2 into $CuA^{\cdot}$, which must then proceed very far before the second dissociation giving $Cu^{\cdot\cdot}$ ions begins. The second dissociation constant of a ternary salt, MX_2, should be very small, in accordance with Ostwald's theory for dibasic organic acids, as the positive charge on the metal in the ion $MX^{\cdot}$ will resist the appearance of a second charge on M.

3. The salts of strong acids are always much paler than those of weak. On dilution the colour deepens, but only slightly. With copper nitrate, the complexes formed in very concentrated solution are of the same blue colour as the copper ion, but deeper.

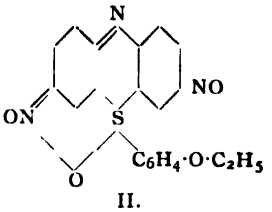
4. It thus seems probable that ionisation affects the intensity of the colour, but not the tint.

262. "*Derivatives of S-Phenylphenazothionium.*" (Part I.). By SAMUEL SMILES and THOMAS PERCY HILDITCH.

The α- and β-dinitro-compounds obtained from thiodiphenylamine by the action of nitric acid (Bernthsen, *Annalen*, 1885, ccxxx., 116) yield the sulphates of bases when condensed with phenetole in presence of concentrated sulphuric acid. Thus Bernthsen's view that these substances are sulphoxides is confirmed. The condensation products referred to are salts of S-phenetyl-3:3′-dinitrophenazothionium (I.); these are converted by aqueous alkali into the reddish brown fluorescent thetine (II.). Hydrolysis of the salts furnishes the crimson sulphonium hydroxide. Derivatives of S-phenetyl-N-methylphenazothionium have been prepared in the same way; here, as with the above-mentioned compounds, the salts are green, but the base is dull brown and not fluorescent. A synthesis of these substances was attempted by the condensation of di-*p*-nitrodiphenylamine and phenetole-*p*-sulphinic acid, but the reaction could not be carried beyond the intermediate stage of the sulphoxide.



I.



II.

263. "*A Colorimetric Method for the Determination of Small Percentages of Iron in Copper Alloys.*" By ARNOLD WILLIAM GREGORY.

The method is based upon the colour reaction given by salicylic acid and ferric chloride. This reaction is modified by using a solution of salicylic acid in acetic acid, and the test is carried out in the presence of sodium acetate. Under these conditions, a deep red colour is produced, which is used as a colorimetric test for iron in small quantities. The interfering action of the blue copper salts is overcome by the addition of a weak solution of potassium cyanide, which results in the formation of the colourless complex cyanide of copper and potassium.

Zinc and antimony do not interfere with the reaction, but lead must be removed as sulphate.

This method has been found to give very accurate results in cases where the percentage of iron in the copper alloys is so low that the ordinary gravimetric methods of estimation involve the use of a large quantity of the alloy.

264. "*The Effect of Heat on the Alkyl Iodides.*" By ZELDA KAHAN.

Experiments an the effect of heating alkyl iodides alone and in the presence of zinc, sodium, silver chloride, and barium peroxide show that the probable course of the reaction is:—

1. The dissociation of the alkyl iodide into hydrogen iodide and an alkylene or alkylidene derivative.

2. If alkylidene is formed, its conversion into an ethylene derivative.

3. The reduction of the ethylene derivative by the hydrogen iodide. When heated alone, ethyl iodide yields ethane, ethylene, and a little hydrogen, but in the presence

of zinc, butane is also formed in amount proportional to the quantity of zinc employed. Methyl iodide decomposes much less readily than any of the alkyl iodides, yielding chiefly methane and ethylene; with zinc, ethane is also formed, but with barium peroxide the chief products are carbon mono- and di-oxides and methane.

The normal and *iso*propyl iodides, when heated alone, yield only propane, but with zinc or sodium much propylene and some hydrogen are also formed.

265. "*The Influence of Acids and Alkalis on the Velocity of Formation of Acetoxime.*" By ERNEST BARRETT and ARTHUR LAPWORTH.

At 0° and at a dilution of 1 grm.-molecule each of acetone and hydroxylamine per 40 litres, the velocity of oxime formation is least with no other base or acid present. The acceleration caused by sodium hydroxide is very large and nearly proportional to the concentration of that substance. The acceleration caused by hydrochloric acid is also considerable, and rises rapidly until when half a grm.-molecule of acid is present the velocity is more than fifty times as great as at first. With more acid, a very rapid fall occurs, and attains a nearly constant velocity when rather more than 1 grm.-molecule of acid is present.

With acetaldehyde, very similar results were obtained.

The measurements were carried out before the appearance of Acree and Johnson's recent paper (*Journ. Am. Chem. Soc.*, 1907, xxxviii., 258).

266. "*Action of Metallic Calcium on Ketones.*" By HERBERT DRAKE LAW and FREDERICK MOLLWO PERKIN.

When metallic calcium is placed in contact with acetone which has previously been dried over calcium chloride, a slow evolution of hydrogen takes place, which becomes brisker in the course of a few hours. The rate of evolution of gas is about 2 litres in twenty-four hours at an average temperature of 16°. If the calcium and acetone are allowed to remain in contact for about one week and the product then fractionated, about 200 to 300 grms. of mesityl oxide are obtained from 2 litres of acetone. More complex substances are also formed in considerable amount. If the acetone remaining after fractionation is again placed in contact with the same quantity of calcium, a further yield of mesityl oxide is obtained. The proportions for which the best results have been obtained are about 150 grms. of metallic calcium and 2 litres of acetone. After standing for four days, 200 to 300 grms. of mesityl oxide are obtained. When acetone is heated with metallic calcium, it is difficult to stop the reaction at the right point to obtain mesityl oxide, and products of high boiling-point are formed.

Methyl ethyl ketone reacts very much more slowly with calcium, and the substances require to be left in contact for several months. When 1500 cc. of methyl ethyl ketone are allowed to remain in contact with 200 grms. of calcium for about one week, the rate of evolution of hydrogen is about 1 litre in twenty-four hours. On fractionation, at the end of eight to ten weeks, a considerable quantity of a fraction boiling at 164—165° is obtained, and also a larger quantity of fractions boiling up to 300°. The lower fraction is probably *γ-methyl-Δγ-heptene-ε-one*, $CH_3{\cdot}CH_2{\cdot}C(CH_3){:}CH{\cdot}CO{\cdot}CH_2{\cdot}CH_3$.

On oxidation with potassium permanganate, acetic acid and methyl ethyl ketone are obtained. This does not actually prove the correctness of the formula just given, because the same results would be obtained by oxidation of the compound $CH_3{\cdot}CH_2{\cdot}C(CH_3){:}C(CH_3){\cdot}CO{\cdot}CH_3$.

The substance is a colourless liquid, having a very fragrant odour resembling that of oil of bergamot.

267. "*The So-called 'Tetrabromodiphenoquinone' and the Constitution of Coerulignone.*" By JAMES MOIR.

The author has continued his researches on Magatti's tetrabromodiphenoquinone (*Proc.*, 1906, xxii., 110), and has studied the action of reducing agents on this compound.

268. "*A Note on Certain Pyrogenic Reactions.*" By NORMAN THOMAS MORTIMER WILSMORE and ALFRED WALTER STEWART.

In the course of some investigations on the effect of a white-hot platinum wire on various organic substances, the authors have made the following observations. The apparatus employed was in essentials the same as the generator used in the case of keten (*Trans.*, 1907, xci., 1938). The results obtained were qualitative only, no analysis being made.

Owing to its possible use as a solvent, the behaviour of benzene was investigated; it was not affected by the wire, and toluene also was unacted on.

When ethyl crotonate is treated pyrogenically. ethylene is liberated, and crotonic acid crystallises from the cooled liquid which remains in the generator. An unsaturated acid, namely, cinnamic, was then tried in benzene solution, but no effect was observed. On the other hand, when saturated ethereal salts were placed in the generator, a mixture of carbon dioxide and hydrocarbons was liberated. The decomposition, in the case of ethyl acetate, appears to take place in the following steps:—

$$CH_3{\cdot}CO_2{\cdot}C_2H_5 \rightarrow CH_3{\cdot}CO_2H + C_2H_4 \rightarrow$$
$$\rightarrow CH_4 + CO_2 + C_2H_4.$$

In the case of ethyl malonate, ethylene is first evolved, as in the foregoing case, and the malonic acid thus formed breaks down into carbon dioxide and acetic acid, which, in its turn, decomposes into methane and carbon dioxide. It is to be noted that whenever any acetyl derivative is formed in the course of any of these stages, some keten is in turn produced from it. In contradistinction to the behaviour of the fatty acids, benzoic acid in benzene solution was not noticeably attacked.

From these results, the authors conclude that the ethylenic linking in the *α*-position with respect to the carboxyl group tends to render the compound more stable with regard to this agent than is an ethane derivative. This view is, of course, supported by the fact that unsaturated hydrocarbons are more stable in the electric arc than saturated ones.

From acetone, keten was obtained, whilst substances of high boiling point, such as anethole and aniline, were decomposed with charring.

FARADAY SOCIETY.

Ordinary Meeting, December 17th, 1907.

Dr. F. MOLLWO PERKIN, Treasurer, in the Chair.

DR. F. G. DONNAN, in the absence of the author, read a paper on "*A Physico-chemical Study of the Complex Copper Glycocoll Sulphates*," by J. T. BARKER, B.Sc. (Will be inserted in full).

Dr. F. MOLLWO PERKIN read a paper on "*The Discovery of the Alkali Metals by Davy: the Bearing of the Discovery upon Industry.*" (The lecture was illustrated with lantern slides).

After a short biographical sketch the author refers to Davy's early experiments on galvanism, which began in 1800, and culminated in 1807 in the electrolytic decomposition of the fused alkalis, caustic soda, and caustic potash, described on November 19th in the Bakerian Lecture before the Royal Society, entitled "On some New Phenomena of Chemical Changes produced by Electricity, particularly the Decomposition of the Fixed Alkalis, and the Exhibition of the New Substances which constitute their Bases, and on the General Nature of Alkaline Bodies." Davy's experiments are described in detail, and it is shown that the E.M.F. of his battery must have been about 220 volts, and the current he used something under 1 ampère. The subsequent experiments on the decomposition of the alkaline earths, by which calcium, strontium, barium, and magnesium in the form of amalgams were obtained, are then described.

The second part of the paper deals, among other matters, with the industrial manufacture by Wöhler in

1827 of potassium, by Ste. Claire Deville in 1854 of sodium, with Watt's suggestions (1851) for electrolysing fused sodium chloride, with Castner's chemical sodium process (1886), and his electrolytic process (1890), Rathenau and Suter's sodium process, Becker's process, and the process of Darling, who electrolysed fused sodium nitrate, using porous partitions.

NOTICES OF BOOKS.

Photographisces Hilfsbuch ("Photographic Guide"). Part II. By Hans Schmidt. Berlin: Gustav Schmidt. 1907.

This book is meant for the serious worker who is willing to give both time and trouble to the preparation of good photographs, and who will not be satisfied with turning out anything but first-class work. Beginners will find it very helpful, more especially as comparatively little is left to the worker's judgment, and nearly always explicit statements and definite rules of working are given. At the same time experienced photographers will no doubt learn something from its perusal. The second volume treats only of the production of the print from the negative. Firstly, processes are described which should be applied to unsatisfactory negatives in order to improve them before printing from them, and the sorting and touching up of negatives are carefully discussed. The value of the different printing papers in use is estimated, and details of printing, toning, and fixing are then given. Various methods of mounting and similar practical questions are also dealt with, and while the book is very full and clear the author avoids verbosity, and shows himself to be an excellent judge of what are the essential points which the uninitiated want constantly emphasised in order that they may get satisfactory results.

MEETINGS FOR THE WEEK.

Monday, 6th.—Society of Chemical Industry, 8. "Preparation of Paratoluidine from Mixed Toluidines by means of Paratoluidine Hydrate," by R. J. Friswell. "The Determination of Small Quantities of Bismuth," by H. W. Rowell.

Tuesday, 7th. Thursday, 9th. } Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "Astronomy, Old and New," by Sir David Gill, K.C.B., F.R.S., &c.

THE CHEMICAL NEWS.

VOL. XCVII., No. 2511.

THE VOLUMETRIC ESTIMATION OF TIN BY MEANS OF POTASSIUM DICHROMATE.

By H. REYNOLDS, B.Sc., Ph.D.

"THE method, originally devised by Streng, for the direct estimation of tin by potassium dichromate or other oxidising agents in acid solution has been found most unsatisfactory from the fact that variable quantities of water or acid seriously interfere with the accuracy of the results. The cause is not fully understood, but that it is owing partly to the oxygen mechanically contained in the water reacting on the very sensitive stannous chloride there can be very little doubt, as the variations are considerably lessened by the use of water recently boiled and cooled in closed vessels." (Sutton, "Volumetric Analysis," 9th Edition, p. 345).

The two points to be considered in the estimation of Sn by means of $K_2Cr_2O_7$ are:—

1. The prevention of oxidation during solution and titration.
2. The determination of the end-point.

1. Streng's method (*Pogg. Ann.*, 1854, xcii., p. 57) of dissolving the metal in boiling HCl and pouring the solution into a beaker for titration could not give exact results. The greatest care is necessary to prevent oxidation, especially if the solution is heated.

The following analyses illustrate this point, the column headed "Difference" giving a measure of the amount of oxidation which took place:—

	Taken.	Found.	Difference.	Per cent.
a.	0·1469	0·1413	0·0056	96·27
b.	0·1417	0·1376	0·0041	97·08
c.	0·1498	0·1253	0·0245	83·6
d.	0·1317	0·1285	0·0032	97·58

Remarks.

a. The metal was dissolved in a boiling tube fitted with a Bunsen valve; after the addition of 22 cc. $K_2Cr_2O_7$, the contents of the tube were transferred to a conical flask owing to the inconvenience of titrating in the tube. The total amount of $K_2Cr_2O_7$ required was 23·75 cc.

b. The gauze basket was removed before titrating, and washed down with a few cc. cold distilled water.

c. The basket was washed with about 20 cc. of warm water on withdrawing it from the flask.

d. The basket was left in until 21 cc. $K_2Cr_2O_7$ had been added (total amount required, 21·60).

In all the analyses the granulated metal was placed in a platinum gauze basket about 1 cm. diameter and 1 cm. deep, which was lowered into 5 cc. concentrated HCl. In the last three analyses a small flask fitted with a Bunsen valve was used instead of the boiling tube.

Fourteen more analyses were carried out in this way, 10 cc. concentrated HCl being used in each case. The solution was made at about 30° C., and when it was complete, or nearly so, the contents of the flask were heated until a brisk evolution of HCl took place, and allowed to cool to the temperature of the room before the flask was opened for the titration. N/10 $K_2Cr_2O_7$ was used for all these analyses, of which the extreme cases are shown below.

Taken.	Found.	Difference.	Per cent.	Remarks.
0·1539	0·1492	0·0047	96·96	Smallest amount of tin taken.
0·2385	0·2339	0·0046	98·07	Largest amount of tin taken.
0·1930	0·1889	0·0041	97·87	Smallest difference.
0·2250	0·2190	0·0060	97·32	Largest difference.

Mean difference, 0·0049

At this point a change was made in the method, the Bunsen valve being no longer used, and instead a current of CO_2 was passed through the conical flask from before the introduction of the metal until the greater part of the $K_2Cr_2O_7$ had been run in. The gas was not passed into the solution but delivered just above it. It escaped through a tube wide at the top and narrow below, with a side hole just below the cork. When the solution was ready for titration the $K_2Cr_2O_7$ was run in through this tube to within about 1 cc. of the correct amount. The necessary quantity of indicator was then added through the same tube, and followed by two or three drops of water. The titration was finished in the open flask, more CO_2 being passed in if necessary.

Five analyses were carried out under these conditions, the quantity of tin taken varying from 0·1974 grm. to 0·2110 grm., and the difference from 0·0018 to 0·0026, with a mean difference of 0·0022 grm. These analyses were all of granulated tin supplied by Merck, and it probably contained about 99·5 per cent Sn. Assuming this, the mean oxidation, using the Bunsen valve, would be 0·0039 grm., and using the CO_2, 0·0012 grm.

Six analyses were made with Kahlbaum tin in the same way; the amount of metal taken varied between 0·1412 grm. and 0·2302, and the difference between the quantity taken and that found varied from 0·0007 to 0·0023 grm., the mean value being 0·0016. For these analyses a weaker solution was used than for those with Merck tin, viz., 1 cc. = 0·0200 grm. Sn, instead of N/10; the volume of solution required is thus greater in the ratio of 6 to 5, and this may account for the slightly greater oxidation which took place.

It thus appears that, if certain precautions be taken, the deficit due to oxidation need not exceed about 0·001 grm. of Sn. This amount can be made unimportant by increasing the amount of tin used for each analysis to about a grm. The precautions to be observed are that the metal shall be dissolved in an atmosphere of CO_2, and that the solution shall be kept in this atmosphere until the titration is almost finished.

2. The determination of the end-point, by observing the colour change caused by the presence of unchanged $K_2Cr_2O_7$, is not practicable with any degree of accuracy. In place of it Streng suggested adding a few drops of KI starch solution to the solution to be titrated. Other available indicators are $FeSO_4$ with KCNS and indigo-carmine. With regard to the latter, the change from the green of the chromic solution to the blue of the indigo-carmine is not always a very easy one to observe; as to the former, it is perhaps doubtful if the KCNS would remain unaffected in the strongly acid reducing solution.

If azobenzene is heated with concentrated H_2SO_4 until the beginning of a violent reaction, and the whole is then poured into a large volume of water, a deep red solution is obtained, containing possibly an oxyazobenzene sulphonic acid. This is reduced to a colourless body by $SnCl_2$, and $K_2Cr_2O_7$ then added restores the colour. If the solution is made alkaline it goes almost magenta coloured, and shows a brick-red fluorescence. The colour is very intense, and the substance is thus a very suitable indicator for use with bichromate when oxidising strong reducing agents. For the red colour to mask the Cr green completely, when oxidising 1 grm. of tin, about 3 cc. of indicator are necessary of a strength = 0·034 cc. of a $K_2Cr_2O_7$ solution, of which 1 cc. = 0·01 grm. Sn. A solution of ferrous sulphate, or of Mohr salt, does not affect the indicator, nor does $Na_2S_2O_3$. It is thus not available for the titration of

weak reducing agents; this has the advantage that a strong reducer like $SnCl_2$ can be estimated in presence of a weak one like $FeCl_2$.

In all the titrations with $K_2Cr_2O_7$ in this work the azo-benzene derivative was used as indicator. In addition the end-point in the ferro-tin analyses was checked by taking out a drop and testing with KCNS.

The general details of the method having been thus settled, analyses were made of pure tin from Kahlbaum, ferro-tin, and Britannia metal with satisfactory results as follows :—

I. *Kahlbaum Tin.*

A. 0·8316 grm. tin was weighed out in the platinum gauze basket, and dissolved in 15 cc. concentrated HCl in a current of CO_2. When solution was complete 41 cc. $K_2Cr_2O_7$ were run in through the short tube, the indicator added, and the titration finished in artificial light.

41·54 cc. $K_2Cr_2O_7$ were required = 0·8308 grm. Sn = 99·90 per cent.

The chromic solution was red in certain lights before the indicator was added, but by reflecting a strong light from a sheet of white paper through a layer 0·5 cm. thick it was quite green. The solution was distinctly green after 41·50 cc. had been run in.

B. 0·7392 grm. tin dissolved in 14 cc. HCl as above, 36 cc. $K_2Cr_2O_7$ added, and then the indicator. The titration was finished in artificial light.

Required, 36·90 cc. = 0·7380 grm. Sn = 99·84 per cent.

For the following analyses the CO_2 was obtained from a cylinder of the gas, and the HCl for the analysis was heated almost to boiling in the flask in an atmosphere of CO_2 to expel any air it might contain. When the acid had cooled, the gauze basket containing the metal was lowered into it.

C. 0·7331 grm. tin was dissolved in 20 cc. HCl, the solution being warmed three or four times during the process. 72·5 cc. $K_2Cr_2O_7$ (1 cc. = 0·01 grm. Sn) were run in, followed by 3·2 cc. indicator. The titration was finished in good daylight, the end reaction being very sharp.

Required, 73·22 cc. = 0·7322 grm. Sn = 99·88 per cent.

D. 0·6383 grm. tin was dissolved in 20 cc. HCl. Solution took about half-an-hour. At the last the acid was heated almost to boiling to dissolve a few remaining specks of tin.

After leaving five minutes to cool, 63·1 cc. $K_2Cr_2O_7$ were run in, and 3 cc. indicator added. The titration was finished in good daylight, the end reaction being very sharp.

Required, 63·77 cc. = 0·6377 grm. Sn = 99·91 per cent.

For this last analysis the CO_2 was passed through a titanous sulphate solution before entering the flask.

Two gravimetric analyses were made by dissolving the metal in HNO_3 and converting into SnO_2.

	I.	II.
Metal taken ..	0·5049	0·4195
SnO_2 found ..	0·6408	0·5321
Sn	= 0·5050 = 100·02 %	= 0·4194 = 99·98 %

Results.

	Volumetric.	Gravimetric.
A.	99·90	I. 100·02
B.	99·84	II. 99·98
C.	99·88	—
D.	99·91	—
Mean ..	99·88	100·00

The method has therefore no serious inherent faults, and the precautions taken against oxidation are not at all complicated or difficult to carry out.

The case of pure tin being thus satisfactorily disposed of, I proceeded to see how far the method was applicable to tin alloys. Ferro tin, manganese tin, phosphor tin, pewter, and Britannia metal have been investigated, and of these manganese tin, pewter, and phosphor tin have so far not yielded good results. The manganese tin gave a very indistinct end reaction, the indicator taking a dirty brown colour on oxidation instead of returning to its original crimson-red, although an aqueous solution of pure $SnCl_2$ and $MnCl_2$ gave a beautiful end reaction. The phosphor tin gave very discordant results, the phosphorus in one instance appearing to take part in the reaction. In this case 0·702 grm. alloy required 82·2 cc. $K_2Cr_2O_7$, corresponding fairly closely to 95 per cent Sn, being oxidised from $SnCl_2$ to $SnCl_4$, and 5 per cent P being oxidised from P_2O_3 to P_2O_5. The end reaction in all cases was slow and was not always distinct.

II. *Ferro-tin.*

A. 0·8451 grm. of the alloy was weighed out in the platinum gauze basket, and dissolved in 20 cc. concentrated HCl, which had been previously heated and cooled in an atmosphere of CO_2. The whole analysis was as usual carried out in the same atmosphere. A slight black flocculent residue remained undissolved, and probably consisted of a trace of C. 77·9 cc. $K_2Cr_2O_7$ were run in through the tube, followed by 3 cc. indicator.

Required, 79·30 cc. = 0·7930 grm. Sn = 93·84 per cent.

B. 0·7359 grm. of the alloy was dissolved as usual, leaving a slight black residue. 68 cc. $K_2Cr_2O_7$ were run in, followed by 3 cc. indicator.

At 68·90 Solution greenish red; no permanent colour with KCNS.

„ 68·95 Green tinge in solution; slight colour with KCNS.

„ 69·00 No green visible in solution; red colour distinct and permanent with KCNS.

Half a drop more made no difference in the appearance of the solution nor in the coloration with KCNS, when a drop was taken out and tested on a tile.

Required, 69·00 cc. = 0·6900 grm. Sn = 93·76 per cent.

C. 0·7043 grm. of the alloy was dissolved as usual. Solution was not quite complete, there being a slight residue of C even after boiling. 63·5 cc. $K_2Cr_2O_7$ were added at once, followed by 3 cc. indicator. At 66·00 cc. the solution was still greenish, and KCNS gave no permanent colour with a drop taken out. At 66·07 there was no green in the solution, and the red with KCNS was permanent.

Required, 66·07 cc. = 0·6607 grm. Sn = 93·81 per cent.

The titration was finished in good daylight.

It will be seen from B and C that the return of the colour of the indicator coincides with the appearance of the colour with the KCNS; that is to say, that the oxidation of the $SnCl_2$ is complete before that of the $FeCl_2$ begins. At the same time, the end reaction is slower than with pure tin, the cause being evidently that—

$$SnCl_2 + Cl_2 = SnCl_4$$

is not the only reaction, the pair of reactions—

$$FeCl_2 + Cl = FeCl_3$$
$$2FeCl_3 + SnCl_2 = SnCl_4 + FeCl_2$$

going on simultaneously with it towards the end of the titration.

D. 0·8158 grm. of the alloy was dissolved as usual. There was the usual slight presumably carbonaceous residue. 76·3 cc. $K_2Cr_2O_7$ were run, followed by 3 cc. indicator. The light was too bad for the colour of the solution to be seen clearly. At 76·54 a drop taken out gave a faint permanent red with KCNS, fainter than, but quite as permanent as, the coloration at 66·07 in C.

Required, 76·54 cc. = 0·7654 grm. Sn = 93·82 per cent.

The CO_2 for the last two analyses and for all the following ones was passed through a Wetzel washing-

bottle containing titanous sulphate before it entered the Erlenmeyer flask.

The control analyses were made volumetrically with iodine and starch in acid solution (*cf.*, S. W. Young, *Journ. Am. Chem. Soc.*, xix., 809), the method of dissolving being exactly as above. The strength of the iodine solution was such that 1 cc. = 0·01904 grm. Sn. It was checked against a N/10 $K_2Cr_2O_7$ solution by means of $Na_2S_2O_3$. The results obtained were :—

Grm.		Cc.		Grm.		Per cent.
1. 0·7362 alloy	required	36·30	I =	0·6911	Sn =	93·88
2. 0·6556	,,	32·35	,,	0·6159	,,	93·96
3. 0·7451	,,	36·72	,,	0·6991	,,	93·84

Results.

	By $K_2Cr_2O_7$.	By iodine.
A.	93·84	1. 93·88
B.	93·76	2. 93·96
C.	93·81	3. 93·84
D.	93·82	—
Mean ..	93·81	93·89

The second iodine estimation had to be finished off in a hurry, and there might have been a few tenths of a milligrm. of metal undissolved when the titration was begun.

III. *Britannia Metal.*

A. 0·6264 grm. of the alloy was dissolved in 20 cc. conc. HCl which had been heated previously in CO_2. A good deal of heating was necessary, and solution was not quite complete, a slight flocculent black residue remaining. 25 cc. $K_2Cr_2O_7$ were run in, and then 3·5 cc. indicator were added. The end reaction was rather slower than with pure tin, but much better than with ferro-tin. The end-point was sharp.

Required, 31·60 cc. = 0·3160 grm. Sn. = 50·45 per cent.

B. 0·6473 grm. was dissolved in 20 cc. conc. HCl which had not been previously heated. The contents of the flask were left cold until the greater part of the metal had dissolved; they were then heated to boiling at frequent intervals until no more gas was given off. 32 cc. $K_2Cr_2O_7$ were run in, followed by 3 cc. indicator.

Required, 32·75 cc. = 0·3275 grm. Sn = 50·55 per cent.

End reaction good, not too slow. End-point sharp. Colour brownish instead of bright crimson.

C. 0·9156 grm. was dissolved as above. 45·5 cc. $K_2Cr_2O_7$ were run in, followed by 3 cc. indicator.

Required, 46·40 cc. = 0·4640 grm. Sn = 50·68 per cent.

In B and C after the indicator had been added, the solution was heated almost to boiling in the current of CO_2 to re-dissolve the $PbCl_2$ precipitated on diluting with the $K_2Cr_2O_7$ solution. The titrations being finished hot the end reaction was fairly fast. The end-point in both cases was sharp.

D. 0·7581 grm. dissolved as above. 37·9 cc. $K_2Cr_2O_7$ were run in, followed by 3 cc. indicator. The solution was heated to re-dissolve $PbCl_2$. The end reaction was fast and sharp, the restored colour brownish.

Required, 38·50 cc. $K_2Cr_2O_7$ = 0·3850 grm. Sn = 50·78 per cent.

E. 0·8509 grm. dissolved as above. 42·5 cc. $K_2Cr_2O_7$ were run in, then 3 cc. indicator. The colour at the end was dirty brown, but on the addition of 1 cc. indicator the red was clear.

Required, 43·02 cc. = 0·4302 grm. Sn = 50·56 per cent.

F. 0·8166 grm. dissolved as above. 41·0 cc. $K_2Cr_2O_7$ run in, followed by 4 cc. indicator, and the solution heated to re-dissolve $PbCl_2$. The end reaction was very good, the colour changed from slightly dirty green to clear red with 0·02 cc.

Required, 41·40 cc. = 0·4140 grm. Sn = 50·70 per cent.

The control analyses were made exactly as in the case of ferro-tin with the following results :—

Grms.		Cc.		Grm.		Per cent.
1. 0·9318 alloy	required	24·78	I =	0·4718	Sn -	50·63
2. 1·0077	,,	26·77	,,	0·5097	,,	50·58
3. 1·0765	,,	28·54	,,	0·5442	,,	50·55

Results.

	By $K_2Cr_2O_7$.	By iodine.
A.	50·45	1. 50·63
B.	50·55	2. 50·58
C.	50·68	3. 50·55
D.	50·78	—
E.	50·56	—
F.	50·70	—
Mean ..	50·62	50·59

Summary of Numerical Results.

	Control.	Found.	Diff. (per cent).
Pure tin	100·00	99·88	+0·12
Ferro-tin.. ..	93·89	93·81	+0·08
Britannia metal	50·59	50·62	−0·03

Summary.

A method has been worked out for the accurate estimation of tin by titration with $K_2Cr_2O_7$.

A sulphonation product of azobenzene was used as indicator, the colour change being from green to red. Kahlbaum tin, which by gravimetric analysis contained 100·00 per cent Sn, gave by this method 99·88 per cent. Ferro-tin and Britannia metal also gave good results.

The Method.

Place 20 cc. concentrated HCl in a 200 cc. Erlenmeyer flask, fitted with a cork, having a long and a short tube passing through it. The long tube should reach to about 1·5 cm. of the bottom of the flask; the short tube should be about 6 mm. wide at the top and 2 mm. at the bottom, which should be cut slantwise. The tube should also have a side hole just below the cork to allow the gas to escape while the $K_2Cr_2O_7$ is running in. Fill the flask with CO_2 from a cylinder, the gas passing first through titanous sulphate to free it from oxygen, and then through a little H_2SO_4 to free it from titanous sulphate. Heat the HCl nearly to boiling, and allow to cool in the current of CO_2. Weigh out 0·6 to 1·0 grm. of the metal in a platinum gauze basket, and lower into the acid. When no more gas is evolved heat nearly to boiling to drive any dissolved hydrogen out of the solution, cool down and run in $K_2Cr_2O_7$ through the short tube to within about 1 cc. of the correct amount. Add indicator in sufficient quantity to be sure that the green colour of the chromic salt will be entirely masked when the colour of the indicator is restored. Remove the basket, and finish by delivering the remainder of the $K_2Cr_2O_7$ direct into the solution.

The Chemical Laboratory,
L.C.C. Paddington Technical Institute,
December, 1907.

Royal Institution.—On Tuesday next, Jan. 14, at 3 o'clock, Dr. A. A. Gray delivers the first of two lectures at the Royal Institution, on "The Internal Ear of Different Animals"; and on Thursday, Jan. 16, Prof. W. W. Watts will deliver the first of two lectures on (1) "The Building of Britain." On Saturday, Jan. 18, Prof. Gisbert Kapp commences a course of two lectures on "The Electrification of Railways." The Friday Evening Discourse on Jan. 17 will be delivered by Prof. T. E. Thorpe, on "The Centenary of Davy's Discovery of the Metals of the Alkalis"; and on Jan. 24 by Colonel David Bruce, on "The Extinction of Malta Fever."

STUDIES ON CHARCOAL AND LIQUID AIR.*

By Prof. Sir JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S., Fullerian Professor of Chemistry, R.I.

(Concluded from p. 8).

Chemical Interactions in High Vacua.

If a piece of pure sulphur (S) is put in one end and some mercury (Hg) in the other end of a U-tube (Fig. 14), both substances being kept at the temperature of liquid air during the time required to reach a high vacuum by the mercurial pump or by charcoal exhaustion, and the whole sealed off and left to stand at the ordinary temperature; then in a few hours, it will be noted that the surface of the mercury which was at first a brilliant reflecting one gets tarnished from the formation of a film of sulphide of mercury. The mercury vapour pressure being much greater than that of sulphur, it would be expected that any formation of sulphide of mercury taking place would be seen on the sulphur side of the U-tube. But the contrary

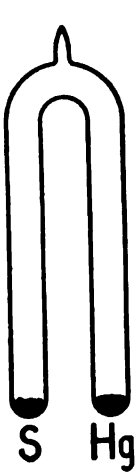


FIG. 14.

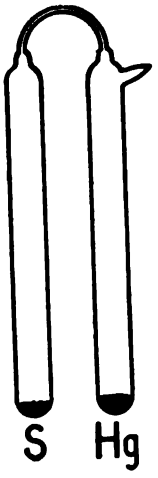


FIG. 15.

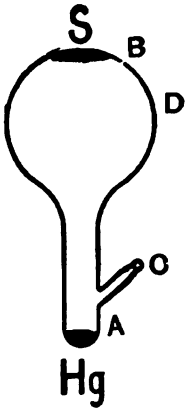


FIG. 17.

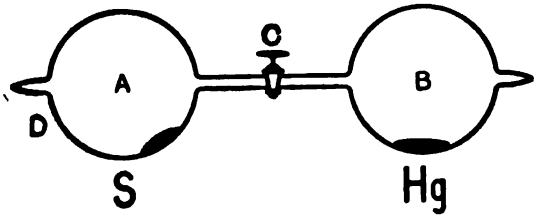


FIG. 16.

is the case, as the sulphide is seen to form at first on the surface of the mercury (Hg). The explanation that suggests itself is that the ordinary molecule of sulphur containing 6 to 8 atoms, dissociates and throws off single or double atoms which make their way rapidly through the mercury vapour without wholly combining with it, until they reach the surface of the liquid mercury, when the conditions for chemical interaction are more favourable. If the tube be constricted as at M (Fig. 15), the activity of the sulphur atoms on the mercury surface is stopped, as they encounter the mercury atoms under the most favourable circumstances for combination in the narrow tube at M, and there form the sulphide which is quite visible after long keeping.

It is interesting to note the excessively small quantities of the respective elements that are interacting in this case. The pressure of mercury vapour at 15° C. is about 1¼ millionths of an atmosphere, whereas that of sulphur is of the order of one-thousandth part of the millionth of an atmosphere.

The same phenomenon was exhibited in an even more striking manner by the following experiment:—Two equal bulbs A B (Fig. 16) were united by a tube containing a finely-ground stopcock C. A small piece of pure sulphur was put into A, and a small quantity of mercury into B, and the whole exhausted through the side-tube D by either a mercury pump or by the use of charcoal cooled in liquid air. While the exhaustion was going on the sulphur in A was fused, and finally the tube D was sealed off. On shutting the stopcock C, and allowing the apparatus to stand for some time, the application of a liquid air sponge to any part of the bulb B at once caused the deposition of a mercury mirror, which disappeared on allowing the cooled spot to regain the ordinary temperature. If the same cooling is applied to any part of the bulb A, no deposit takes place; but, if the sulphur has been recently fused so as to get it deposited on a portion of the glass surface in what is called the *utricular* state, then, in a short time a fine film of highly refracting sulphur is seen to have distilled to the cooled part, just like what takes place with the mercury in the other bulb. Now let the stopcock C be opened for a few seconds and shut again, and the local liquid air cooling on parts of both A and B repeated. On the cooled part of B nothing but mercury will be deposited as before; but on the cooled part of A a brilliant metallic deposit will be noticed, which is, however, not wholly mercury, for, on heating it with the finger, it is only partially volatilised, the portion which remains being sulphide of mercury. On repeating the operation on another part of A, in about a quarter of an hour all metallic deposition has disappeared. Thus, mercury vapour requires time to react with sulphur, but ultimately all the mercury vapour is removed by the sulphur. The apparatus enables the experiment to be repeated at any time.

Shortly after the discovery of oxygen by Priestley some Dutch physicists began the study of the gases absorbed and given off by living plants; and for this purpose the plants were covered by bell-jars whose lower edge was laid in a channel of mercury. But a difficulty arose, as it was found that the plants in these circumstances soon became sickly and died. Then the remarkable discovery was made that if sulphur was sprinkled over the leaves and the surface of the vessel, the deleterious effect of the mercury was overcome and the plants became healthy. Boussingault repeated and confirmed these results in 1868, and made many experiments to elucidate the remedial action of sulphur. He explained this action by pointing out that the poisoning of the plants arose from the presence of mercury vapour, and that as one volume of sulphur vapour was able to combine with six volumes of mercury vapour, the sulphur, although less volatile, was able effectually to neutralise the deleterious effects of the mercury vapour.

Now, the ratio of the pressure of mercury vapour to that of sulphur at the temperature of 115° C., when both bodies are in the liquid condition, is as 10 to 1. Seeing the sulphur molecule is S_6 to S_8, one volume of sulphur vapour is sufficient to neutralise or combine with six to eight volumes of mercury vapour, so that an excess of mercury pressure of from six to eight times that of the sulphur vapour can always be removed by combination with the sulphur. If, on the other hand, we compare the relative pressures of mercury at 100° C. to that of solid prismatic sulphur at the same temperature, this ratio is 37 to 1, so that the removal of the mercury vapour at the ordinary temperature, when the pressure ratio is still higher, cannot be fully explained. The effect of air and water vapour complicates the action in the case of plants, as the molecules of sulphur and mercury have not the free play they have when no inert gas is present. It would seem that in high vacua the S_2 molecule of sulphur may be considered as produced by molecular dissociation, and that moving with great rapidity relatively to the mercury

* A Discourse delivered at the Royal Institution, June 8, 1906.

gas molecules soon gets at the surface of the liquid mercury and coats it with a thin layer of mercury sulphide, which acts as a trap, stopping the exit of further mercury molecules. The effect of such a coating in preventing the escape of mercury vapour may be shown by the use of an inverted boiling-point flask like Fig. 17 containing a layer of fused sulphur at B, and mercury at A. Before and during very complete exhaustion, the mercury at A is kept in liquid air, and finally the flask is sealed off at C. On standing at the ordinary temperature, the surface of the mercury gets acted upon by the sulphur, and if the mercury is not shaken so as to crack the film of mercury sulphide, a little sponge of liquid air placed upon the surface at D shows no metallic deposit; but the moment the mercury is slightly shaken to break the surface film of the liquid mercury, metallic deposit is instantly formed by the local cooling.

Fig. 18.

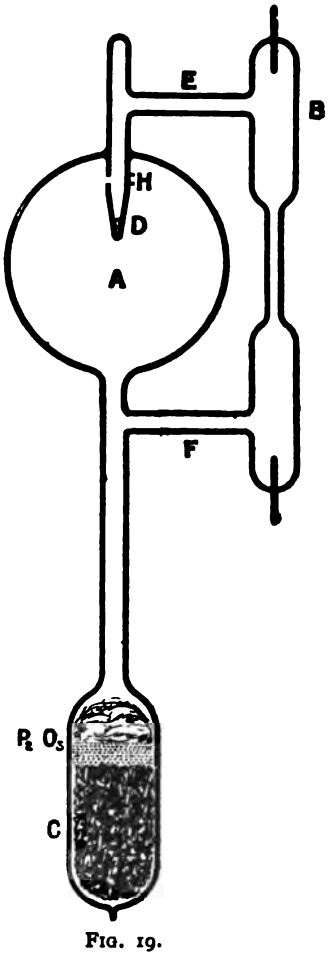


Fig. 19.

This deposit is not all mercury, but partly sulphide, because on taking away the sponge and heating the cooled spot by contact with the hand, a permanent brown part remains, whereas, if it had been all mercury it would have completely volatilised. On standing for a little time the liquid air cooling causes no metallic mirror, as all the mercury vapour has been removed by combination with the sulphur, and the sulphide film reforms on the mercury, when the experiment may be repeated.

Oxidation of Phosphorus in High Vacua.

In the Friday Evening Address of 1905 an experiment was shown illustrative of the well-known fact that the phosphorous glow caused by oxidation does not take place in dry oxygen at atmospheric pressure, and that it was only when the pressure was very considerably reduced that such action took place. This may be shown more clearly in the following way:—A globe (Fig. 18), A, has a small capillary-side tube, P, attached, containing a little phosphorus, that has been melted at its end, and is at the same time connected by another tube to a reservoir, D, containing charcoal covered with a layer of phosphoric anhydride to absorb all traces of moisture. To the side of this tube a small mercury gauge, G, is attached. After the whole vessel is thoroughly exhausted it is filled up to atmospheric pressure with pure oxygen gas, and the whole sealed off. On immersing the charcoal bulb in liquid air the pressure falls rapidly to a fraction of a millimetre pressure, and soon the globe A becomes filled with a phosphorescent glow, showing that chemical action is taking place. As the absorption of the oxygen by the charcoal continues the phosphorescence becomes less, and at last disappears, nothing finally filling the bulb but the vapour of phosphorus as it distils from P into the liquid air condenser. Meanwhile the gauge G shows that the pressure at which the phosphorescence begins must be only a fraction of a millimetre, and that it continues at a pressure below what could be measured on the gauge. When the charcoal is taken out of the liquid air, and the temperature allowed to rise, the course of the experiment is inverted, the oxygen occluded in the charcoal being given off, and as it meets the vapour of phosphorus in the bulb A, suddenly combines with it in a few oscillating flashes, and soon all is dark again. The experiment may be repeated after weeks of keeping with the same uniform results. The same thing is also very beautifully shown by the arrangement in Fig. 19. Here the gauge is replaced by a sparking tube B, having free access to the globe A by the tubes E and F, the former having communication by means of the small hole H; D is the phosphorus. The high vacuum at which the glow takes place in the bulb is shown by the character of the discharge taking place in B. A curious phenomenon is observed on stopping the electric discharge; now the glow travels from the bulb along E and F, and meets in the middle of B. It looks as if the electric discharge expelled all the phosphorus vapour from the discharge tube, and that the moving phosphorescent stream is due to the vapour of phosphorus coming back again. While the electric discharge is passing in B, the spectroscope reveals only the oxygen bands.

Separation of the Volatile Gases Neon, Hydrogen, Helium.

Attention has already been called to the selective nature of the absorption when a mixture of gases is presented to cooled charcoal, and it has been noted that the gas obtained from the charcoal after absorption of air has the quantity of oxygen increased from 21 to 50 or 60 per cent, The general law of this absorption is that the lower the boiling-point, in other words, the more volatile or less condensable the gas, the less is the absorption. Thus for air, nitrogen with the lower boiling-point is not absorbed to so great a degree as oxygen, which has the higher boiling-point. This is beautifully shown in the following experiment:—A number of spectroscopic tubes connected in

series with a large charcoal U-tube, are highly exhausted by cooled charcoal so that the discharge will hardly pass. The charcoal tube is now placed in liquid air, and a slow current of air is allowed to enter the system. The less volatile gases, oxygen, nitrogen, argon, are absorbed by the charcoal, while the more volatile gases, helium, neon, and hydrogen, are allowed to pass. In a short time, when the pressure of the latter gases has risen sufficiently, the first tube begins to glow with the well-known rich orange hue of neon. As the air-absorption progresses, the characteristic discharge of neon and helium gradually extends to the other tubes, the slowness of the current

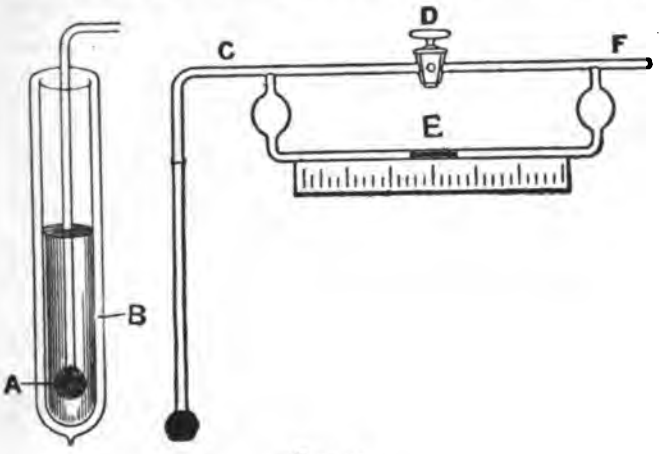


FIG. 20.

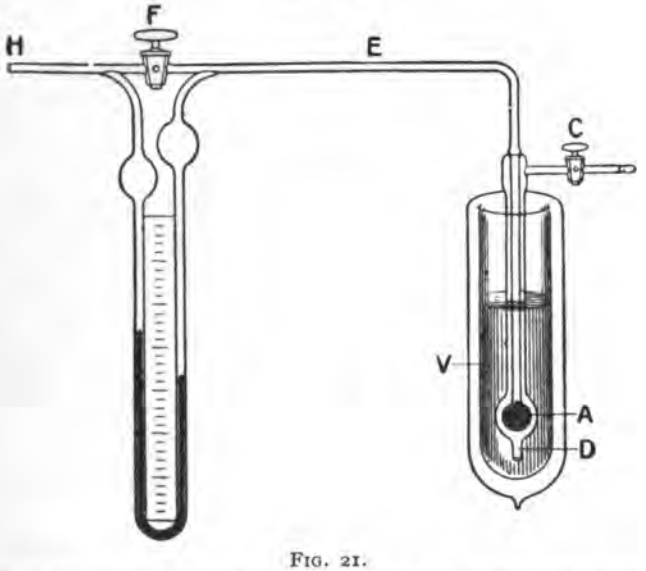


FIG. 21.

displaying vividly the march of the neon and helium glow. In this connection the sensitivity of the neon tube to induced electric oscillations from a coil of wire placed at right angles to the tube, was shown. This property of neon Professor Fleming makes use of in his ingenious wave-detector for wireless telegraphy—the cymometer.

The most volatile gases being neon, hydrogen, and helium, when a charcoal bulb attached to a sparking tube filled with helium was placed in liquid air, the nature of the luminosity remained unchanged, thus indicating that hardly any absorption had taken place at the temperature of liquid air. But on replacing the liquid air by liquid hydrogen under exhaustion, the pressure was so much reduced that the discharge no longer passed. This observation corroborates the statement already made that the boiling-point of hydrogen is a temperature for helium which corresponds with the boiling-point of air for hydrogen, and leads us to infer that the boiling-point of helium is about 5° to 6° absolute.

Measurements made in 1902, by what was called the float-method of separation, showed that the atmosphere contained as a minimum one part in 70,000 of neon, and one part in 362,000 of helium. Recent determinations by the charcoal method, made by Sir William Ramsay, give these proportions as one part in 80,790 of neon and one part in 245,300 of helium, or one part in 61,000 of both these gases together. The absorption of 30 litres of air by 500 grms. of charcoal gives a residuary pressure amounting to between 1·4 and 1·5 mm. of mercury pressure; thus representing a partial pressure of unabsorbed gases—helium, neon, and hydrogen—amounting to 1/5300 of the volume of the original air used in the experiment.

Separation of the Less Volatile Gases, Krypton and Xenon, by Charcoal.

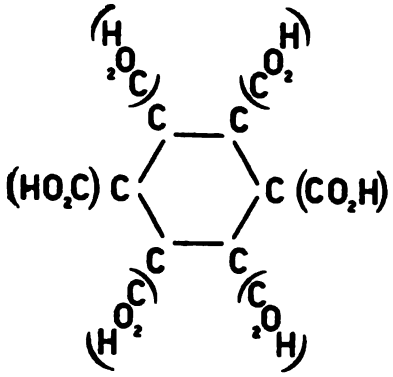
The method of separating carbonic acid from air shown in the Friday Evening Address for 1905 is equally applicable to the separation of krypton and xenon. A current of air passes through a series of tubes immersed in liquid air for the purpose of purification, the final tube containing cotton-wool in order to retain any dust of the solid condensed impurities. This pure air is passed through a tube containing about 100 grms. of charcoal, the current being maintained for at least twenty-four hours. The charcoal tube is now removed and placed in solid carbonic acid, any gas coming off being allowed to escape. The gas remaining in the charcoal at −78° C. is now got out by heating and exhaustion, and all the carbon compounds and oxygen removed from it. The remaining gas, nitrogen containing krypton and xenon, is separated into its constituents by condensation and fractionation. Instead of passing a current of air over charcoal at −183° C., a few hundred grms. of charcoal may be covered with old liquid air, and the latter allowed to evaporate in a silver vacuum vessel, the gases remaining in the charcoal being separated as above. In this way krypton and xenon are readily separated from air and spectrum tubes easily prepared.

Charcoal Thermometer and Calorimeter.

Charcoal saturated with gases at low temperatures may be used as a thermoscope or calorimeter. Attention has been called to the law of absorption, that when the volume is constant, the pressure falls very rapidly with the temperature; in fact, the curve connecting them, when pressure is plotted as ordinate to temperature as abscissa, drops almost vertically as the temperature diminishes to the absolute zero, and a similar relation holds for the volume absorption at constant pressure. Hence, a small change of temperature is accompanied by a great change of pressure or volume absorption as the case may be. This was exemplified in the following experiment:—A charcoal bulb A (Fig. 20) previously saturated with air at −185° C. or hydrogen at −253° C. at any required pressure, the most convenient being atmospheric pressure, was immersed in a bath, B, of the corresponding liquefied gas

contained in a vacuum-jacketed vessel; and a tube, C, was led from it to a Leslie thermometer containing a sulphuric acid cylinder used as a registration instrument for volume. The gauge consisting of a U-tube, with bulbs on each side, to prevent any sudden sucking back of the drop of sulphuric acid, E, renders visible the slightest alteration of the volume of gas occluded in the charcoal. The upper ends of the U-tube were connected by a by-pass containing a stop-cock D. On shutting this stopcock after the complete saturation of the charcoal with air has been effected, equilibrium of pressure between C and F could be obtained, while the sulphuric acid drop E occupied a convenient position in the gauge. On the approach of a candle-flame to the charcoal bulb, the gauge immediately showed a considerable expansion, notwithstanding that the radiant heat had to traverse a considerable quantity of liquefied gas and several thicknesses of glass tubing. In the same manner a beam of light thrown on the charcoal bulb when charged with hydrogen instead of air immediately affected the gauge in a striking way.

The apparatus can be rendered still more sensitive by the following device (Fig. 21):—The charcoal bulb, A, saturated with air at −185° C., is surrounded with another larger bulb giving an annular space that can be filled with



Mellitic Acid

Fig. 22.—Graphical Formula of Mellitic Acid.

liquid air by opening the stopcock C, the orifice D being open while immersed in a large vacuum-jacketed reservoir, V, of liquid air. The tube E leading from A passes to a sulphuric acid manometer, with by-pass and stopcock, F, as before, thence to the open end, H. The apparatus works thus:—Before the radiant beam is turned on A, the annular space between the bulbs is cleared of liquid by blowing a little air through the tube C, and shutting the stopcock, thus forcing the liquid air out by the aperture D. The charcoal bulb is now surrounded by an atmosphere of liquid air vapour, or hydrogen, as the case may be, maintained at the boiling-point by the liquid in V. In these circumstances the maximum effect of any heat given to the charcoal bulb is obtained. The effects are magnified two or three times compared with those given by the charcoal bulb left in direct contact with the liquid.

The special value of this instrument for thermometric measurements is that it becomes more sensitive as the temperature falls, thus placing in our hands a most efficient thermometer for the lowest temperatures which can possibly be reached. Thus, when the charcoal is saturated with hydrogen gas at the boiling-point of hydrogen, the instrument has its maximum delicacy under ordinary circumstances; but provided helium was absorbed in charcoal at and below the temperature of solid hydrogen, then we can predict that the instrument would be still more sensitive to radiant energy.

If, further, the charcoal occupies an annular space surrounding another smaller bulb, into the interior of which any small heated object is inserted, the apparatus becomes a very sensitive calorimeter.

Much investigation is still necessary to clear up the nature of the various charcoals and their properties. One chemical character they possess, and that is that, by powerful oxidising agents like concentrated nitric acid or permanganate of potash, they seem all capable of giving a greater or less yield of an acid called mellitic acid, the graphical formula of which is represented in Fig. 22, which occurs in nature as the aluminium salt commonly called honeystone. This acid, we know, is a derivative of benzol, and its production from charcoal suggests that the latter has a structure of double benzine rings, each containing twelve atoms of carbon, such as is shown in Fig. 23. This gives a fundamental molecule containing a

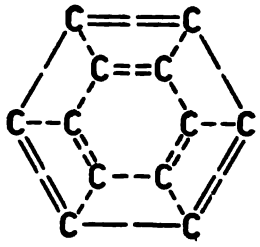


Fig. 23.—Graphical Formula of Charcoal Molecule.

large number of latent valences available for chemical or physical combination, and this structure may have something to do with the general absorptive power of charcoal.

The Professor thanked his assistants, Mr. R. N. Lennox and Mr. J. W. Heath, for valuable aid in the conduct of these experiments.

A METHOD OF DEPOSITING COPPER UPON GLASS FROM AQUEOUS SOLUTIONS IN A THIN BRILLIANTLY REFLECTING FILM, AND THUS PRODUCING A COPPER MIRROR.*

By F. D. CHATTAWAY, F.R.S.

Many organic substances which undergo oxidation easily are able to reduce various metallic oxides. The oxygen is removed with very different degrees of readiness, and the property is in consequence often used as a means of recognising particular compounds or atomic groupings.

Silver oxide is especially easily reduced, and if it is dissolved in an aqueous solution of ammonia the metal, by an appropriate agent, as Liebig first observed (*Annalen*, 1835, xiv., 133), may be obtained attached to the glass walls of the containing vessel as a brilliant reflecting film.

This observation has received an important industrial application in the manufacture of mirrors, and silver thus deposited has now practically replaced the tin amalgam formerly used, which so often seriously affected the health of the workers.

With the view of improving the processes originally used, many chemists have studied the conditions under which glass is coated with silver, but their investigations have generally had for their object the preparation of a liquid which would deposit a uniform and coherent layer of the metal over a large glass surface at the ordinary temperature. Liebig (*Annalen*, 1856, xcviii., 132) was the first to solve the problem satisfactorily, and his method, in which milk sugar is the reducing agent, was formerly extensively used.

Other metals are not so easily laid down upon glass in a firm reflecting film as is silver, and in particular copper, which is so closely related to it, is not in similar cir-

* A Paper read before the Royal Society, November 21, 1907.

cumstances so deposited. Metallic copper has been attached to glass in various ways. Faraday (*Phil. Trans.*, 1857, p. 145), about the time when silver mirrors were attracting much attention, made the interesting observation that a mirror-like deposit of the metal upon glass having the proper metallic lustre and colour by reflection could be obtained by dissolving a little oxide of copper in olive oil and heating plates of glass in a bath of this liquid up to the decomposing temperature of the oil. Mirrors, however, obtained by Faraday's method, if of any size, are liable to be stained and discoloured in patches by decomposition products of the oil, and they are, moreover, generally lacking in brilliancy. Further, as the deposition of the metal only takes place at a temperature above that at which the oil decomposes, the process is excessively disagreeable to carry out, and, as the oil is spoiled, it is somewhat costly.

Faraday also discovered (*Phil. Trans.*, 1857, p. 154) that a fine deposit of copper upon glass could be produced by deflagrating the metal in the neighbou hood of the glass by a Leyden battery in an atmosphere of hydrogen, and Wright, employing a method essentially the same (Silliman, *Amer. Journ.*, 1877, [3], xiii., 49), obtained small brilliant mirrors of copper on the inner surface of exhausted glass tubes by passing through them an electric discharge between copper electrodes.

Everyone who has reduced Fehling's solution with excess of grape sugar must have noticed that occasionally the metal produced adheres to the sides of the beaker or flask in somewhat reflecting patches, and much brighter patches are obtained when certain copper salts such as formate or acetate are heated in glass vessels. The firm of Weisskopf, in Morchenstein, has further succeeded in depositing copper upon glass by reducing the hydroxide in presence of zinc chloride together with gold or platinum chloride by a somewhat complicated liquid mixture containing cane-sugar, glycerin, and formaldehyde.

These facts lead to the conclusion that copper should be capable of deposition in the same way as silver, if a suitable reducing agent were forthcoming; this I have recently found in phenylhydrazine.

Phenylhydrazine, as I have elsewhere showed (*Trans. Chem. Soc.*, 1907), especially in presence of caustic potash, which greatly accelerates the action, is easily oxidised by free oxygen, there being produced in all likelihood hydroxyphenylhydrazine, which immediately breaks down into a molecule of benzene, a molecule of nitrogen, and a molecule of water thus:—

$$C_6H_5{-}N(H){-}N(H){-}H + O = C_6H_6{-}N(H){-}N(OH){-}H = C_6H_6 + N_2 + H_2O.$$

Copper oxide acts similarly upon the base, and under suitable conditions the metal can be deposited upon glass in the form of a fine mirror.

The operation may be carried out in a variety of ways, using finely divided black copper oxide suspended in a boiling saturated solution of phenylhydrazine or a liquid made by mixing the latter with a solution of copper hydroxide in alkaline tartrates or ammonia.

The following procedure, which resembles that employed in silvering glass, gives a uniformly excellent result:—Heat a mixture of one part of freshly distilled phenylhydrazine and two parts of water till a clear solution is obtained. To this add about half its bulk of a warm saturated solution of cupric hydroxide in strong ammonia. Nitrogen is freely evolved during the addition, and the cupric is reduced to cuprous hydroxide, which remains dissolved in the ammoniacal liquid, and does not undergo any immediate appreciable further reduction until heated. Add next a hot 10 per cent solution of potassium hydroxide until a slight permanent precipitate of cuprous hydroxide is produced. If this colourless or pale yellow liquid be cautiously heated in contact with a perfectly clean glass surface, metallic copper is deposited upon it in the form of a thin coherent perfectly reflecting lamina.

As nitrogen is evolved during the reduction, and as tarry by-products are formed in small quantity and float with the benzene produced to the surface of the liquid, if flasks or tubes are to be coppered, devices have to be adopted to keep the inner surface completely covered by the liquid from which the metal is being deposited, whilst allowing the gas to escape.

If the glass in any part is not perfectly coated, the process may be repeated, but a uniform deposit is seldom obtained unless the whole surface is covered in one operation. To obtain a film of sufficient thickness to be permanent, and to prevent its superficial oxidation, it is best to allow it to remain for an hour or so in contact with the warm reducing fluid, and not to pour this off till it has cooled to the temperature of the air. The surface of the deposited copper should then be well washed, first with water, and afterwards with alcohol and ether, and finally should be protected from the slow oxidising action of the air by one or two coats of some quick-drying varnish.

Very little of the phenylhydrazine is actually used up in the reduction, and the same fluid may be employed again and again after filtering while warm through cotton-wool and mixing with more solution of copper hydroxide, adding fresh phenylhydrazine when necessary to compensate for the dilution. If required for future use, the liquid must be kept in a stoppered bottle carefully protected from the air, as free oxygen is very readily absorbed by it and the phenylhydrazine thereby destroyed.

The mirrors obtained by this method are very beautiful, for they show the pleasing red colour of copper, and are as perfect in reflecting surface and as lustrous as the similar mirrors obtained by the deposition of silver.

To carry out the operation successfully, it is essential to cleanse very thoroughly the surface of the glass; this is best done by well rubbing in turn with a strong solution of soap, with strong nitric acid, and with strong caustic potash, using a pad of cotton-wool soaked in these liquids, and washing well between the successive operations.

Surfaces of blown glass are more readily coated with copper than polished surfaces. In any case old glass should not be used, at least without the surface being carefully re-polished.

Ammonia in excess hinders the deposition of copper, as it does that of silver, while caustic alkali accelerates it.

It is interesting to note that the copper is in the monovalent or cuprous state, in which it is analogous to silver, when it shows a similar tendency to be deposited in a metallic film upon glass.

Little is known as to the reasons why, when metallic oxides are reduced in aqueous solutions, the metals under certain conditions are deposited upon glass in a thin reflecting lamina, while under others, apparently equally favourable to such deposition, they separate in a spongy or flocculent state. Vogel (*Journ. Prakt. Chem.*, 1862, lxxxvi., 321) concludes from his experiments with silver oxide that when complete reduction takes place in one stage, a mirror or crystalline deposit is obtained, whilst granular or finely-divided silver is produced in two stages, a lower insoluble oxide separating as the primary product of the reduction, and being afterwards itself further reduced.

The behaviour of copper oxide on reduction makes it, however, very improbable that the various stages of the process affect the result.

For the production of a mirror it appears rather to be essential that the compound undergoing reduction shall be in solution, and that its concentration shall be small, that the liquid in which it takes place shall be alkaline, and that action shall be more rapid at the surface of the glass than elsewhere.

It is certain that the nature of the surface on which the metal is deposited plays an important part in the process, since both silver and copper are deposited much better upon blown than upon polished glass and upon surfaces which have not for long been exposed to the action of the air or of water.

It seems probable that the glass surface itself acts a catalyser and locally accelerates the action.

Oberbeck, some years ago, measured the electric resistances of a number of silver films deposited upon glass from aqueous solution (*Ann. der Physik und Chemie*, 1892, p. 282).

He made the interesting discovery that such resistances, although very large immediately after the metal had been deposited, continually diminished with time, and although a minimum was not reached in two years, ultimately approximated to the resistances which would have been shown by films of ordinary silver of corresponding thickness and size. The films during this change of resistance altered neither in reflecting power nor in appearance when viewed by transmitted light.

As reflecting silver films of very different thickness and initial resistance and produced under very different conditions all showed this great increase in conductivity, Oberbeck concluded that when silver is first deposited from aqueous solution in the form of a mirror, it is in a different molecular condition from ordinary silver, but that in time its state approaches that of the latter more and more.

THE RAPID DETERMINATION OF NICKEL IN THE PRESENCE OF CHROMIUM, IRON, AND MANGANESE.

By C. M. JOHNSON.

IN applying the method of T. Moore (CHEMICAL NEWS, lxxii., 92) to the determination of nickel in steel, the directions given by Brearley and Ibbotson on p. 183, "Analysis of Steel Works Materials," were followed:—One grm. of steel was dissolved in a 150 cc. beaker with 10 cc. of concentrated hydrochloric acid diluted with an equal volume of water.

When action ceased 10 cc. of nitric acid (1·20) were added and the contents of the beaker were boiled to about one-half. 16 cc. of dilute sulphuric acid were poured into the solution and also 3 grms. of powdered citric acid. The solution was stirred until the citric acid was dissolved, transferred to a 600 cc. beaker, and rendered faintly but distinctly ammoniacal.

The nickel was titrated with a standard solution of potassium cyanide, using a measured amount of standard silver nitrate and 2 cc. of a 20 per cent solution of potassium iodide as an indicator. The deep red colour of the citrate of iron greatly obscures the end-point. The authors complain of this colour and recommend the use of a condensing lens to cast a beam of light through the darkness. In the presence of chromium the writer found that a still more sombre gloom settled down over the close of the reaction. The authors mentioned also state that this element retards the union of the cyanide and the nickel, causing the recurrence of the cloud of silver iodide.

After struggling with the process for some time and always carefully separating the chromium, and with it the iron, in chrome steels, an attempt was made to dispel the darkness and also to avoid these tedious separations:—Less citric acid per grm. of steel was taken and the dark red shaded to blackness.

Naturally, the amount of citric acid per grm. of steel was then increased, that is, 6 grms. of citric acid per grm. of steel were used, and a marked improvement was noted. Still more citric acid caused a complete lifting of the shadows.

The following modified procedure was finally adopted for nickel steels after having been thoroughly tested with plain carbon steels to which known amounts of nickel had been added: Dissolve 1 grm. of steel drillings in a 150 cc. beaker with 20 cc. of hydrochloric acid (1:1). When action ceases add 10 cc. of nitric acid (1·20).

Reduce the volume of the solution to about 15 cc., keeping the beaker covered during the boiling. Remove the beaker from the fire and pour into it 8 cc. of concentrated sulphuric acid diluted with 24 cc. of water. The presence of the sulphuric acid is essential to a sharp end reaction between the cyanide standard and the silver iodide in the subsequent titration.

Transfer the contents of the beaker to one of 600 cc., capacity containing 12 grms. of powdered citric acid. Stir until the citric acid is dissolved. Render this solution *faintly* but *distinctly* alkaline with ammonia, using one part of concentrated ammonia diluted with one part of water. A large excess of ammonia causes low results. Stand the beaker in running water until it is cold. The volume of the solution should now be about 300 cc. Much larger volumes than 300 cc. should be avoided, as great dilution retards the end-point, causing the cloud of silver iodide to disappear and then to reappear again in a few minutes.

The faintly ammoniacal condition can be easily controlled by adding the ammonia rather slowly and noting the changes of colour that ensue: The first change is to amber, then to yellowish-green, then to distinct green, then to a light shade of green, then to a yellow almost matching the yellow colour of the acid solution. The reappearance of the yellow tint indicates that alkalinity is nearly attained.

A little more ammonia now causes a brownish shade, which is evidence that the ammonia is in slight excess. The moderately alkaline citrate of iron obtained in the proportion of 1 grm. of iron to 12 grms. of the citric acid yields a bright greenish-yellow solution in plain nickel steels instead of being of a dense dark red shade!

To the cold solution, 2 cc. of a 20 per cent solution of potassium iodide are added. From a 50 cc. burette a standard solution of silver nitrate is dropped into the same beaker, producing with the iodide a white turbidity. The standard potassium cyanide is added with constant stirring until the cloud of silver iodide just disappears, which it does on being converted into silver cyanide. Nickel cyanide is first formed and then the silver cyanide is produced:—

1. $Ni(NO_3)_2 + 4KCN = Ni(CN)_2.2KCN + 2KNO_3$;
2. $AgNO_3 + 2KCN = AgCN.KCN + KNO_3$.

If the directions are followed as given, the titration can be accomplished at almost the full speed of the burette. If the titrated solutions are permitted to remain in the open beakers for a time, a film usually appears on the surface of the liquid. No account is taken of it as its presence is most likely due to a superficial loss of ammonia. The reactions are always found to be completed when the body of the solution is freed of the iodide precipitate.

Standards.—From the equations as given, 5·85 grms. of silver nitrate are equivalent to 4·4868 grms. of potassium cyanide. This weight of cyanide dissolved in one litre of water gives a value of 1 cc. equals about 0·001014 grm. of nickel.

As comparatively little silver nitrate is needed with each analysis, it is not advisable to prepare more than a-half litre of the water solution of this salt, using 2·925 grms. per 500 cc. of distilled water.

The potassium cyanide standard should contain about 5 grms. of potassium hydroxide to the litre, which renders it quite permanent. The solutions are readily standardised by applying them to a plain steel to which a known amount of nickel has been added. The chemically pure double sulphate of nickel and ammonium is a convenient standardising medium. For example, 0·2 grm. and 0·25 grm. of the double sulphate can be weighed into 150 cc. beakers together with 1 grm. of plain carbon steel drillings.

This mixture is then put through all of the foregoing manipulations and titrated with the cyanide solution that is to be standardised. The number of cc. of the silver nitrate and of the potassium cyanide solution used in this titration are noted. An excess of 10 cc. of the cyanide is now added and in turn titrated with the silver nitrate solution until a distinct cloud of silver iodide is produced.

This second titration gives the relation between the silver solution and the cyanide.

An actual case will illustrate the calculations:—In Sample No. 3477, 1·7 cc. of standard silver nitrate solution were required to produce a distinct turbidity and also to combine with any excess of potassium cyanide standard. In all 35 cc. of the cyanide were consumed in the titration. When the cloud of silver iodide had just been dispelled an excess of 9·8 cc. of cyanide was allowed to flow into the clear solution. Just 10·1 cc. of silver nitrate standard were needed to produce a reappearance of the cloudiness. Therefore 9·8 ÷ 10·1 = 0·97, or 0·97 cc. of cyanide standard solution equals 1 cc. of silver nitrate. Hence instead of deducting 1·7 cc. from 35 cc., 1·7 × 0·97 or 1·65 cc. were deducted, leaving 33·35 cc. of cyanide combined with the nickel in this steel.

To a plain carbon steel 0·200 grm. of double sulphate of nickel and ammonium were added, put through all of the steps of a regular analysis. This mixture required 28·75 cc. of cyanide. The nickel salt contains 14·86 per cent of nickel or 0·200 + 0·1486 = 0·02972 grm. of nickel were present. Hence 0·02972 ÷ 28·75 = 0·00103 or 1 cc. of standard cyanide solution is equivalent to 0·00103 grm. of nickel. No. 3477, as has been stated, required 33·35 cc. of the cyanide standard, and therefore contains 0·00103 × 33·35 = 0·03435 or 0·03435 grm. of nickel or 3·435 per cent.

Chromium-Nickel Steels.—When chromium is present proceed exactly as in plain nickel steels except that 24 grms. of citric acid per grm. of steel are used. This proportion of citric acid is adequate to render the end-point quite as easy to see as in ordinary nickel steels. The action is prompt and free from recurrence of turbidity. Of course cloudiness through the entire solution will occur, as the ammonia is dissipated from it, after it has stood for some time in an open beaker.

Table I. furnishes satisfactory proof that chromium does not interfere with the successful technical estimation of nickel in its presence.

TABLE I.

Sample No.	No chromium added. Nickel found, per cent.	Per cent of chromium added to a portion of the same steels.	Nickel found after the addition of varying amounts of chromium.
525	5·09	4·0	5·10
2991	4·44	2·0	4·45
7239	3·24	1·0	3·28
3017	4·96	1·0	5·03
612	3·47	0·5	3·47
7273	3·29	1·0	3·31
622	3·56	0·5	3·56
7288	3·32	2·0	3·41
7289	3·11	2·0	3·16
663	3·57	6·0	3·59
2991	4·44	3·0	4·47

The chromium was introduced in the form of re-crystallised chemically pure potassium dichromate. The dichromate crystals were mixed with a weighed amount of nickel steel drillings before the addition of the 20 cc. of hydrochloric acid. The combined action of the nascent hydrogen from the steel, the excess of boiling hydrochloric acid, and the ferrous chloride reduced the chromate to chromic chloride, thus duplicating the conditions found when a chromium-nickel is similarly treated.

Determinations by this modification of the cyanide method can be finished in from forty-five to fifty minutes, either in the presence or absence of any per cent of chromium likely to be met with in steels or alloys soluble in the acids given. In this laboratory *duplicate* determinations in nickel or nickel-chromium steels are made in the time just specified. By the process one can decide in a few minutes whether or not nickel is present in a given steel and just how much. Tungsten, if present, does not interfere appreciably, as has been noted by the authors mentioned in this article. The writer had two different amounts of nickel added to a steel containing several per cent of chromium and 16—17 per cent of tungsten. This steel was then carried through exactly as though no tungsten or chromium were present, using the method as given for chromium-nickel steel.

Nickel added (grm.) ..	0·0297	0·03715	None
Nickel found	0·0299	0·0372	0·0006

Tests were then made in the same manner in the presence of molybdenum and vanadium as follows:—

TABLE II.

Name.	Kind of steel or mixture.	Nickel added. Grm.	Nickel found. Grm.
J. R. steel. ..	Contains 10 per cent ± Mo	0·0297	0·0295
		0·0222	0·0223
		None	0·0002
Bxx—173 steel.	Contains 4 per cent Mo and 4 per cent Cr	0·0223	0·0222
		0·0297	0·0296
		None	0·0004
A mixture. ..	0·920 grm. of steel .. 0·030 „ nickel .. 0·018 „ vanadium	0·0297	0·0298
A mixture. ..	0·840 „ steel .. 0·022 „ nickel .. 0·035 „ vanadium	0·0223	0·0227
A blank	1·000 „ steel .. 0·035 „ vanadium	None	0·0008

Table II. demonstrates that neither vanadium, tungsten, chromium, nor molybdenum, when present in the amounts given, interferes appreciably in technical analysis. These amounts represent extreme cases, especially for the vanadium, it being equivalent in one instance to 3·5 per cent V when 1 grm. of steel is taken.

As copper also forms cyanides, its presence would cause results to be too high, but copper is religiously avoided in good steel making. Its presence is extremely unlikely in greater amounts than 0·06 per cent, although the writer, on one occasion, found as much as 0·25 per cent in a low carbon steel, not a *crucible* steel, however. Crucible steel rarely contains over 0·04 per cent copper. The choice brands are under 0·02 per cent in copper.

Wishing to test the extent to which nickel could be titrated in the presence of large percentages of chromium, iron being also present, the mixtures as given in Table III. were titrated with potassium cyanide. The various salts were weighed into 150 cc. beakers, together with the proper amounts of steel drillings. The same proportions of hydrochloric, nitric, citric, and sulphuric acids were employed as are herein given for nickel-chromium steels, and were applied in the same manner.

A sufficient quantity of the salts of chromium and nickel, and of the steel drillings, were taken to give a total of one-half grm. of metals in the mixture.

Double sulphate of nickel and ammonium [$(NH_4)_2SO_4.NiSO_4.6H_2O$], potassium dichromate, and steel drillings free from nickel were used as sources of nickel, chromium, and iron, respectively.

To obtain the nickel value of the cyanide standard under conditions similar to those existing in the mixtures tested, standardising mixtures of these salts were prepared varying from the mixtures tested as much as 1 per cent to 20 per cent in the different constituents.

For mixtures exceeding 10 per cent of nickel, a standard cyanide solution with a nickel value of 1 cc. = 0·0031 grm. of nickel was used. The standardising mixtures were dissolved and treated exactly as the mixtures tested. The same method of standardisation was observed in the work recorded in Table IV.

TABLE III.

Per cent of metals. Ni.	Cr.	Fe.	Grm. of nickel added.	Grm. of nickel found.	
30	40	30	0·1499	0·1494	0·1495
60	20	20	0·2999	0·3003	0·2989
20	40	40	0·1029	0·1022	—
5	90	5	0·0250	0·0248	0·0244
4	92	4	0·0200	0·0199	—
1·5	95	3·5	0·00749	0·00805	0·00822
0·5	99	0·5	0·00249	0·00225 0·00247	0·00243 0·0026
0	98·9	1·0	None	None	

Table III. demonstrates that nickel may be estimated by the foregoing modified cyanide process, using the proportions of citric acid as given, with sufficient accuracy for works analysis, and indeed for most practical purposes; even when the percentage of chromium is as much as 99 per cent, and the nickel content is but one-half of 1 per cent.

The titration of the mixtures given in Table III., and containing the larger amounts of chromium, requires considerable practice on the part of the operator. The work should always be carried out in duplicate. The disappearance of the cloudiness in the presence of 0·100 to 0·450 grm. of chromium in a volume of 350—400 cc., is much more exactly observed when the mixture containing the iodide cloud is compared, from time to time, with a *similar* mixture which is perfectly free of this milky turbidity. The dilution of the deep purple, or wine colour, of these ammoniacal mixtures of citrates to more than 300 to 400 cc., renders the end-point but slightly more distinct, and has the great objection of retarding the reaction between the cyanide and the nickel. The increase above 24 grms. of citric acid in the solution, even to the extent of adding 60 grms. of citric acid, did not relieve the density of colour to any perceptible extent.

When titrating with a standard, 1 cc. of cyanide = 0·0031 grm. of nickel (three times the strength used for steels) do not also increase the strength of the silver standard to equal it, but still retain the silver nitrate standard as given for steels. A silver nitrate solution sufficiently concentrated to be equivalent, volume for volume, to the cyanide standard (1 cc. =0·0031 grm. of nickel), on being dropped into the solution containing the potassium iodide, does not produce the usual opalescence alone, but also forms curds of iodide that do not readily combine with the cyanide standard. The end-point is reached and the main body of the solution is free of cloud while curds of silver iodide still lie on the bottom of the beaker. The weaker silver nitrate standard, or 5·85 grms. of silver nitrate to the litre, produces with the potassium iodide a finely divided cloud of precipitate that combines promptly with the strong cyanide standard, giving a sharp end-point. Weigh, therefore, 2·925 grms. of silver nitrate, diluting to 500 cc., and 13·4604 grms. of the best grade of potassium cyanide, diluting to 1000 cc., for titrations of solutions containing from 0·100 to 0·300 grm. of nickel; 1 cc. of this silver nitrate solution should be equivalent to one-third cc. of the concentrated cyanide standard (1 cc. cyanide = 0·0031 ± grms. of nickel).

The titration of nickel by potassium cyanide in mixtures containing large percentages of manganese with varying amounts of chromium and iron was also tried.

As in the experiments outlined in Table III., mixtures were prepared to contain one-half grm. of metallic substances. The same nickel and chromium salts were employed. Potassium permanganate crystals supplied the manganese.

The crystals of double sulphate of nickel and ammonium, potassium dichromate and potassium permanganate, were weighed into a 150 cc. beaker with the steel drillings. To this were added 20 cc. of dilute hydrochloric acid. The contents of the beaker were then boiled, after the first action was completed, until the chromate and permanganate were reduced. An addition of 10 cc. of nitric acid (1·20) followed, and the analysis was carried out exactly as given for chromium-nickel steels, using 24 grms. of citric acid. The results obtained are given in Table IV. Sulphuric acid was added as in the process for steels.

TABLE IV.

Per cent of metals. Ni.	Mn.	Cr.	Fe.	Grm of nickel. Added.	Found.
41	20	10	30	0·2059	0·2058
20·6	40	20	20	0·1029	0·10228
15	60	15	10	0·0750	0·0752
1·5	95·5	1	2	0·00749	0·00762
0·25	94·9	2	2·9	0·00124	0·00122
—	94·9	2	4	None	0·00006

Table IV. gives evidence of the fact that nickel can be accurately determined in the presence of large percentages of chromium and manganese, if the conditions herein given are carefully observed. In the hands of a practised operator no difficulty was experienced in the analysis when as much as 95 per cent of manganese was in solution with but 0·25 per cent of nickel.—*Journal of the American Chemical Society*, xxix., No. 8.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 23, December 2, 1907.

This number contains no chemical matter.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 16, 1907.

Electrolytic Reduction of Ethyl Barbituric Acids.—Julius Tafel and Herbert Bryan Thompson.—When 5 . 5-diethyl barbituric acid (veronal) is reduced electrolytically only one crystalline substance is produced. This is 5 . 5-diethyl-4 . 6-dioxy-2 . 5-dihydropyrimidine—

$$\begin{matrix} NH—CO \\ CH_2 \quad C(C_2H_5)_2. \\ NH—CO \end{matrix}$$

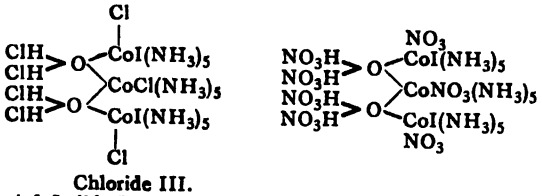
5-Monoethyl barbituric acid under the same circumstances yields 5-ethyl hydrouracyl and 5-ethyl trimethylene urea. It is much more easily reduced than the diethyl derivative. Barbituric acid itself yields hydrouracyl and trimethylene urea. This striking difference in the behaviour of barbituric acid and its monoethyl derivative on the one hand, and the diethyl derivative on the other, is undoubtedly due to the fact that in the two first compounds the malonyl carbonyl is much more easily reduced electrolytically than urea carbonyl, but that the introduction of a second ethyl group into the molecule makes the carbonyl of the carbon chain less easily reducible than the urea carbonyl.

Cobaltic Pentammins.—J. Sand and G. Bokman.—When nitric acid acts upon ammoniacal solutions of cobaltous salts two different series of compounds result. The salts of one group, the cobaltous-nitroso-pentammins, contain divalent cobalt and form glittering black crystals. These black compounds isomerise to the red cobaltic-nitroso-pentammins, which contain trivalent cobalt, and unlike the black compounds are very stable towards water. The black chloride and nitrate, when treated with alcoholic iodine solution, yield green substances which belong to a hitherto unknown type of condensed cobaltic pentammins. It was found that the iodide contained considerable

quantities of chlorine. The quantitative analysis of the substances leads to the following complicated formulæ :—

I. Precipitated with KI $Co_3I_2Cl(NH_3)_{15}I_6.2H_2O$
II. Precipitated with HNO_3 .. .. .. $Co_3I_2Cl(NH_3)_{15}(NO_3)_6.2H_2O$
III. Precipitated with HCl .. .. .. $Co_3I_2Cl(NH_3)_{15}(Cl_6.2H_2O$
IV. Black nitrate + I; boiled with HNO_3 $Co_3I_2(NO_3)(NH_3)_{15}(NO_3)_6.2H_2O$

The conductivity of a freshly prepared solution of the green chloride III. was found to be three times as great as that of a ternary electrolyte. Hence this salt must contain to one cobalt atom two ionisable acid radicles. In the complex cation there are always present 2 I and 1 Cl to 3 Co, or 2 I and 1 NO_3, in non-ionogenic combination, as well as the fifteen purpureo ammonia residues. It is noteworthy that all four salts after being dried in vacuo contain 2 H_2O molecules for 3 Co. Probably these water molecules join the three cobalt atoms in the complex. The possible structural formulæ are—



Chloride III.
(*cf.* Iodide I., Nitrate II.).

Compounds of Tetravalent Molybdenum.—J. Sand and Johanna Maas.—The electrolytic reduction of molybdic acid in hydrogen sulphocyanide solution gives, besides sulphocyanides of pentavalent molybdenum, very complex salts in which a central molybdenum atom with four principal valencies is present. A very characteristic zinc salt, $[Mo(SCN)_6(NH_3)_4]Zn$, can be prepared by saturating the reduced solution with ammonia and precipitating the filtrate with ammoniacal zinc chloride solution. From this zinc salt a series of salts of the type $Mo(SCN)_6(NH_3)_3H_2$ can be obtained. Salts of this constitution yield addition products with acetic acid, ethyl alcohol, and propyl alcohol. The tetravalency of the molybdenum can be proved by heating weighed quantities of the zinc salt in carbon dioxide, cooling, adding manganese sulphate, and dilute sulphuric acid, and titrating the solution with permanganate.

MISCELLANEOUS.

The Andrew Carnegie Research Scholarship.—A Research Scholarship or Scholarships, of such value as may appear expedient to the Council of the Iron and Steel Institute from time to time, founded by Mr. Andrew Carnegie (Past-President), who has presented to the Iron and Steel Institute eighty-nine one-thousand dollar 5 per cent Debenture Bonds for the purpose, will be awarded annually, irrespective of sex or nationality, on the recommendation of the Council of the Institute. Candidates, who must be under thirty-five years of age, must apply on a special form before the end of February to the Secretary of the Institute. The object of this scheme of Scholarships is not to facilitate ordinary collegiate studies, but to enable students, who have passed through a college curriculum or have been trained in industrial establishments, to conduct researches in the metallurgy of iron and steel and allied subjects, with the view of aiding its advance or its application to industry. There is no restriction as to the place of research which may be selected, whether university, technical school, or works, provided it be properly equipped for the prosecution of metallurgical investigations. The appointment to a Scholarship shall be for one year, but the Council may at their discretion renew the Scholarship for a further period instead of proceeding to a new election. The results of the research shall be communicated to the Iron and Steel Institute in the form of a paper to be submitted to the Annual General Meeting of members, and if the Council consider the paper to be of sufficient merit, the Andrew Carnegie Gold Medal shall be awarded to its author. Should the paper in any year not be of sufficient merit, the medal will not be awarded in that year.

MEETINGS FOR THE WEEK.

Tuesday, 14th.—Royal Institution, 3. "The Internal Ear of different Animals," by Dr. A. E. Gray, F.R.S.E.

Wednesday, 15th.—Microscopical, 8. "The Microscope as an Aid to the Study of the Biology of Insects, with Special Reference to the Foods," by W. Wesché. An improved type of Mercury Vapour Lamp for Use with the Microscope will be exhibited and described by Mr. J. E. Barnard.

—— Society of Arts, 8. "Screen-plate Processes of Colour Photography," by Dr. C. E. K. Mees.

Thursday, 16th.—Royal Institution, 3. "The Building of Britain," by Prof. W. W. Watts, F.R.S., &c.

—— Society of Arts, 4.30. "Indian Agriculture," by Henry Stavely Lawrence, I.C.S.

Friday, 17th.—Royal Institution, 9. "The Centenary of Davy's Discovery of the Metals of the Alkalis," by Prof. T. E. Thorpe, C.B., F.R.S.

Saturday, 18th.—Royal Institution, 3. "The Electrification of Railways," by Prof. Gisbert Kapp, Dr.Eng., M.Inst. C.E.

THE CHEMICAL NEWS.

VOL. XCVII., No. 2512.

THE ATOMIC WEIGHT OF TELLURIUM.

By W. MARCKWALD.

EVER since the periodic system of the elements was established the atomic weight of tellurium has repeatedly been the subject of thorough investigation, because it had been found to be higher than that of iodine, and thus the element did not fit in well with the system.

A. Gautbier (*Sitzungsber. d. Physik.-medizin. Soz. in Erlangen*, 1905, xxxvii., 270) has recently prepared a complete summary of all the publications which have appeared on this subject, and thus it is not necessary for me to go over the same ground again. I shall only touch upon the most important results.

The conversion of tellurium into the oxide by means of nitric acid is not satisfactory for the determination of the atomic weight. B. Brauner (*Monatsh. für Chem.*, 1898, x., 411) thinks that this is because tellurium dioxide does not give up the last traces of oxides of nitrogen until the temperature at which it begins to volatilise is reached (*cf.* also McIvor, CHEMICAL NEWS, 1903, lxxxviii., 17). He obtained results which agreed very well when he determined the bromine in tellurium tetrabromide by titration. His value was 127·71. This value was approximately confirmed by M. Chikasige (*Journ. Chem. Soc.*, 1896, lxix., 881) by the same method.

(NOTE.—All the results given in this paper are calculated with the values given in this year's Table of the International Atomic Weight Commission).

A greater number of workers have studied the quantitative transformation of tellurium dioxide into tellurium. Staudenmaier (*Zeit. Anorg. Chem.*, 1895, x., 189) effected the reduction by a current of hydrogen, and in two experiments, in which altogether only 3·5 grms. of substance were used, found a mean value of Te = 127·57. Almost the same number is obtained when the mean of G. Pellini's (*Ber.*, 1901, xxxiv., 3807) three results, obtained by the same method as Staudenmaier's, is calculated, but the numbers vary from 127·30 to 128·02. K. B. Heberlein (Inaugural Dissertation, Basel, 1898), employing the same reaction, obtained two concordant results, but the value was much lower, viz., 126·99, while Gutbier (*loc. cit.*) in five determinations found 127·55 to 127·68, which agreed best with Staudenmaier. Gutbier obtained almost the same result when he reduced tellurium dioxide in the wet way by means of hydrazine. The differences in the results of different observers are very remarkable. The material used, TeO_2, can easily be obtained pure. On the other hand, it is questionable whether the reduction in the dry way is complete, and whether the occlusion of hydrogen can be entirely prevented. The water formed in the reaction has unfortunately never been weighed.

The basic nitrate, $(TeO_2)_2HNO_3$, which can be converted into dioxide by igniting, has also been used as the starting point of a large number of atomic weight determinations. This method, which was first recommended by Norris, Fay, and Edgerly (*Am. Chem. Journ.*, 1900, xxiii., 105) is evidently closely allied to the method rejected by Brauner, viz., the oxidation of tellurium with nitric acid. While in a long series of experiments in which more than 80 grms. of substance were used, P. Koethner (*Ann. d. Chem.*, 1901, cccxix., 1) obtained exceedingly concordant results, which only varied from 127·55 to 127·66, Gutbier (*loc. cit.*) in eight experiments obtained values from 125·8—127·8. On the other hand, J. F. Norris (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1675) has recently confirmed Koethner's results.

Another point must be taken into consideration in the use of the basic nitrate for atomic weight determinations. It is very sensitive to moisture, so that it can only be freed from the nitric acid mother-liquor by means of absolute alcohol.

Telluric acid was first used by Staudenmaier (*loc. cit.*) to determine the atomic weight of tellurium. He transformed the hydrate, $H_2TeO_4+2H_2O$ or H_6TeO_6, into tellurium oxide by igniting it. From a long series of experiments, in which altogether 22·5 grms. of substance were used, the value 127·16 was calculated. The numbers obtained lay between 127·08 and 127·27. When telluric acid was reduced to tellurium the same author in three experiments, using 4·8 grms. of substance, found the mean value 127·28. Gutbier (*Ann. d. Chem.*, 1902, cccxx., 52), using the first reaction and only 1·5 grms. of substance in two experiments, weighed the water formed in a calcium chloride tube, and not the TeO_2, and found Te = 127·65, and when telluric acid was converted into tellurium obtained the mean value 127·34 (127·00—127·80). Finally, Heberlein transformed 3 grms. of telluric acid into dioxide and weighed the latter; in two experiments he found 126·72 (126·60 and 126·84).

Besides the methods described above many others have been used for the atomic weight determinations. It is not necessary to give details of them here, because either they were described too shortly to be criticised, or else the quantities of substance used were too small.

As those methods which were carried out with the greatest exactitude were always those which give a higher atomic weight for tellurium than that of iodine, many of the above authors have endeavoured to find out whether tellurium is accompanied by an element of higher atomic weight; this assumption was first suggested by Mendeleeff, and Brauner thought he had obtained experimental confirmation of it. However, all attempts to decompose tellurium have given a negative result. Their value has lain in the fact that they have given us excellent methods of preparing pure tellurium. Koethner's method cannot be excelled for this purpose.

Mendeleeff's hypothesis also suggested the experiments I now propose to describe. Telluric acid was subjected to fractional crystallisation on a large scale by the column system, in order to test whether any differences could be observed in the different fractions. Staudenmaier (*loc. cit.*) had already separated telluric acid from its solutions in some fractions, and found that it was not complex, and F. Mylius (*Ber.*, 1901, xxxiv., 2208) had confirmed this result in the course of his complete investigation of telluric acid; but these experiments did not take sufficient account of the possibility of the existence of an isomorphous mixture, which could be split up only by a systematic crystallisation process. I therefore decomposed about 1500 grms. of telluric acid by several hundred crystallisations into twenty fractions of approximately equal size, and found not the least difference between the first and last fractions. If we remember that a similar research which Norris, Fay, and Edgerly (*loc. cit.*) had carried out with potassium tellurium bromide, K_2TeBr_6, on a somewhat smaller scale, also gave a negative result, like all other attempts to decompose tellurium by chemical methods, we can no longer entertain any doubt about its simple nature.

As by these experiments I obtained a large quantity of very pure telluric acid I decided to use it to determine the atomic weight of tellurium, under better conditions than Staudenmaier.

Preparation of the Material.

1¼ kilogrms. of raw tellurium containing more than 75 per cent of tellurium, which had been obtained from the Royal Hungarian Foundries in Selmeczbanya, was first converted into the dioxide, and roughly freed from impurities (copper, lead, silver, &c.). The dioxide was oxidised to telluric acid by chromic acid by a modification of Staudenmaier's method. For this purpose one part by weight of TeO_2 was suspended in 1¼ parts by weight of

nitric acid (sp. gr. 1·4), and the theoretical quantity of chromic acid anhydride, dissolved in five times the quantity of water, was added in small portions. The reaction evolves much heat. Finally, the solution was heated on the water-bath till it had become clear. On cooling, the greater part of the telluric acid formed crystallised out; the residue was obtained by evaporation and then by the addition of strong nitric acid. The telluric acid thus obtained was subjected directly to the above crystallisation process only because it must have been purified in the course of these operations. The last mother-liquors were always re-precipitated with nitric acid, and thus, finally, nearly 1½ kilogrms. of perfectly pure telluric acid was obtained almost without loss. It was not until no impurity except nitric acid could be detected in the last liquors, and in particular no further trace of a sulphuretted hydrogen reaction appeared, that the further crystallisations were undertaken with special precautions. Little flasks of Jena glass were used; they had previously been boiled with water and acids, and finally rinsed out with water vapour. Into these the warm fairly concentrated solutions were filtered, so that on cooling crystals formed in large quantities on the bottom. The narrow necked flasks were protected against dust by means of covers. Then the mother-liquor of each crystallisation was poured without filtration on to the following fraction, the last liquor was concentrated in platinum dishes, and then poured into a Jena flask. If the first crystallisation, which was always re-crystallised from fresh quantities of pure water, had become too small, it was added to the subsequent fraction, previously re-crystallised from pure water. The same process was repeated with the final mother-liquors, except that the last residues, in which nitric acid had accumulated, were finally put aside, by which only a few grms. of telluric acid were removed from the crystallisation process. After about twenty equal fractions had thus been obtained, the last of which was quite free from nitric acid, the material for the atomic weight determinations was separated. For this purpose the fraction chosen was brought into solution by warming with its mother-liquor, the solution was poured into a platinum dish, and allowed to cool quickly, being stirred with a platinum spatulum. The acid separated in a fine crystalline mass. This was well drained on a Nutschen filter, the bottom of which was covered with hardened filter-paper, and dried in a desiccator over sulphuric acid. The only impurity which could still remain in the material was mother-liquor and water. Hence the greatest care was taken to dry the telluric acid. Some of it was allowed to stand in a thin layer in a vacuum over phosphoric acid anhydride until its weight was constant, which was always the case after twenty-four hours, and the rest was very finely powdered and sifted through a fine-meshed gauze sieve, and then treated similarly. Of the following atomic weight determinations Nos. 1, 2, and 5 were carried out with unsifted and the others with sifted material. No difference could be detected. Finally, in one case, No. 6, the telluric acid was allowed to stand for two months in a vacuum over phosphoric acid anhydride. It might have been expected that in this case the telluric acid would have shown some loss of weight, but it did not; 15 grms. of the substance showed a loss of only 0·3 mgrm., *i.e.*, its weight was practically constant.

The Atomic Weight Determinations.

The atomic weight was determined from the telluric acid by transforming it into dioxide, according to the equation $H_6TeO_6 = TeO_2 + O + 3H_2O$. Staudenmaier had used the same reaction, and for this purpose had heated the acid in a hard glass flask, the neck of which was closed by an asbestos stopper. This method seems rather too rough for an atomic weight determination, and I therefore altered it as follows:—

A pear-shaped platinum vessel was employed for the heating, such as F. W. Hinrichsen (*Zeit. Physik. Chem.*, 1902, xxxix., 311) used in determining the atomic weight of calcium and has described fully. As counterpoise a second vessel of exactly the same shape and weight was used. Thus, not only were the reductions of the weighings to vacuo simplified, but also I was independent of errors which might be caused by the increase of weight of larger vessels during the weighing, owing to the formation of a layer of water.

The heating was performed in an electric resistance furnace, which was arranged so that the bottom could be specially heated. The platinum vessel rested on three platinum supports fastened on the bottom, and about three quarters of its height projected above the furnace through a platinum ring. The temperature of the bottom of the vessel was measured by means of a Le Chatelier element with a millivoltmeter. In the upper parts of the platinum vessel the temperature remained a good deal lower, which was necessary in order that the tellurium dioxide might not volatilise. During the experiments the temperature was very slowly raised in the course of two to three hours from 100—160°, because between these temperatures two molecules of water escape, and care had to be taken that the powdery mass did not cake together. This was always successfully avoided when the above method was adopted. Experiment 4, however, was intentionally carried out much more quickly than the others in order to find out when the acid was transformed into the dioxide rather more rapidly, the final result obtained would be nearer Staudenmaier's. The opposite was the case. Hence, in calculating the final result this experiment is excluded as obviously and purposely incorrectly performed.

Then during the next three or four hours the temperature was gradually raised to 650°, and this temperature was maintained for about an hour. The residue then always appeared perfectly white, and was thus free from TeO_3, which, when present even in the minutest quantity, always gives the dioxide a yellow colour. After weighing, the heating was repeated for an hour, sometimes increasing the temperature by 80°, and no decrease of weight was observed.

During the heating in the first four experiments the platinum vessel was kept open until the temperature had risen to 300°, so that the water vapour could escape easily. Then a well-fitting cover was placed loosely on, and taken off when the vessel was taken from the furnace. During the cooling the excess of oxygen contained in the vessel diffused into the atmosphere.

(Note.—Staudenmaier heated in a narrow necked glass flask loosely closed with asbestos. As he did not expel the oxygen by air after heating, the weight of his residue must have been a little too high).

In the last two experiments the method was altered. In order to find out whether some telluric acid volatilised with the water vapour, or some tellurium oxide with the oxygen, the cover described by Hinrichsen (*loc. cit.*) was placed on the platinum vessel, so that a current of dry air could be led through the apparatus during the heating. The escaping water vapour condensed in a platinum tube and dropped into a platinum crucible. The cover, tube, and crucible were weighed before the experiment. After the heating they were heated to 150° in a drying oven and then weighed again. No loss of weight exceeding 0·1 mgrm. was ever observed.

It need hardly be mentioned that all the necessary precautions and corrections were applied to all the weighings. Dry telluric acid is not so hygroscopic that there is any difficulty in weighing accurately in the covered platinum crucible. When allowed to stand in air it does gain considerably in weight.

First of all, a middle fraction of the different crystallisations, viz., the ninth, was used for the experiments. One part of this acid served for the preliminary experiments to perfect the method. In the following table all the results are collected which were obtained in experiments which had atomic weight deterimations for their special aim. The first experiment was performed with the ninth

fraction, the next two with the first, and the last three with the twentieth. The results showed that it was unnecessary to do more experiments. Experiment 4 was excluded for the reasons given above. In the calculation O was taken = 16, H = 1·008.

No.	Fraction.	Weight of H_6TeO_6.	Weight of TeO_3.	Loss of weight (per cent).	Te.	Deviation from mean.
1.	IX.	8·6277	5·9884	30·591	126·93	+0·08
2.	I.	12·2680	8·5135	30·604	126·84	±0·01
3.	I.	13·0051	9·0244	30·609	126·80	−0·05
4.	XX.	8·6415	5·9947	30·629	126·65	—
5.	XX.	8·4588	5·8696	30·6095	126·80	−0·05
6.	XX.	8·0113	5·5599	30·591	126·94	+0·09
		50·3699	34·9558	30·602	126·85	

The experiments thus led to the unexpected result that the atomic weight of tellurium is—

126·85 ± 0·02 (probable error),

thus lower than that of iodine (I = 126·97), and 0·75 units (0·6 per cent) lower than the value given by the International Commission.

It is very improbable that my method could be affected by so large an error. The purity of the material is guaranteed by the agreement in the values obtained with the first and last fractions. It can hardly be supposed that a constant amount of moisture caused the greater loss on ignition, since the result remained the same, whether the telluric acid was left *in vacuo* over phosphoric anhydride either in a coarse mass for one day or in a fine powder for two months. It is equally unlikely that in the experiments described the greater loss on ignition was due to the volatilisation of a tellurium compound. Other sources of error which might give too low a value seem to be absent.

As may be seen from the figures given at the beginning of this article, other workers have found an atomic weight of tellurium differing but little from the value obtained by me. Allusion need only be made to the researches of Staudenmaier and Heberlein. Other facts in the chemistry of tellurium seem to confirm the lower atomic weight. O. Steiner (*Ber.*, 1901, xxxiv., 570) determined in a series of analyses the carbon contained in very carefully purified diphenyl telluride, and calculated from it the atomic weight of tellurium. The results lie between 126·1 and 126·7, while two control experiments with diphenyl selenide gave for Se 78·8 and 79·3 instead of 79·2. In his article the author rightly states that his numbers, even if they have not the importance of trustworthy atomic weight determinations, nevertheless argue against an atomic weight of over 127 for tellurium.

The results which B. Brauner (*Monatsh. fur Chem.*, 1890, xi., 526; 1891, xii., 29), and Gooch and Peters (*Zeit. Anorg. Chem.*, 1899, xxi., 405) obtained in the determination of tellurium dioxide, are very noteworthy. The first-named carried out a very thorough investigation of the subject, and found that all the methods he tested gave too high a value. These methods, which proved to be the best, gave in a long series of experiments 0·20—0·47 per cent, or on an average 0·35 per cent too much. If the value found by me for the atomic weight of tellurium is used in the calculation, Brauner's deviations are −0·27 to ± 0·00 per cent, or an average of −0·12 per cent. Gooch and Peters at the end of their article state that the average found by them would agree with the theory if tellurium was taken to be 127 instead of 127·5, the value employed in their calculation. The atomic weight of tellurium must now be checked by a titration method.

The cost of this research was defrayed by means put at my disposal in 1905 by the Jagor Fund. The unpleasant physiological effects due to working with tellurium (*cf.* Mylius, *loc. cit.*) have considerably delayed the investigation.—*Berichte*, 1907, xl., 4730).

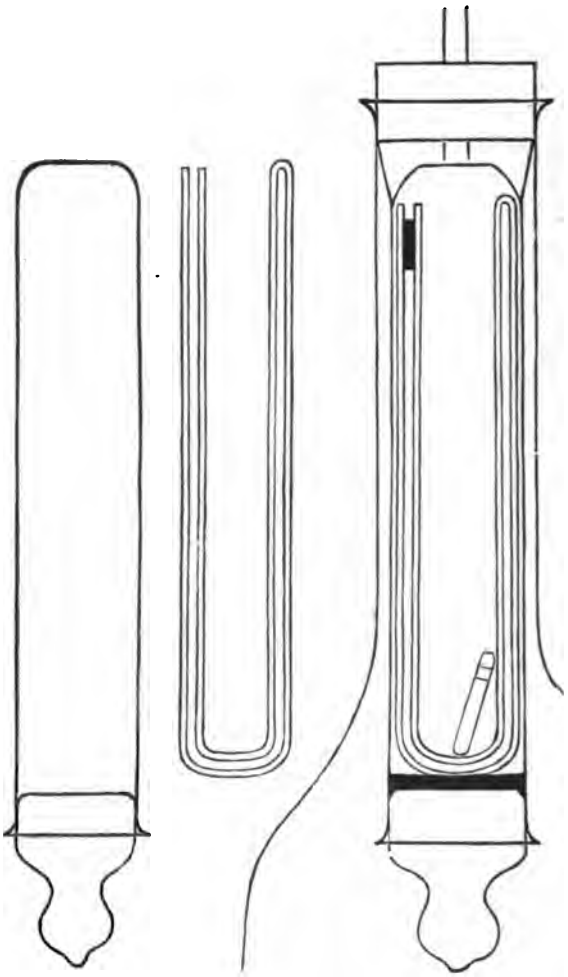
A NEW METHOD SUGGESTED FOR DETERMINING VAPOUR DENSITIES.

(SECOND COMMUNICATION).

By PHILIP BLACKMAN.

THE apparatus described by the author in the CHEMICAL NEWS, 1907, vol. xcvi., p. 223, may be simplified as here detailed.

The apparatus consists of a long vessel with an air-tight stopper. The manometer is a U-capillary tube, with one end closed, and of a size that it fits conveniently into the vessel; it has a scale of cm. (divided into tenths and



numbered) marked right round it facing outwards, so that when it is fixed in the vessel the readings can be easily observed from the outside.

The open end of the U-tube is placed in mercury, the other end warmed and then cooled, and a thread of mercury thus introduced. The U-tube is placed in the vessel, some mercury (5 cc.) poured in to help to seal the stopper, the weighed substance introduced, the stopper fixed and wired on, and the whole heated.

It would perhaps be more advantageous to have the U-capillary tube open at both ends; two threads of mercury would in this case have to be introduced, one at each end.

MELTING-POINTS OF THE IRON GROUP ELEMENTS BY A NEW RADIATION METHOD.*

By G. K. BURGESS, Associate Physicist, Bureau of Standards.

RECENTLY Dr. Waidner and the author suggested two radiation methods for the determination of high melting-points of substances in minute quantities ("On the Determination of Melting-points by Radiation Method," *Phys. Rev.*, 1906, xxii., 359). The first depends on the total radiation from a surface as measured in terms of some instrument making use of the Stefan-Bolzmann law. The second method is based on the measurement of the intensity of a particular monochromatic radiation from platinum or other substance; that is, it makes use of an instrument based on Wien's equation. (A discussion of the laws of radiation will be found in *Bulletin*, Bureau of Standards, 1905, i., 189.)

Some preliminary measurements made at that time by the second method on the metals of the iron group showed it to possess considerable accuracy and to be particularly applicable to the easily oxidised elements if the melts were obtained in an atmosphere of pure hydrogen It was also demonstrated that a compound of one of the refractory elements, which could be reduced to the metal by hydrogen, might serve as material for determining the melting-point of the pure metal.

The present paper is an account of the application of this second method to the determination of the melting-points in hydrogen of the members of the iron group, using, for the measurement of temperature a Holborn-Kurlbaum optical pyrometer, and the data on the monochromatic radiation from platinum published by Waidner and Burgess in *Bulletin*, Bureau of Standards, 1907, iii., 1.

Experimental Method.—The arrangement of the apparatus is shown in Fig. 1, and is as follows:—Within the blackened brass cylinder C is a strip of pure platinum P, about 6 cm. long, 4 mm. wide, and 0·02 mm. thick. This platinum strip is heated electrically to any desired temperature, and by means of a rheostat, which has a fine adjustment, very delicate control of the temperature of P is obtained. The cylinder C is connected to an electrolytic hydrogen generator in series with an alkaline pyrogallate solution and a drying tube of calcium chloride. At M is a removable window of thin mica, giving access to the cylinder and permitting observation of P both with the microscope N and the optical pyrometer H.

To take an observation of a melting-point, a minute quantity of a metal or its oxide, usually about 0·001 mgrm. in the form of powder, is placed at the centre of the platinum strip P, the window M screwed down, the cylinder closed and filled with hydrogen, and then the electric circuit is made through P. One observer watches the metallic speck or dust through the microscope and gradually increases the current until the melting-point is reached, while, simultaneously, another observer reads this temperature with the pyrometer. Only one melt is taken on a given platinum strip.

Temperature Scale.—The Holborn-Kurlbaum pyrometer was calibrated by sighting upon an improved form of the electrically heated experimental black-body due to Lummer and Kurlbaum, the temperature of which was given by the electromotive forces of two platinum, platinum-rhodium thermoelements as measured on a potentiometer. The temperature scale of the thermoelements was obtained by assuming the following melting-points: Zn = 419·0° C., Sb = 630·5°, Cu = 1084·0°, all these metals being of "Kahlbaum" purity. As an upper fixed point, the melting-point of platinum was taken as 1753° C., determined from measurements with the optical pyrometer. In the optical pyrometer two lamps were used which gave practically identical values for every temperature observed. As the establishment of the high temperature scale of the Bureau of Standards is treated at length elsewhere in this Bulletin, further discussion of this scale need not be given here (Waidner and Burgess, *Bulletin*, Bureau of Standards, 1907, iii., 1).

The indications of the optical pyrometer, when sighted upon platinum through a mica window, are subject to two corrections, one for the reflection and absorption of the

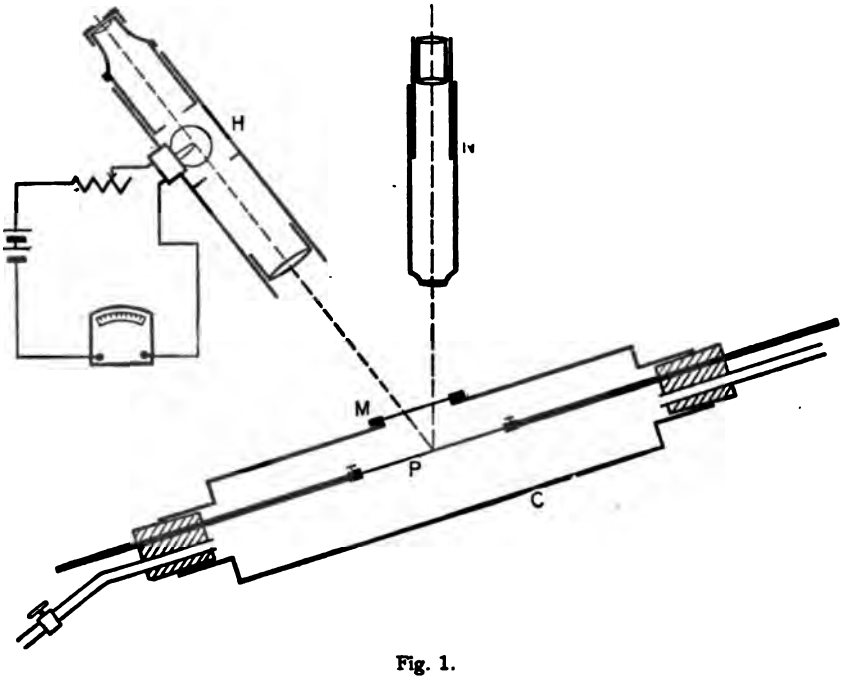


Fig. 1.

* From *Bulletin* of the Bureau of Standards, vol. iii., No. 3.

mica, the other for the selective emission of the platinum for the light used—in this case, red light $\lambda = 0.66\mu$. The former correction, which is about 15°, is easily determined and checked between measurements of the melting-points by taking observations of the platinum brightness at a definite temperature both with and without the mica interposed, with a second mica strip always in place to prevent air currents.

The correction for the selective emission of platinum is discussed in the paper above cited. The magnitude of this correction varies from 110 to 160° C. and is known to at least 10° within the temperature range here used.

Sources of the Materials.—Chemically pure elements are difficult to get, and it is desirable to use products from different sources and of known analyses. These experiments were greatly facilitated by the willingness of scientists possessing very pure samples to put them at our disposal.

H. Copaux, of Paris, who has recently completed a most comprehensive study of the properties of cobalt and nickel, and produced these metals containing less than 1/2000 part impurities, furnished samples of these elements ("Recherches Experimentales sur le Cobalt et sur le Nickel," *Ann. Chim. Phys.*, 1905, vi., 508). Dr. H. Goldschmidt, of Essen Ruhr, Germany, sent pieces of his pure aluminothermic metals, namely, chromium and manganese, all of an average purity of 98 to 99 per cent; and Prof. C. F. Burgess, of the University of Wisconsin, supplied samples of his pure electrolytic iron. The other samples were from Kahlbaum and of "Kahlbaum" grade except as otherwise noted.

Iron.

Iron from two sources was used, "Kahlbaum" iron in the form of powder, and electrolytic iron in lumps, from Prof. C. F. Burgess, from which particles weighing slightly more than 0·001 mgrm. were chipped. This electrolytic iron had the following composition, as determined from an analysis of a similar sample by Mr. A. A. Blair, of Wisconsin:—

Sulphur	None.
Silicon	0·013 per cent
Phosphorus	0·004 „
Manganese	None.
Carbon	0·012 „
Hydrogen	0·072 „

Iron as it approaches the melting-point becomes plastic, so that the actual temperature of melting is not sharply defined, there being a considerable transition region.

The very considerable variation in the separate melts appears to be due mainly to the influence of size and shape of the particles on the viscosity and surface tension; also lack of homogeneity in chemical constitution of such minute samples may play some *role*, as well as variations in the temperature of adjacent areas of the platinum strip. That the electrolytic iron melts at a slightly higher temperature seems probable. Any impurity likely to be formed in iron will lower its melting or freezing point; but the total impurities in the electrolytic iron here used will not cause a lowering as great as 5° C.

The corrected values found for all the separate melts are given in Table I.

TABLE I.—*Melting-point of Iron.*

C. F. Burgess (electrolytic).	"Kahlbaum" (powder).
1493°	1509°
1519	1494
1518	1512
1512	1483
1512	1507
1514	1491
1489	
1508	
1508	
1494	
Means.. 1507	1499

Among previous determinations of the melting-point of iron have been the following:—

Roberts-Austen, 1899 ..	1600°
Le Chatelier, 1901	1575°
Osmond	1550°
Tammann, 1904	1555° (1490°)

The value given by Tammann, 1555° (Guertler and Tammann, *Zeit. Anorg. Chem.*, 1905, xlv., 205), is that, assuming the nickel point to be 1484°, as determined by Holborn and Wien (*Wied. Ann.*, 1895, lvi., 360). Tammann's value as obtained by extrapolation of his own thermocouple calibration from the gold point (= 1064°) would be about 1490°.

Cobalt.

Three kinds of cobalt were used; chips from M. Copaux's sample, "Kahlbaum" cobalt, and the metal obtained from Kahlbaum's nickel-free cobalt-carbonate transformed to cobalt-oxide by heating in air, and reduced to metallic cobalt by hydrogen, in place on the platinum strip on which the melt was taken.

In great contrast to iron, cobalt possesses a very sharp melting-point, and the resulting precision is correspondingly increased, showing that the greater deviations in the measurements on iron are not due to the fault of the method nor to its lack of sensitiveness.

TABLE II.—*Melting-point of Cobalt.*

Co from $CoCO_3$. (Kahlbaum Ni-free).	"Kahlbaum." Powder.	Copaux pieces from crucible melt.
1456°	1470°	1457°
1472	1466	1468
1467	1468	1463
1468	1466	1466
1453	1459	1462
1470	1461	
Means 1464	1465	1463

Copaux himself gets 1530° for the cobalt point by interpolation between the gold and platinum points, assuming the latter to be 1780°. Recent measurements of the platinum point show 1780° to be high by about 70° on the thermocouple scale, or by about 30° on the optical scale, as usually defined in terms of Wien's law. (Harker, CHEM. NEWS., 1905, xci., 62; Holborn and Henning, *Sitzber. Berlin Akad.*, 1905, xii., 311; Nernst, *Berichte Deut. Phys. Ges.*, 1906, iv., 48; Waidner and Burgess, *loc. cit.*) Holborn and Valentiner (*Ann. der Physik.*, 1907, xxii., 1), however, have recently obtained 1789° for the melting-point of platinum, using Wien's equation, the constants of which were newly determined by comparison with the indications of a gas thermometer up to 1600°. Guertler and Tammann get 1505° for cobalt on the Holborn and Wien scale, or reduced, as explained in the case of iron, their value for cobalt would be about 1455° on the thermoelectric scale.

Nickel is usually present in cobalt to at least 2 per cent, causing a proportional lowering of the freezing point of less than 1° C. (Guertler and Tammann, *Zeit. Anorg. Chem.*, 1904, xlii., 353). Iron, even if present in considerable quantities, has a negligible effect on the cobalt melting-point. Cobalt is less oxidised in the air at high temperatures than are the other elements of the iron group, and cobalt oxide is only slightly soluble in the metal (Copaux, *loc. cit.*). These properties, taken together with its very sharp melting-point, the insignificant effect of its usual impurities on this temperature, and its relative cheapness as compared with the platinum metals, make cobalt, even of a commercial purity, a desirable metal to use for a fixed point in pyrometric measurements.

Nickel.

The melting-point of nickel was determined with the pure metallic nickel of M. Copaux and with Kahlbaum's cobalt-free nickel oxide reduced by hydrogen on the

platinum strip. The melting-point is about as well defined as that of cobalt.

TABLE III.—*Melting-point of Nickel.*

Pressed nickel (Copaux).	Ni from the oxide (Kahlbaum).
1434°	1433°
1435	1434
1434	1439
1436	1434
1436	
Means.. 1435	1435

The preliminary measurements of Dr. Waidner and the author showed that "Kahlbaum" nickel also gave the same value as the above.

The following thermoelectric determinations of the nickel point may be noted :—

Le Chatelier, 1887.. ..	1420°
Holborn and Wien, 1895	1484°
Harker, 1905	1427°
Tammann, 1905	(1425—1430°)
Copaux, 1905	1470°

The measurements of Copaux and of Holborn and Wien are subject to the same corrections as discussed under cobalt. Le Chatelier's determination is based on a too low value of the gold point. Tammann's value is that deduced from his own observations as in the case of cobalt and iron. According to the measurements of Waidner and Burgess (*loc. cit.*) the optical is 8° higher than the usual thermoelectrie scale at 1427°, so that the nickel freezing point, as determined by Harker using thermocouples, is in exact agreement with the above optical determination.

The presence of cobalt in nickel as impurity will raise the melting-point, while iron as an impurity in nickel will lower its melting-point (Tammann, *loc. cit.*).

Chromium.

Crystallised chromium from Kahlbaum was used and also Dr. Goldschmidt's aluminothermic chromium of 98—99 per cent purity and carbon free. As Table IV. shows, it is about as difficult with chromium as with iron to get a sharp melt. Possibly the greater impurity of the crystallised chromium increases this effect for that sample.

TABLE IV.—*Melting-point of Chromium.*

Chromium crys. Kahlbaum.	Chromium, 98—99 per cent. Goldschmidt.
1501°	1497°
1472	1483
1480	1486
1505	1484
1475	1494
Means.. 1487	1489

A thermoelectric determination of the chromium melting-point has been made by E. A. Lewis (CHEM. NEWS, 1902, lxxxvi., 13), using 99 per cent chromium obtained by the Goldschmidt process. The melt was made in a lime crucible in an oxy-coal-gas flame; two melts gave 1510° and 1520°.

Manganese.

Two samples of manganese were used: "Kahlbaum" manganese, and a sample from Dr. Goldschmidt, 98 per cent manganese, carbon free and technically iron free. The manganese point, although the lowest in the series, is the least satisfactory to determine on account of the very great temperature interval (over 25° C.) in which the melt takes place.

First signs of melting were evident as low as 1195° C., and the melt of relatively large pieces was not complete at 1220° C.

TABLE V.—*Melting-point of Manganese.*

Manganese. "Kahlbaum."	Mn. 98 per cent. Goldschmidt.
1226°	1207°
1203	1210
1197	
1198	
Mean. .. 1207	

Heraeus found 1245° (*Zeit. Elec. Chem.*, 1902, viii., 185), by observing with a telescope the melt in hydrogen within an electric furnace, whose temperature was given with a thermoelement and pyrometer-galvanometer. Levin and Tammann, also using a thermo-element, get between 1190° and 1200° for the manganese melting-point (*Zeit. Anorg. Chem.*, 1905, xlvii., 136).

Conclusion.

The values found by the radiation method described above, for the melting-points, in an atmosphere of hydrogen of the elements of the iron group in contact with platinum, are as follows :—

TABLE VI.—*Approximate Melting-points of the Iron Group.*

Metal.	Melting-point.	Purity.
Iron..	1505° C.	99·95
Chromium ..	1489	98—99
Cobalt	1464	99·95
Nickel	1435	99·95
Manganese ..	1207	98—99

Of these, the cobalt and nickel melting-points appear to be correct to within 5°, while the uncertainty of the iron, chromium, and manganese points is probably less than 10° C. It is not probable that any of these metals combines with platinum, or alloys with it until the metal is melted at its natural melting-point. The fresh melts are all white, changing to the colour characteristic of each metal after standing in the air.

It is not claimed that the above numerical values are final, and they are given mainly as an illustration of the possibilities of a method which may be the only one available in certain cases. The above values are, however, in excellent agreement with certain of the latest determinations by the thermoelectric method, notably Harker's determination of the nickel-point, and the determinations of Tammann and his associates for iron, nickel, cobalt, and manganese, when these latter results are reduced by extrapolation from the gold point and account is taken of the difference between the thermoelectric and optical scales (Waidner and Burgess, *Bulletin*, Bureau of Standards, 1907, iii., 1). It would be highly desirable to determine the melting-point of cobalt with the greatest accuracy for use as a fixed point in pyrometry.

By this radiation method less than 0·001 mgrm. is required for a single observation, making it readily applicable for the relatively exact determination of the melting-points of the rarer refractory elements, and it is the only sensitive method yet suggested when the pure element can be obtained only in very small quantities. It is our intention to continue such determinations whenever it is possible to obtain the refractory elements of sufficient purity.

There may be considerable variations in size of the particles to be melted without appreciable change in the apparent melting-point. Furthermore, the method gives the same melting-point for the pure metal, and for the metal reduced from the pure oxide by hydrogen in the apparatus used, and requires no transfer or handling of the microscopic quantity of the metal so formed.

For the determination of the melting-points of those elements having a higher fusing point than platinum, iridium strips may be used and in some cases perhaps carbon; but it is hoped that we may shortly be able to use tungsten strips. Tungsten, as we have found (Waidner and Burgess, "Temperature and Selective Radiation of Incandescent Lamps, *Electrical World*, Nov. 10, 1906,

915; *Bulletin*, Bureau of Standards, 1906, ii., 319), appears to have the highest melting-point—above 3000° C.—of any element that can be melted without considerable previous evaporation, and appears to possess the further advantage of being unattacked by hydrogen. The above apparatus could evidently be arranged, if necessary, to work with a vacuum instead of an atmosphere of hydrogen or other gas.

It might also be possible, as in the case of steels, to apply the method to a determination of carbon or other content from the melting-point measurements.

To Mr. J. R. Fehr credit is due for efficient aid in carrying out the above experiments.

THE DETERMINATION OF SILICA AND ALUMINA IN IRON ORES.

By G. W. DEAN.

Further experience with the method which was described in the *Journal of the American Chemical Society*, vol. xxviii., 882, has led to its modification in two or three important particulars. It has been found that the ore may be ignited directly instead of separating and igniting the residue from digestion with hydrochloric acid. It has also been found that a porcelain crucible is the most suitable for the ignition, since the ore is less liable to be overheated and the alumina rendered insoluble. When the determination of alumina is not required, the use of stannous chloride aids greatly in dissolving the ore. It has also been found that by heating the ore with sulphur it is partly reduced in such a manner that it is more easily soluble in hydrochloric acid and the whole method can be used when it is desired to determine both silica and alumina. The methods which are now used are as follows:—

Determination of Silica alone.—Weigh 0·5 grm. of the finely pulverised ore (100 mesh), transfer to a 20 cc. porcelain crucible, cover and heat over a Dangler burner until the contents of the crucible are dull red, raise the temperature for a few seconds and then remove the crucible from the source of the heat. The whole operation should take not more than two or three minutes. Transfer the ignited ore when cold to a beaker, add 20 cc. strong hydrochloric acid containing 1 grm. of stannous chloride in 225 cc. Boil vigorously until solution is apparently complete, and for five or ten minutes longer. Twenty or thirty minutes will usually be enough. If the ore is very difficult to dissolve, a stronger solution of stannous chloride or more of the same solution may be used. Dilute slightly, filter, and wash thoroughly first with dilute hydrochloric acid and then with water. Ignite and weigh the silica as usual.

2. *Determination of both Silica and Alumina.*—Weigh 0·5 grm. of the finely pulverised ore (100 mesh), transfer to a 20 cc. porcelain crucible, and place on top 0·25 to 0·40 grm. of sulphur; heat gradually until the ore is dull red and then raise the temperature slightly for ten seconds. Transfer to a beaker, pulverise the mass with a glass rod, add 25 cc. of hydrochloric acid, and boil vigorously for fifteen minutes. Then add enough nitric acid to clear the solution and decompose the sulphides and boil vigorously for another five or ten minutes, repeating the addition of nitric acid and boiling if required. If dark particles remain undissolved after this treatment, it is probable that further treatment will not decompose them. Dilute, filter, wash, and determine the silica, as before, and in the filtrate determine the alumina by any one of the various methods which are suitable. In this method the ignited mass is treated with hydrochloric acid, first to gain the advantage of the reducing action of the hydrogen sulphide liberated from the sulphide of iron formed by the action of the sulphur. If the nitric acid is added at first, the advantage of this reducing action is lost, and the oxides of iron are often very difficult to dissolve.

The methods have been applied to the determination of silica in the following ores:—(1) Arizona hematite; (2) Wyoming low grade hematite; (3) Alabama limonite; (4) Alabama hematite; (5) Magnanite from Llano County, Texas; (6) Michigan magnetite; (7) Michigan hematite; (8) Mesabi limonite; (9) Mesabi decomposed hematite; (10) Swedish hematite; (11) Swedish magnetite; (12) Highly aluminiferous hematite from Baraboo iron district; (13) Hematite from Port Arthur field in Canada; (14) Bog iron from Nova Scotia. The results are as follows (Determinations are in duplicate):—

	Per cent silica by Na_2CO_3 fusion.	Per cent silica by hydrofluoric acid method.	Per cent silica by above method.
1.	12·06—12·20	12·08—12·10	12·09—12·13
2.	21·27—21·22	21·11—21·20	21·26—21·23
3.	13·77—13·68	13·69—13·72	13·73—13·62
4.	11·99—11·82	11·88—11·94	11·92—11·83
5.	14·28—14·33	14·32—14·31	14·36—14·41
6.	9·91— 9·99	9·82— 9·89	9·80— 9·81
7.	10·55—10·40	10·49— —	10·50—10·52
8.	8·02— 8·00	8·15— 8·10	7·99— 8·08
9.	17·82—17·74	17·85—17·77	17·86—17·88
10.	7·09— 7·13	7·00— 7·04	7·06— 7·01
11.	6·72— 6·84	6·72— 6·67	6·74— 6·77
12.	31·12—31·18	31·09—31·12	31·08—31·11
13.	4·44— 4·52	4·40— 4·52	4·38— 4·40
14.	2·06— 2·05	2·08— 2·03	2·09— 2·00

It is evident from the above that the method gives accurate results when applied to a great variety of ores.—*Journal of the American Chemical Society*, xxix, No. 8.

THE CORROSION OF IRON AND STEEL.

By WILLIAM H. WALKER, ANNA M. CEDERHOLM, and LEAVITT N. BENT.

Some time ago an investigation was undertaken in the Research Laboratory of Technical Chemistry of the Massachusetts Institute with a view to throwing some light upon the much discussed question as to whether wrought iron is more resistant to corrosion than is steel. To this end a relatively large quantity of pure iron was prepared, and with this as a basis, alloys of iron and varying amounts of the different elements occurring in commercial iron and steel were made by melting the constituents in alumina crucibles heated by an electric furnace operating under a high vacuum. In studying the specimens so produced, it early became apparent that a more complete understanding of the factors which occasion corrosion and the conditions under which corrosion proceeds was necessary in order that our results could be intelligently interpreted. A study of the literature on the subject showed it to be so voluminous and so altogether contradictory, that as a first step in our investigation of the general subject of the influence of the constituents of iron or steel upon its corrosion, we decided to determine, if possible, the mechanism of the reactions by reason of which corrosion takes place.

(Since this part of the work was undertaken we have learned that Dr. Allerton S. Cushman, Assistant Director, Office of Public Roads, Washington, has also been investigating this subject. Although contemporaneous, the investigations have been carried on entirely independently, except in regard to the ferroxyl indicator, and it is believed that Dr. Cushman's work will be found to confirm in many respects the results herein recorded.

Theories of Corrosion.

The more important theories of the corrosion of iron and steel which seem to be worthy of discussion may be considered under three heads, the first, when taken up chrono-

* Read before the New York Section of the American Chemical Society, May, 1907. From the *Journal of the American Chemical Society*, xxix., No. 9.

logically, being the *carbon dioxide theory*. Although the subject of corrosion had been investigated by a number of workers, Dr. Crace Calvert in 1871 seems to have been the first to have carried on a systematic study of the factors entering into the reaction, and concludes that at least three reagents are essential, viz., water, oxygen, and carbon dioxide. This work received a complete endorsement at the hands of Crum Brown in 1888, who summarised the successive changes in the process of corrosion in the following equations :—

$$4(Fe + H_2O + CO_2) = 4FeCO_3 + 4H_2.$$
$$4FeCO_3 + 6H_2O + O_2 = 2Fe_2(OH)_6 + 4CO_2.$$

Two important facts regarding corrosion may be so easily explained by this theory that it has been very generally accepted by text-book writers and thus gained credence. These facts are, first, that the presence of carbon dioxide accelerates corrosion, and, second, that alkalis such as calcium hydroxide entirely prevent corrosion.

The latest and possibly most convincing work to be done on this subject is that of Gerald T. Moody, which apparently proves that no corrosion of iron will take place without carbon dioxide (*Journ. Chem. Soc.*, lxxxix., 720).

Moody's principal experiment consisted in exposing a bright piece of pure iron immersed in water to a stream of oxygen, the utmost precautions having been taken to exclude the presence of carbon dioxide. The different parts of the apparatus were connected by glass seals, and in order to free them from carbon dioxide, air, after passing through a most elaborate washing and purifying system, was drawn for three weeks through the apparatus. Notwithstanding these precautions, rust in small amounts was found to develope on the specimens after a few days. When, however, air from which the carbon dioxide had not been absorbed was drawn through the water in which the iron was immersed, corrosion rapidly increased.

Moody concluded that the very small amount of rust which he had observed before the unwashed air was led in, was due to a trace of carbon dioxide which had been introduced with the piece of iron. He therefore immersed his specimens in a 1 per cent solution of chromic acid in order that they might be protected from the carbon dioxide until the apparatus had been swept entirely free from this gas. After again drawing carbon dioxide-free air through the system for three weeks, the chromic acid was displaced by passing through the tube containing the iron a large quantity of pure water, introduced in such a manner as to insure no contamination with carbon dioxide. This water entirely removed all traces of this protective chromic acid solution. Carbon dioxide-free air was then drawn through the water and over the iron for five weeks, and at the end of that period no rust could be observed. The connection between the washing system and the specimen was then broken and unwashed air drawn through the water. Very considerable corrosion was observed after three days.

Electrolytic Theory.—In 1903, W. R. Whitney (*Journ. Am. Chem. Soc.*, xxv., 394) published the results of an investigation, which furnished data on which he based a theory of corrosion in accordance with the conceptions of Nernst and the modern theory of solutions. In accordance with this theory metals can dissolve only by entering the solution as electrically charged ions. This escaping tendency of a metal is measured by a force known as the electrolytic solution pressure, which will operate in any solution until counterbalanced by the osmotic pressure of the metal already in solution. In passing into the ionised state, the ions assume their positive charges while the residual negative charges remain upon the metal. Action is therefore immediately arrested on account of the difference of potential which would exist between the positively charged ions and negatively charged metal. In the case when iron is immersed in a solution of copper sulphate, there are present the positively charged copper ions which have a smaller solution pressure than the positively charged iron ions, and hence when the former are attracted to the negatively charged metallic iron their charges are neutralised and metallic copper is precipitated. Since its solution pressure is less than that of the iron, there is little tendency for the copper ions to again dissolve in the presence of iron, and the action continues.

Hydrogen acts as a metal and has an electrolytic solution pressure which places it between iron and copper in the series of metals. Iron placed in a solution containing hydrogen ions will therefore dissolve at a velocity dependent in general upon the concentration of the hydrogen ions and the ease with which the gas can be liberated upon the iron surface. Water is dissociated to a small extent into hydrogen and hydroxyl ions, and hence, if this theory holds, iron should pass into solution to a slight extent, with the liberation of an equivalent amount of hydrogen. Any reagent which increases the concentration of the hydrogen ions, such as an acid, will increase the corrosive action, while any agent which will decrease this hydrogen concentration will inhibit corrosion. In this way is explained the protecting effect of the alkalis and of any substance, for example, borax, which by hydrolysis yields hydroxyl ions, inasmuch as the product of the hydrogen and hydroxyl ions must remain a constant. The formation of rust is thus seen to be a secondary action, brought about by the oxidation of the already dissolved iron by the action of atmospheric oxygen. The role of carbon dioxide is but that of any acid, increasing by its presence the concentration of the hydrogen ions and to this extent accelerating the action.

Hydrogen Peroxide Theory.—Dunstan, Jowett, and Goulding (*Journ. Chem. Soc.*, 1905, lxxxiv., 1584) repeated the work of Whitney and failed to get any evidence that iron dissolved in pure water free from oxygen and carbon dioxide. They therefore considered this theory untenable, and advanced a theory based upon the fact that when some metals oxidise in water, hydrogen peroxide is frequently formed. The chemical action taking place when iron corrodes in water with access of oxygen is represented by these authors as follows :—

$$Fe + H_2O = FeO + H_2.$$
$$H_2 + O_2 = H_2O_2.$$
$$2FeO + H_2O_2 = Fe_2O_2(OH)_2 \text{ (rust)}.$$

Although a great deal of experimental work was done, these investigators failed in every instance to get evidence of the presence of hydrogen peroxide in the oxidation of iron. This theory explains the fact that when zinc corrodes in water hydrogen peroxide may be detected, by the supposition that hydrogen peroxide can exist upon the surface of zinc, while when iron corrodes the hydrogen peroxide is incapable of existence on the surface of the iron long enough to make detection possible. Support for this idea is found in the fact that, in every case, those reagents which inhibit rusting are also substances which decompose hydrogen peroxide.

Experimental.

Evidently the first question to be settled is—Is carbon dioxide essential to corrosion? To this end we repeated the experiments of Moody, duplicating his apparatus and method in every possible particular. In general, our observations coincide with his. Our explanation of the phenomena observed, however, differs radically from his. It is well known that pure water attacks with considerable ease all glass except that which has been most carefully prepared, producing an alkaline solution. It is also well established that in pure water a relatively small amount of free alkali will inhibit rusting. We therefore again repeated Moody's experiment, but constructed the apparatus so that a little phenolphthalein could be introduced after the water had been passed through the tube containing the iron. Both the water which was on the iron and also that which had passed over the iron into a flask beyond showed a distinct bright red when the indicator was added. When air containing carbon dioxide was passed through the solution this alkali was converted into the acid carbonate and the corrosion accelerated. When Jena glass which had been steamed for two days was employed, the

iron corroded almost as readily as when left in the open air. We feel satisfied that in our experiments (and we believe the same to be true of Moody's) the tardy corrosion of the iron was due to the inhibiting effect of the free alkali present, and that iron does rust in the presence of air containing no carbon dioxide.

All those experiments of Moody in which chromic acid was used are rendered worthless, so far as showing the preservation of iron in the absence of carbon dioxide is concerned, by the fact, apparently overlooked by Moody, that immersing iron in chromic acid or potassium dichromate will render it relatively passive. We have repeated these experiments a number of times, carrying on simultaneously a check experiment in which we treated a specimen of the same iron with a portion of the same chromic acid solution, but drew ordinary unwashed air through the apparatus. No difference could be observed in the latter case. The fact that iron is preserved by solutions of the chromates was mentioned by Wood in 1894 (*Trans. Am. Soc. Mech. Eng.*, xvi., 384), and later by a number of writers including Moody himself. No one seems to have noticed, however, that the passivity imparted to iron by such a solution is retained by the specimen after it is washed with pure water and dried. Without going further into this phenomenon we can but give it as our opinion that the apparent non-corrosion of iron in the absence of carbon dioxide is due, not to the fact that no carbon dioxide is present, but to the fact that the iron is protected by the as yet not clearly understood condition of passivity, brought about by its immersion in a chromic acid solution. (Since the above was written, a short notice of an article by Wyndham R. Dunstan appeared in *Journ. Chem. Soc.*, xxii., 63, in which the experiments of Moody without chromic acid have been repeated. Dunstan confirms his previous results and those stated above, in that iron rusts freely in the presence of oxygen and water containing no carbon dioxide). A further proof that carbon dioxide is not essential to corrosion will be given later under the consideration of the influence of oxygen on corrosion.

The failure of the writers already noted to duplicate the results of Whitney, probably accounts for the fact that the electrolytic theory has not been more generally accepted. Even so valuable a text-book as "General Inorganic Chemistry," by Alexander Smith, does not mention the possibility of this explanation, although it makes very general use of the newer theories of chemistry involved in Whitney's work. The carbon dioxide theory and the peroxide theory of Dunstan are given sufficient space, while the electrolytic theory is ignored.

Evidently the theory of Whitney must stand or fall with the truthfulness of his statement that iron dissolves in pure water entirely feee from oxygen and carbon dioxide. Although we employed a number of types of apparatus in studying this question, the following is both very simple and satisfactory. A round bottom Jena flask of about one litre capacity is inverted on a nozzle supplying live steam, for at least twenty-four hours. This insures the removal of any easily soluble alkalis, which would otherwise destroy the neutrality of the liquid. The flask is fitted with a carefully cleaned rubber stopper through which extends a glass tube drawn down to a moderate-sized capillary at its upper end. The flask is three-fourths filled with ordinary distilled water (not conductivity water) which has previously been boiled for several hours in a block-tin heater. The water in the flask is boiled for about ten minutes, and while steam is still rapidly passing out of the opening, the stopper is removed and a piece of bright iron introduced. The stopper is again inserted, the boiling continued for another ten minutes, and while boiling the capillary is sealed. The flask is allowed to cool after thickly coating the stopper with molten paraffin. If this experiment be carefully performed, no action will be observed, the iron remaining bright and the water clear even after standing several days. When the stopper is removed and the water concentrated in a platinum dish, using every precaution to prevent contamination from dust, a strong test for iron can always be obtained by the addition of a drop of ferrocyanide or sulphocyanate of potassium solution.

Thinking that possibly enough gas had been occluded in the iron to effect the reaction, the above experiment was repeated a number of times under conditions which allowed of introducing pieces of iron which had been heated to low redness and cooled in hydrogen. In every case the presence of iron was easily detected when the content of the flask was evaporated to a few drops.

This experiment was again repeated with the additional precaution of using water which had been allowed to stand for a number of days over a large quantity of spongy metallic iron, the water being introduced into the reaction flask by distilling it from the iron in an atmosphere of hydrogen. Notwithstanding all these precautions, a distinct test for iron was obtained after the water had been concentrated. In all these experiments "blanks" were run which in no case showed that sufficient iron had been dissolved either from the glass or from the platinum to furnish the test which was obtained.

We therefore support Whitney in his statement that iron will dissolve in water which contains not more than a trace of electrolyte, no oxygen, and only that amount of carbon dioxide which is not retained by a strong alkaline hydroxide. In explanation of the failure of the investigators previously cited to detect dissolved iron, we would state that usually it is not possible to obtain an indication of iron with potassium ferricyanide; for example, in the water as it comes from the flask; concentration is generally necessary.

(To be continued).

A STANDARD OF RADIO-ACTIVITY.

In the early part of 1906 the Röntgen Society appointed a Standards' Committee to systematise as far as possible the various methods already in use for determining the dosage of X-rays, and, if possible, to establish a unit for the measurement of radio-activity. The work has been carried out largely in the laboratories of Lord Blythswood and Mr. C. E. S. Phillips. In the former the properties of X-rays bearing on the problem have been investigated, and in the latter an effort has been made to obtain a radio-active standard. The Committee have been in touch with the Intensitats Commission of the Berlin Röntgen Society, as well as with similar societies in London and on the Continent.

At the last meeting of the Society on January 2nd an interim report was presented. The Committee laid it down that the conditions essential to a radio-active standard were constancy and homogeneity. The study of the transformation products of radium showed that the Alpha and Beta rays changed with time, but that, on account of the Gamma rays all being emitted by radium C, that radiation might for all practical purposes be regarded as constant. The Gamma rays from radium are also believed to be nearly homogeneous, and therefore the Committee thought that this form of radiation appeared to fulfil the conditions essential to a standard, and that it was only necessary to eliminate the Alpha and Beta rays by passing the radiation through a thickness of lead. They therefore recommended that 1 mgrm. of pure radium bromide should be regarded as a standard, and that the ionisation produced by the Gamma rays from that quantity after passing through 1 cm. of lead should be taken as the measure of the unit of radio-activity. They went on to suggest that multiples of this standard could then be prepared, feebly active standard solutions containing 1/10, 1/100, 1/1000 mgrm. of the active salt being conveniently obtained by the method described by Rutherford for comparisons based upon "emanation methods." The Committee was of opinion that a fundamental C.G.S. unit of radio-activity was not at present feasible, but suggested

that it might ultimately be possible to define the standard in C.G.S. units as that weight of radium which radiated energy at the rate of, say, one erg per second.

A number of interesting letters from well-known scientists were read at the meeting, and revealed certain differences of opinion, principally on the question of the atomic weight of radium, the correct thickness of the lead screen to be used in filtering out the Alpha and Beta rays, and the purity of radium preparations. Professor Silvanus Thompson asked whether an organic reaction could be made use of as at least an approximate test of possible therapeutic effect—whether there was no coloured organic substance which would give a reaction in presence of radium. Sir William Ramsay wrote that, according to experiments now being carried out at University College, it appeared probable that the atomic weight of radium is more than 240. (Mdme. Curie's estimate was originally 225, and has been more recently modified to 226). It appeared to him that we must wait till we have a sample of radium bromide of undoubted purity which had been re-crystallised often. Prof. E. Rutherford suggested a lead screen thickness of 5 mm. instead of 1 cm., stating that the former thickness was sufficient to mask the inconstant rays, and would at the same time extend the lower limit of comparison of quantities of radium by this method. Prof. Rutherford added that he thought the Society would be doing a good work by fixing a temporary radio-active standard for radium, both for the advantage of physicists and professional men. The number of people in the past who had paid for pure radium and been given nearly pure barium was legion.

A discussion ensued, in which Mr. C. E. S. Phillips, replying to some of the criticisms in the letters, said that the choice of 1 cm. as the screen thickness was made because that distance was more easily expressed and remembered than an odd number of millimetres. Mr. F. H. Glew questioned whether the Committee had done wisely in selecting radium as the standard of radio-activity. He thought uranium would have been better. Mr. W. Duddell, the President, said that any standard of radio-activity must be constant and capable of reproduction. As in electrical work a practical sub-standard might be made and compared from time to time with the fundamental standard which it was hoped would be in the National Physical Laboratory.

NOTICES OF BOOKS.

Town Gas and its Uses. By William Hosgood Young Webber. London: Archibald Constable and Co., Ltd. 1907.

The well-informed general public will find that this book gives them an excellent opportunity of acquiring a knowledge of the manufacture and uses of town gas. The early history of the industry is narrated, and the difficulties with which it had to contend will provide food for thought on the part of that conservative section of the public which is always ready to oppose new schemes which appear to threaten old interests. A sufficiently detailed description of the interior of modern gas-works is given to enable the reader to form a clear idea of the general structure and arrangement of the plant, and the great importance of the by-products of the manufacture is emphasised. An excellent discussion of the different systems of lighting and the various burners upon the market is well illustrated by photographs, and in the chapter on the cost of gas lighting the construction and method of reading a meter are described. The author writes in glowing terms of the great advantages to be gained by the use of gas for heating and cooking, and possibly some of the figures given relating to both uses will surprise his readers. The healthfulness and safety of town gas and its use for power generation are considered in two chapters, in the latter of which an account is given of the value of an engine, supplied with town gas, for the generation of electricity for private installations. Finally, the author gives a short summary of the legal relations of gas suppliers, consumers, and the public, and clears up some common misapprehensions on this subject.

Die Flechtenstoffe. ("The Lichens.") By Dr. W. Zopf. Jena: Gustav Fischer. 1907.

This work is a pioneer in biochemical literature, being the first treatise yet published devoted exclusively to the lichen acids and their derivatives. The student who wishes to explore that inaccessible and little known region where botany and chemistry meet, has every reason to be grateful to Dr. Zopf for thus clearing the way for him. The book will probably be most appreciated by the botanist whose knowledge of chemistry is deficient. The first short section gives a summary of the chemical and physical properties of the lichen acids in general, and in the second section, which fills the greater part of the book, a detailed account is given of all the known substances belonging to this category. The occurrence of each acid and its preparation and properties are discussed, and the decomposition products, where these have been studied, are described in full. The following section on the physiology and biology of the lichens might well have been rather fuller and more detailed. The technical importance of those lichens which have application in dyeing is discussed in a short section, and an excellent index is provided. Although the author has had to adopt a somewhat restricted definition of lichen substances, and has only taken into account the crystallising lichen acids, his book is a valuable summary of the present state of our knowledge of a subject which possesses a very scattered literature, and which up to the present has found no competent chronicler.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 24, December 9, 1907.

Direct Hydrogenation of the Aromatic Diones.—Paul Sabatier and A. Mailhe.—Benzile, $C_6H_5.CO.CO.C_6H_5$, may be hydrogenated in presence of nickel by an excess of hydrogen at 220—230°. The reaction is complete, and the only products are water and symmetric diphenylethane or dibenzyl:—

$$C_6H_5.CO.CO.C_6H_5 + 4H_2 = C_6H_5.CH_2.CH_2.C_6H_5 + 2H_2O.$$

Under the same circumstances (temperature, 210—220°) benzoïn yields the same products. The β-dione, benzoylpropanone, when similarly reduced, yields chiefly butyl benzene,—

$$C_6H_5.CO.CH_2.CO.CH_3 + 4H_2 = C_6H_5.CH_2.CH_2.CH_2.CH_3 + 2H_2O,$$

as well as small quantities of hexahydrobutyl benzene.

Action of Incandescent Electric Conductor upon surrounding Gases.—M. Couriot and Jean Meunier.—Incandescent electric conductors of small diameter have been shown by the authors to be incapable of causing the explosion of mixtures of fire-damp and air, even under conditions most favourable to such explosions. The explanation now put forward for this phenomenon is as follows:—The incandescent filament attracts the molecules of oxygen and repels those of the hydrocarbon. Thus a sort of protective zone is formed round the filament, and as the molecules of hydrocarbon become fewer in the immediate neighbourhood of the filament, the concentration necessary for explosion is not reached. If, however, the

incandescent conductor is large enough it may radiate sufficient heat to penetrate this protective zone, and thus an explosion is caused.

Non-existence of a common Solvent for Yellow and Red Phosphorus.—Alb. Colson.—The author has investigated the action of essence of terebenthene upon the two varieties of phosphorus, and finds that, although it is a good solvent for yellow phosphorus, neither the liquid itself nor any polymer obtained from it by the action of heat, can dissolve the red variety. Since the vapours of the two modifications have the same density, corresponding to the molecule P_4, if it is assumed that the dissolved state is similar to the state of vapour, it would necessarily follow that if it were possible to dissolve it in essence of terebenthene it would be transformed into the yellow variety.

Apparatus for producing the Spark Spectra of Solutions.—A. de Gramont.—The negative electrode is surrounded by a capillary tube of fused silica, and a second capillary of the same material is arranged above the first, and inclined at an angle of 45° to it; this tube contains the positive electrode, and is fed with the liquid to be examined from a reservoir. The ends of the platinum electrodes are at least 5 mm. from the ends of the capillary tubes. The whole arrangement, to prevent splashing and loss of liquid, is surrounded by a glass tube fitted with a window for observing the spark. The vapours formed during the operation can be drawn off by gently heating a raised side tube connected with the glass tube.

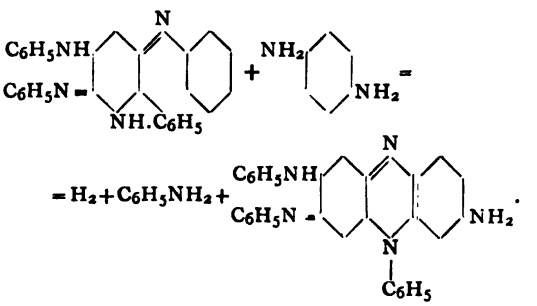
Graphite and Graphitic Carbon in Cast-Irons.—Georges Charpy.—A specimen of cast-iron was liquefied and separated into two parts. One was allowed to solidify slowly, and thus grey cast-iron was obtained. The other part was cooled rapidly, thus forming white cast-iron, which was then tempered to form grey cast-iron. The carbon was separated in each case by dissolving out with boiling nitric acid, and it was then found that each specimen was transformed into graphitic acid at the same rate. Both specimens behaved similarly when subjected to the action of a current of hydrogen at 1000°. Thus graphite and graphitic carbon separated by tempering form a single phase in the iron-carbon systems.

Action of Gaseous PH_3 on Mercuric Chloride and Bromide.—P. Lemoult.—When gaseous PH_3 acts on mercuric chloride, care being taken to avoid the presence of excess of the gas even locally, a compound of the formula PHg_3Cr_3 is obtained. Mercuric bromide, however, gives a brown compound, the formula of which is $P_2Hg_5Br_4$. Apparently the reactions can be represented by the equations $PH_3+3HgCl_2 = 3HCl+PHg_3Cl_3$, $2PH_3+5HgBr_2=6HBr+P_2Hg_5Br_4$. To check these conclusions, since the analysis of the products presented considerable difficulties, the author determined how much mercuric salt was consumed by one molecule of PH_3, when the former was in excess. With the chlorine compound he found one molecule PH_3 used up 2·93 molecules $HgCl_2$, and with the bromine compound one molecule PH_3 = 2·54 molecules $HgBr_2$, which agrees very well with the theoretical numbers obtained from the equation. The chloride and bromide of mercury are excellent absorbers for the gas PH_3, and this fact might be employed in qualitative and quantitative analysis.

Transformation of Barbaloïn into Isomeric β-Barbaloïn.—E. Léger.—When barbaloïn is heated for three hours to a temperature of 160° to 165° it is converted into a modification β-barbaloïn. This modification does not crystallise, but readily yields a crystalline chlorinated derivative, the formula of which is $C_{21}H_{16}Cl_4O_9$. The chloride obtained from the original barbaloïn differs in crystalline form from this compound, and also contains one and a-half molecules of water. Thus aloïn is one of the numerous substances which are optically active and are transformed into their optical isomers under the action of heat. When the barbaloïn in Cape aloes is removed, and the amorphous residue is chlorinated, chlor-β-barbaloïn is obtained. Thus Cape aloes are much richer in aloïn than is generally supposed, but one part of the aloïn occurs in the amorphous or β-form. Other aloes, *e.g.*, those from Uganda, give the same result.

Dissociation of Compounds of Acid and Basic Dyes by Adsorbent Substances.—L. Pelet-Jolivet.—The aqueous solutions of basic dyes are precipitated by many acid dyes, the dye in excess determining the colour of the solution. A definite compound is thus obtained, which may be regarded as a compound of the basic dye with the organic residue of the acid dye. The molecular weight of these compounds, determined by the cryoscopic method in paratoluidine or phenol, is one-quarter to one-third lower than the theoretical molecular weight; hence, pronounced dissociation occurs. When adsorbent substances, such as wool or animal charcoal, are added to the aqueous solution of the coloursd compound, it is found that in neutral or faintly alkaline solution the adsorbent solid dissociates the coloured compound, and fixes only the basic element; the solution retains the colour of the acid dye. In acid solution the absorbent substance dissociates the compound, but fixes the acid dye, and the solution has the colour of the basic dye. The colloidal theory of dyeing explains these facts. The adsorbent substances are in the colloidal state. In a neutral or alkaline bath their charge is negative, and they precipitate and fix only the positive basic dye. In an acid bath the adsorbent is positively charged, owing to the H^+ ions of the acid added, and in this case fixes the negative acid dye.

Synthesis of Symmetrical Phenylated Anilido-phenosafranine.—Ph. Barbier and P. Sisley.—When an alcoholic solution of a mixture of azophenine and para-phenylene diamine is heated in a closed vessel to 165° for six or seven hours a violet-blue liquid is obtained, from which, by distillation in a current of steam, the symmetrical phenylated chlorhydrate of anilido-phenosafranine, $C_{30}H_{23}N_5.2HCl$, may be separated. The following scheme shows the formation of this substance.



Condensation of Water Vapour in presence of Radium Emanation.—Mdme. Curie.—The author has already shown that when a gas under atmospheric pressure contains radium emanation, the induced activity in suspension in the gas behaves like matter having weight, and the particles not only travel towards the wall but also have a slow movement downwards. This phenomenon may not occur when the gas is perfectly dry, and hence the author concluded that the presence of water vapour favours the formation of agglomerations which have as nuclei the particles of induced activity, and which may attain sufficient mass to acquire an appreciable downward velocity. Damp air containing radium emanation is always more or less opaque, owing to the presence of particles of mist which can easily be seen when it is lighted by an electric arc light. The air need not be saturated with moisture, but no mist is produced in perfectly dry air. When bulbs of 35 to 50 cc. capacity contained the maximum quantity of emanation furnished by a solution of 0·05 grm. of pure radium chloride, the conditions of the formation of the mist were as follows:—1. When the bulb contained a few cc. of distilled water. It was still visible after twenty

days. 2. When the bulb contained a solution of sulphuric acid in water. 3. When the bulb contained crystals of sodium phosphate, for which the equilibrium pressure of water vapour at 17° is about 1 cm. of mercury. 4. When the bulb contained a little phosphoric anhydride the mist appeared when the emanation was introduced, but disappeared in a day owing to the absorption of the water by the anhydride. 5. When the bulb contained a little petroleum ether and a small piece of phosphoric anhydride. The mist produced was much more marked than with distilled water. The bulbs contained two platinum electrodes. If a difference of potential of some hundreds of volts was established between these electrodes the mist disappeared. This action of the electric field seems to show that the condensation of vapour occurs round the particles of induced radio-activity which in an electric field move rapidly towards the cathode. On the suppression of the field the mist re-forms, becomiug visible in five minutes. If the bulb contained distilled water and air, but no emanation, the little drops of moisture formed round any dust present on the least variation in temperature. These drops, however, were rapidly deposited, and new droplets were formed only with difficulty and in very small numbers. From these experiments it must be concluded that the particles of induced radio-activity of radium possess the property of condensing water vapour, either by electrostatic attraction or by chemical affinity. The same phenomenon is observed with the vapour of petroleum ether; it must not be confused with the phenomenon of the condensation of vapour by the gaseous ions which are produced in large numbers by radium emanation. In this case the condensation only occurs when the pressure of the water vapour becomes momentarily about four times as great as the equilibrium pressure.

MISCELLANEOUS.

The late Lord Kelvin.—In an appreciative obituary notice of Lord Kelvin, which appeared in a recent number of the *Chemiker Zeitung*, an unfortunate error has been perpetrated. Owing, no doubt, to the similarity of surname, confusion has arisen between the late Lord Kelvin and Prof. J. J. Thomson, who is still happily with us, and in the full tide of activity of mind and body. The error is perhaps the more painful and serious in that it occurs, not in the letterpress, in which a laudatory account of Lord Kelvin's achievements is given, but in the accompanying portrait, which is that of the distinguished Professor of Experimental Physics at the University of Cambridge.

NOTES AND QUERIES.

Electrolytic Deposition of Bismuth.—I should be greatly obliged if any of your readers could give me the following information:—(*a*) The best solution for electrically depositing bismuth from. (*b*) Best current density for depositing. (*c*) Is the oxide of bismuth conductive to the electric current, like that of silver?—E. G. Middleton.

MEETINGS FOR THE WEEK.

Monday, 20th.—Society of Arts, 8. (Cantor Lecture). "Theory and Practice of Clock Making," by H. H. Cunynghame, C.B.

Tuesday, 21st.—Royal Institution, 3. "The Internal Ear of different Animals," by Dr. A. E. Gray, F.R.S.E.

—— Society of Arts, 8. "The Art of Jewellery," by Mrs. Hadaway.

Wednesday, 22nd.—Society of Arts, 8. "Siam and its People," by Harry Hillman.

Thursday, 23rd.—Royal Institution, 3. "Recent Light on Ancient Physiographies," by Prof. W. W. Watts, F.R.S.

Friday, 24th.—Royal Institution, 9. "The Extinction of Malta Fever," by Col. David Bruce.

—— Physical, 5. "Recalescence Curves," by W. Rosenhain. "An Experimental Examination of Gibbs' Theory of Surface Concentration regarded as the Basis of Adsorption, and an application to the Theory of Dyeing," by W. C. M. Lewis.

Saturday, 25th.—Royal Institution, 3. "The Electrification of Railways," by Prof. Gisbert Kapp, Dr.Eng., M.Inst. C.E.

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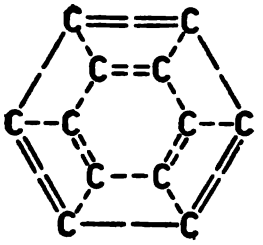
NOTE ON THE CONSTITUTION OF THE CARBON MOLECULE FROM THE STANDPOINT OF THERMO-CHEMISTRY.

By H. STANLEY REDGROVE, B.Sc., F.C.S.

PROF. SIR JAMES DEWAR has recently brought forward the interesting suggestion (CHEMICAL NEWS, xcvii., 19) that the constitution of the carbon molecule is represented by the formula—



It will be of interest to see how far this formula is supported by thermo-chemical data.

Using the author's notation (CHEMICAL NEWS, xcv., 193 and 301), the heat of combustion of a grm.-mol. of carbon is represented by $12\alpha - 12\beta - 6\gamma = 2529{\cdot}6$ cals. $- 630{\cdot}0$ cals. $- 534{\cdot}0$ cals. $= 1365{\cdot}6$ cals. Accepting the value 97·0 cals. as the atomic heat of combustion of carbon we we get 1164·0 cals. for the molecular heat of combustion, assuming that the carbon molecule contains twelve atoms, as above. The above formula therefore gives an error of 201·6 cals.

The formula is derived from the fact that, on oxidation of carbon, mellitic acid can be obtained, but it also assumes that Kekulé's formula is the true one for benzene derivatives, or at least mellitic acid.

Without making this assumption as to the nature of the benzene molecule, suppose the carbon molecule to consist of two condensed benzene molecules, its molecular heat of combustion would be represented by twice the molecular heat of combustion of benzene $- 6\mathfrak{z}$ cals. $= 2 \times 797{\cdot}9$ cals. (*i.e.*, Thomsen's experimental value corrected for constant volume) $- 315{\cdot}0$ cals. $= 1280{\cdot}8$ cals.

The error in this case is therefore 1280·8 cals. $- 1164{\cdot}0$ cals. $= 116{\cdot}8$ cals. This is a large error, but much less than when Kekulé's formula was assumed. In both cases the effect of the intramolecular tension due to the tetramethylene rings has been neglected; the effect would be to increase the molecular heat of combustion, and thus the errors are actually greater than the above.

The general formula for a carbon molecule containing "single" links only is $n(\alpha - 2\beta)$, with a molecular heat of combustion of 105·8 n cals. The most likely of these formulæ from the mellitic acid standpoint is $12\alpha - 24^{1}$, with a molecular heat of combustion of 1269·6 cals., giving an error of 105·6 cals., which is also large. Such a carbon molecule could be derived from either Ladenburg's or Claus's benzene formulæ, but in each of these intramolecular tension would be introduced, which would cause the error to be higher; such a formula as $12\alpha - 24\beta$, or, indeed, any formula for the carbon molecule, without intramolecular tension appears to be geometrically impossible. It is, of course, not unlikely that the various modifications of carbon may possess different molecular structures. A perfectly satisfactory solution of the benzene mystery and a fuller knowledge of valency might, however, throw light on the question of the constitution of the carbon molecule.

The Polytechnic, Regent Street, W.

A PHYSICO-CHEMICAL STUDY OF THE COMPLEX COPPER-GLYCOCOLL SULPHATES.*

By J. T. BARKER, B.Sc.

IT is well known that addition of glycocoll to aqueous solutions of copper sulphate produces a fine blue colour, similar in general character to that produced by excess of ammonia. That the concentration of the cupri-ions has been lowered by the presence of the glycocoll is rendered probable by the fact that caustic potash does not precipitate cupric hydroxide from solutions containing moderate amounts of glycocoll, whereas potassium ferrocyanide and ammonium hydrosulphide throw down precipitates of cupric ferrocyanide and sulphide respectively. It seemed probable that the reduction in the concentration of the cupri-ions is caused by the formation of complex cupri-glycocoll cations. The experimental work described in the present paper was undertaken with the object of investigating this question.

1. *Electrometric Measurements.*

In order to arrive at some idea of the degree of complex formation, the following preliminary measurements of potential were made:—A series of solutions one-tenth molecular normal with respect to copper sulphate, but respectively $n/2$, $n/5$, $n/10$ with respect to glycocoll, was made up. By Poggendorff's compensation method, using a slide-wire bridge and a Lippmann capillary electrometer, the potential difference between a clean copper rod and each of these solutions was determined. For this purpose each copper electrode was connected through a KCl solution with a normal calomel electrode, and the cells so constructed were measured with and against a standard cadmium cell in the usual manner. Taking the potential of the calomel electrode as $+0{\cdot}56$ volt, and the E.M.F. of the cadmium cell as 1·0186 volt, the results shown below were obtained at 17° C.

In calculating these values the potentials at the liquid junctions have been neglected (as a first rough approximation).

By means of the formula $\pi = \frac{0{\cdot}000198\,T}{2} \log \frac{c_1}{c_2}$ we can now obtain approximate values for the ratios of the cupri-ion concentrations in the several solutions examined. In the above formula π denote the E.M.F. of a cell such as—

$$Cu \mid CuSO_4 \mid KCl \mid CuSO_4 + \text{glycocoll} \mid Cu,$$

and c_1 and c_2 denote the respective cupri-ion concentrations.

Solution.		Potential of copper electrode (volt).
Concentration of $CuSO_4$.	Concentration of glycocoll.	
$n/10$	0	$+0{\cdot}558$
$n/10$	$n/10$	$+0{\cdot}549$
$n/10$	$n/5$	$+0{\cdot}537$
$n/10$	$n/2$	$+0{\cdot}512$

Thus for the cell $Cu \mid n/10 - CuSO_4 \mid KCl \mid n/10\,CuSO_4 + n/10$ glycocoll $\mid Cu$ $\pi = 0{\cdot}558 - 0{\cdot}549 = 0{\cdot}009$ volt.

Calling the concentration of the cupri-ion in the $n/10 - CuSO_4$ solution 100, we obtain in this way the relative values given in Table I.

These figures, though not pretending to be very accurate, suffice to show the progressive decrease of the $Cu^{\cdot\cdot}$-concentration on continued addition of glycocoll, and appear to

* A Paper read before the Faraday Society, December 17, 1907. From the Muspratt Laboratory of Physical and Electro-chemistry, University of Liverpool. Communicated by Dr. F. G. Donnan.

warrant the assumption that with a large excess of glycocoll the cupri-ion will be practically completely converted into some complex ion (or neutral compound).

TABLE I.

Molar ratio of glycocoll to $CuSO_4$.	Relative concentration of $Cu^{\cdot\cdot}$-ion.
0	100
1	48
2	19
5	3

We shall assume first of all, as seems most probable, that a complex cupri-glycocoll ion cation is formed, and that its formula may be represented as $CuG_x^{\cdot\cdot}$, *i.e.*, that it contains x mols. of glycocoll for every atom of copper. If the glycocoll be present in large excess relatively to the copper sulphate, we may assume, with a fair degree of probability, that practically all the copper sulphate will be converted into complex copper-glycocoll sulphate, and that, to a first approximation, we may take the final concentration of the glycocoll as equal to its initial concentration. Furthermore, if the solution be pretty dilute with respect to total dissolved copper salts, the complex sulphate (or sulphates) may be regarded as completely ionised, in which case the final molar concentration of the cupri-glycocoll ion will be equal to the initial molar concentration of the copper sulphate. Let us suppose that the complex ion $CuG_x^{\cdot\cdot}$ dissociates (non-electrolytically) into glycocoll and cupri-ions. Denoting molar concentrations by square brackets, and writing i for initial total concentration of copper sulphate, we have—

$$[Cu^{\cdot\cdot}]_1.[G]x = k[CuG^{\cdot\cdot}{}_x]_1 = ki_1.$$

For another solution—

$$[Cu^{\cdot\cdot}]_2.[G]_2 = ki_2.$$

Whence, dividing and taking logarithms—

$$\log \frac{[Cu^{\cdot\cdot}]_1}{[Cu^{\cdot\cdot}]_2} + x \log \frac{[G]_1}{[G]_2} = \log \frac{i_1}{i_2} \quad . \quad . \quad 1.$$

Although $[Cu^{\cdot\cdot}]_1$ and $[Cu^{\cdot\cdot}]_2$, may be very small, their ratio is a definite quantity, which is found by measuring the potentials of a copper electrode in each of the two solutions, and then applying the formula—

$$\pi = \frac{RT}{2F} \log \frac{[Cu^{\cdot\cdot}]_1}{[Cu^{\cdot\cdot}]_2}.$$

The only unknown quantity in Equation 1 is, then, x. In order to obtain the most accurate values, two corrections must be applied to Equation 1. In the first place, an allowance must be made for the amount of free glycocoll removed from the solution as complex ion; and, secondly, if the complex copper-glycocoll sulphate be not completely ionised, the concentration of the complex copper-glycocoll ion is not equal to the initial total concentration of copper sulphate. The second correction will be dealt with later.

Equation 1, with the first correction, takes the form—

$$\log \frac{[Cu^{\cdot\cdot}]_1}{[Cu^{\cdot\cdot}]_2} + x \log \frac{[G]_1 - xi_1}{[G]_2 - xi_2} = \log \frac{i_1}{i_2} \quad . \quad . \quad 2.$$

In solving this equation, an approximate value of x is first obtained from Equation 1, and then the value of x which satisfies 2 is found by successive approximations.

In the case of the preliminary data already given, any potential differences existing at the liquid junctions were ignored. These potential differences can probably be for the most part eliminated by comparing only solutions having the same total copper content and a varying, though very large, relative excess of glycocoll; for in this case the two solutions will contain practically only complex sulphate, and that of practically the same concentration in both cases. It will be seen that the method here employed is substantially that first introduced by Bodländer.

The results of the first measurements are contained in the following two tables. The E.M.F's. of the concentration cells have been calculated from direct measurements of cells of the type Cu | $CuSO_4$ + glycocoll | $3{\cdot}5n - NaNO_3$ | calomel electrode.

The value 1·35 is evidently too low. For the rest, the values of x given in Table III. are seen to be considerably higher than those in Table II. Probably only the values in Table III. are deserving of weight, since these are derived from measurements of pairs of solutions of equal total copper content.

TABLE II.—*Temperature* 13° C.

First solution. $CuSO_4$	First solution. Glycocoll	Second solution. $CuSO_4$	Second solution. Glycocoll	E.M.F. of combination.	x Calculated from Equation 1.
$n/200$	$n/1$	$n/100$	$2n$	0·0138	2·62
$n/200$	$n/2$	$n/100$	$n/1$	0·0030	1·35
$n/200$	$n/2$	$n/100$	$2n$	0·0421	2·97
$n/200$	$n/1$	$n/100$	$2n$	0·0135	2·58

TABLE III.—*Temperature* 13° C.

$n/100$	$n/1$	$n/100$	$2n$	0·0351	4·12
$n/100$	$n/1$	$n/100$	$2n$	0·0391	4·59
$n/200$	$n/2$	$n/200$	$n/1$	0·0289	3·39

More accurate measurements were now carried out, in which every effort was made to eliminate disturbing influences. The calomel electrode was dispensed with, the E.M.F's. of the concentration cells being directly measured with $3{\cdot}5n$ $NaNO_3$ solution as connecting liquid. The concentration cell was combined with a standard cadmium cell, and the E.M.F. of this combination determined, with the concentration cell acting both with and against the cadmium element. From these measurements the E.M.F. of the concentration cell was calculated. The means of the two values so obtained are given in the following table. As the E.M.F's. of the concentration cells do not amount to more than 3 to 4 hundredths of a volt, and small errors in the values of the E.M.F's. produce considerable errors in the values of x, it was found necessary to introduce corrections for any inequality of potential of the two copper electrodes when dipping in the same copper solutions. This inequality of potential did not ever appreciably exceed 1 millivolt. On making this correction, it was found that the values whose means are given in the following table did not differ by more than a few tenths of a millivolt. In order to eliminate errors due to the liquid potentials or to a varying degree of ionisation of the complex sulphate, only solutions of the same total copper content were compared, and these solutions contained large relative excesses of glycocoll.

Since $i_1 = i_2 = i$, Equations 1 and 2 reduce to—

$$\log \frac{[Cu^{\cdot\cdot}]_1}{[Cu^{\cdot\cdot}]_2} + x \log \frac{[G]_1}{[G]_2} = 0 \quad . \quad . \quad 3.$$

$$\log \frac{[Cu^{\cdot\cdot}]_1}{[Cu^{\cdot\cdot}]_2} + x \log \frac{[G]_1 - xi}{[G]_2 - xi} = 0 \quad . \quad . \quad 4.$$

TABLE IV.—*Final E.M.F. Measurements.*

Concentration of $CuSO_4$ in both solutions.	$[G]_1$.	$[G]_2$.	E.M.F. of concentration cell.	Temperature.	x Calculated from 3.	x Calculated from 4.
$n/80$	$5n/2$	$5n/4$	0·0335	19°	3·85	3·75
$n/100$	$2n$	$n/1$	0·0339	19°	4·12	4·00
$n/200$	$n/1$	$n/2$	0·0355	20·5°	4·05	3·95
$n/250$	$4n/5$	$2n/5$	0·0318	20·5°	3·63	3·54
$n/250$	$4n/5$	$2n/5$	0·0309	21°	3·53	3·45
$n/300$	$2n/3$	$n/3$	0·0327	19°	3·76	3·65
			Mean values		3·82	3·72

It will be observed that the ratios of glycocoll to copper sulphate are the same for the different pairs of solutions, so that any pair of solutions could be obtained from a more concentrated pair by dilution. This was done with the intention of seeing whether the value of x varied with the

dilution, the ratio of glycocoll to copper sulphate being constant. No variation within the above range of concentrations can be said with certainty to occur.

The E.M.F. measurements point to the existence of complex ions of the formula $[CuG_4]^{\cdot\cdot}$ and their dissociation products. To this ion corresponds the complex sulphate $[CuG_4]SO_4$. The fact that x comes out somewhat less than 4 is probably due to the partial dissociation of the complex ion $CuG_4^{\cdot\cdot}$ into less complex ions such as CuG_3, &c., *i.e.*, the elementary $Cu^{\cdot\cdot}$-ions are converted by the excess of glycocoll partly into complex ions containing less glycocoll than $CuG_4^{\cdot\cdot}$.

This conclusion requires to be supported by evidence obtained from some independent method, and with this object in view the freezing-point measurements described in the next section were undertaken.

2. *Freezing-point Measurements.*

A few preliminary measurements of the freezing-points of aqueous glycocoll solutions gave as a mean value for the molecular weight 73·5 (theoretical value, 75), thus confirming the already known result that glycocoll exists *substantially* as simple molecules in aqueous solution.

In order to investigate the complex formation, the freezing-points of a series of strong glycocoll solutions of gradually decreasing concentration were determined, and the *rise* of freezing-point produced by the addition of small quantities of copper sulphate to these solutions measured very carefully. Let γ denote the net number of active individuals removed from the solution per mol. copper sulphate added. As before, let x denote the number of glycocoll molecules which combine with the Cu-atom to form a complex. We shall now assume that practically all the copper sulphate added is converted by the large excess of glycocoll present into complex sulphate, and that at the fairly high dilution used the value of van 't Hoff's factor i for the complex sulphate is the same as that for copper sulphate of the same total molar concentration. Then, per grm. mol. copper sulphate added, i new individuals enter the solution, whilst x individuals (glycocoll molecules) are removed. Hence $x-i=\gamma$, or $x=\gamma+i$. If the solution employed is so dilute with respect to total copper that we can assume complete ionisation of the complex or simple sulphate, $x=\gamma+2$.

The practical range of this method of procedure is limited by the following considerations:—The rise of freezing-point actually measured being dependent upon the amount of $CuSO_4$ present, as much of this salt as possible must be added, in order to reduce the percentage error of the readings. But as it is imperative to have the glycocoll in large excess of the copper sulphate to ensure as complete as possible a formation of complex salt, the amount of copper salt that can be added will depend on the solubility of glycocoll at the temperature of the freezing-points. The cryohydrate point of glycocoll was found to be approximately $-3°$, so that at this temperature the saturated glycocoll solution must contain about 2·3 grms. of glycocoll per 20 grms. water. In the experiments to be described the amount of glycocoll taken varied from 1·2 to 2·1 grms. per 20 grms. water, whilst the rises of freezing-point observed varied from 0·021° to 0·088°. Supposing the probable error of any one reading to be 0·001° and of any measured rise to be 0·002°, the percentage error of the latter must vary from 9·5 per cent to 2·3 per cent.

In order to obtain values of x of sufficient accuracy for our purpose it is clearly necessary that the rises of freezing-point must be determined very carefully. In the apparatus used the cooling bath of ice and brine was surrounded by a vessel containing finely crushed ice, the outer walls of which were enveloped in felt, so that its temperature did not vary as much as one-tenth degree during a series of measurements. The stirring was done by an automatic stirrer driven at a constant rate, the Beckmann thermometers were kept in ice for several hours before a measurement, and for every series of measurements with one solution the temperature of the ice-brine bath was carefully adjusted so as to give a convergence-temperature as nearly as possible equal to the freezing-point to be measured. The supercooling was kept within the limits 0·1—0·2°. The following example well shows the general accuracy of the results:—

Freezing-point of Pure Glycocoll Solution.

Temp. of cooling bath.	Freezing-point.	Supercooling.
−4·5°	2·393	0·178°
−4·5°	2·390	0·150°
−4·5°	2·392	0·167°
−4·5°	2·394	0·162°
	Mean .. 2·392	

Freezing-points of Glycocoll-copper Sulphate Solution.

−4·5°	2·415	0·175°
−4·5°	2·413	0·171°
−4·5°	2·412	0·157°
	Mean .. 2·413	

Rise of freezing-point = 0·021°.
Concentration of copper sulphate = 0·000886 grm. mol. per 100 grms. water.
i for copper sulphate at this dilution = 1·89.
Total number of mols. glycocoll present in the solution per mol. $CuSO_4$ = 89·5.
Calculated value of x = 3·17.

The following table contains the results of the freezing-point measurements.

TABLE V.—*Freezing-point Measurements.*

Concentration of $CuSO_4$ in grm. mols. per 100 grms. water.	Mols. glycocoll per mol. of $CuSO_4$.	Rise of freezing-point.	Values of i for $CuSO_4$.	Values of x when— i for complex salt has same value as for $CuSO_4$.	Values of x when— i for complex salt is taken as 2.
0·000886	89·5	0·021°	1·89	3·2	3·3
0·00146	84·4	0·0355°	1·81	3·1	3·3
0·00194	63·5	0·0555°	1·75	3·3	3·5
0·0023	60·6	0·055°	1·70	3·0	3·3
0·00182	54·4	0·0393°	1·76	2·9	3·2
0·00297	46·5	0·072°	1·63	2·9	3·3
0·00346	40·0	0·0885°	1·59	3·0	3·4
0·00298	33·3	0·0643°	1·64	2·8	3·2
		Means		3·0	3·3

The values of i for solutions of $CuSO_4$ have been previously determined, but it was deemed advisable to redetermine these cryoscopically for the present purpose, so as to ensure a high degree of comparability in the measurements. The values given in the above table have been obtained by graphical interpolation and extrapolation from the following measurements:—

TABLE VI.

Concentration of $CuSO_4$ in mols. per 100 grms of water.	Lowering of freezing-point.	Value of i.
0·0031	0·095°	1·62
0·0067	0·172°	1·38
0·0109	0·247°	1·22
0·0194	0·407°	1·14
0·0227	0·457°	1·09
0·0264	0·523°	1·07

The values of x in Columns 5 and 6 of Table V. do not differ to any very considerable extent. The true mean will lie undoubtedly between 3·0 and 3·3. It will be observed that this number is considerably lower than 3·72, the mean of the values obtained from the electrometric measurements recorded above. This divergence admits, however, of explanation, when we consider that for the solutions used for the cryoscopic measurements the ratio of mols.

glycocoll to mols. $CuSO_4$ varied from 33 to 89, whilst in the case of the solutions employed in the electromotive force measurements, this ratio varied from 100 to 200. It is to be expected that in the former case the non-electrolytic dissociation of the complex ion or ions would be greater owing to the smaller excess of glycocoll present. In accordance with this explanation, it will be seen that the values of i given in Column 5 of Table V. show a general tendency to decrease with decreasing values of the ratio mentioned above.

3. *Further Electrometric Measurements.*

In order to obtain a more direct comparison between the results of the electrometric and cryoscopic measurements, pairs of solutions were taken in which the molar ratios of glycocoll to copper sulphate were 30 and 90. In other respects the same procedure was followed as described under the final measurements of Section 1 of this paper. The results obtained are given in the following table :—

TABLE VII.—*E.M.F. Measurements in Solutions diluter with respect to Glycocoll.*

Concentration of $CuSO_4$ in both solutions.	Concentration of glycocoll in— First solution.	Second solution.	E.M.F. of combination.	Temp.	Value of x from— Equation 3.	Equation 4.
$n/80$	$3n/8$	$9n/8$	0·0458	14°	3·38	3·15
$n/80$	$3n/8$	$9n/8$	0·0471	11°	3·51	3·30
$n/160$	$3n/16$	$9n/16$	0·0390	12°	2·90	2·75
$n/160$	$3n/16$	$9n/16$	0·0422	14°	3·12	2·95
			Mean totals		3·23	3·04

The mean value of x calculated from these E.M.F. measurements agrees very well with the mean value obtained from the freezing-point measurements, which shows that the explanation of the previously noted divergence given at the end of Section 2 is probably the correct one.

(To be continued).

A NEW COLOUR TEST FOR MOLYBDENUM.

By WILLIAM BETTEL.

IN 1903, while engaged upon the examination of so-called "refractory" ores containing molybdenum, I had occasion to add hydrogen peroxide to an aqueous solution of ammonium molybdate, rendered faintly alkaline with ammonia, with a view to converting the lower oxides of molybdenum —colouring the solution blue—into molybdate. The result of the experiment was the production of an intense brownish red colour (slightly redder than the colour produced by the Nessler test in weak ammonia solutions), the salt produced being, presumably, a permolybdate. This reaction, I believe, has not hitherto been published. On testing a sample of "chemically pure" ammonium molybdate with peroxide of hydrogen, one merely obtains the yellow colour (permolybdic acid ?) given by acid solutions of molybdenum trioxide when treated with hydroxyl. On rendering the solution slightly alkaline with ammonia, the yellow colour is replaced by the reddish brown colour previously observed. This colour is partly discharged by dilution, and disappears on standing, oxygen being evolved.

The colour is instantly discharged by addition of excess of alkalis; a moderate excess of ammonia has little action on the colour, but a large excess of ammonia discharges it. The colour is produced in aqueous solutions of alkaline molybdates (K and Na), quite neutral, or containing a mere trace of free alkali; this reaction is therefore a good indicator of neutrality when forming neutral molybdates.

For detection of molybdenum the solution to be tested is evaporated nearly to dryness, tested for neutrality by litmus; if alkaline, neutralised by nitric or sulphuric acid and solution of peroxide of hydrogen added. If a yellow colour is observed, add a small drop of dilute ammonia; the brownish red colour will then appear if molybdates are present.

To test the delicacy of the reaction various amounts of a standard solution of ammonia molybdate containing 5 mgrms. MoO_3 per 100 cc. were taken, evaporated to nearly dryness in porcelain capsules, cooled, the small drop rendered faintly ammoniacal, and two drops of a 5 per cent solution of pure peroxide of hydrogen added.

1. = 0·00005 grm. MoO_3 Strong reaction.
2. = 0·000005 „ Distinct reaction.
3. = 0·000001 „ Very faint tint, unmistakeable reaction.

Although I have found this reaction useful for approximately estimating molybdenum in rocks and ores, the instability of the permolybdates renders the method unsuitable for *accurate* quantitative work.

As a confirmatory test in qualitative analysis, and for detecting the presence and approximately estimating the percentage of molybdenum in tungsten trioxide, obtained in analysis of scheelite, wolframite, hubnerite, and other tungsten minerals, the reaction has frequently been made use of in my laboratories since 1903, with satisfactory results.

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THE CORROSION OF IRON AND STEEL.

By WILLIAM H. WALKER, ANNA M. CEDERHOLM, and LEAVITT N. BENT.

(Concluded from p. 33).

Ferroxyl Indicator.—That the corrosion of iron is an electrolytic phenomenon is shown by a very simple experiment devised by Dr. Allerton S. Cushman and ourselves. A piece of iron is immersed in ordinary water to which has been added a little phenolphthalein and a trace of potassium ferricyanide. Within a very few minutes the iron is seen to divide itself into zones or surfaces which exhibit opposite polarity. Those portions where the iron is anodic will become coated with a precipitate of Turnbull's blue, owing to the escape of the iron ions at those points. Those portions on which hydrogen is being liberated, acting as cathodes, will become bright red owing to the formation of hydroxyl ions. This action may be more easily studied if this reagent (for which Dr. Cushman has proposed the name "ferroxyl") be thickened by the addition of neutral gelatin or agar-agar. We will return to this phenomenon later in this paper.

Function of Oxygen.—The rapidity with which iron will pass into solution in water depends not only upon the electrolytic solution pressure of the iron and hydrogen, and the osmotic pressure of the iron ions already in solution, but also upon the "excess voltage" (uberspannung) which is required in order that the hydrogen ion which passes from the ionised condition may be set free (Nernst, *Theoretische Chemie*, 5th Ed., p. 712). In this case there is a counter electromotive force which must be overcome before the hydrogen can be liberated. It is possible, therefore, that the quantity of iron which can dissolve in water is limited to that amount which is equivalent to the hydrogen necessary to polarise that portion of the specimen which acts as the cathode. If this is the case, we should be able to make this solvent action continuous by the addition of any reagent which will depolarise the hydrogen-covered cathode portion. This reaction may be shown by the following very simple apparatus.

* Read before the New York Section of the American Chemical Society, May, 1907. From the *Journal of the American Chemical Society*, xxix., No. 9.

Two unglazed porcelain cups are placed concentric with each other and within a small Mason fruit jar, in the zinc top of which is soldered a small piece of copper tubing. The three vessels are filled with hundredth-normal potassium chloride solution free from oxygen and carbon dioxide, and the whole placed upon a hot plate of a temperature to insure continuous boiling. Two pieces of clean, pure iron, joined by an iron wire, are introduced into the central and outside compartment, and the whole while still boiling is sealed by screwing on the metallic cap. Hydrogen is allowed to enter the jar as it cools, in order to relieve the vacuum and prevent leakage of air. Such a cell may be maintained many hours without dissolving enough iron in either compartment to be detected by potassium ferricyanide in its unconcentrated condition. When reduced to a few drops, however, iron may always be shown to be present. Portions of each iron plate may be assumed to be anodic with iron tending to go into the ionised form, and other portions cathodic, being polarised by a film of hydrogen. If, now, a substance which will dissolve away the hydrogen be added to one compartment, the cathodic portion of the iron contained therein should be depolarised and the action should result in the solution of the anodic portions. Since the two pieces of iron are short-circuited above by a wire, and below by the electrolyte, that piece which is continually depolarised would be expected to become the cathode, and the other the anode. Hydroxylamine serves as such a depolariser, and from an apparatus as above described, after standing for forty-five hours at room temperature, the following results were obtained :—

	Blank.	Hydroxylamine.
Increase in weight of cathode	0·0005 grm.	0·0380 grm.
Decrease in weight of anode	0·0002 „	0·0393 „

When a 5 per cent solution of potassium dichromate is used as a depolariser, and the cell allowed to stand at room temperature for forty hours, the results were :—

	Blank.	$K_2Cr_2O_7$.
Increase in weight of cathode	0·0001 grm.	0·0212 grm.
Decrease in weight of anode	0·0000 „	0·0217 „

By passing a stream of hydrogen gas through all three cups iron will not dissolve in six hours sufficiently to give directly the ferricyanide test. If the hydrogen stream in one compartment be replaced by oxygen, iron will immediately begin to dissolve at an appreciable rate in the other compartment, separated though it is by the intermediate compartment through which hydrogen is passing. The dissolved iron in the anode compartment remains in solution as a ferrous salt, while the cathode compartment becomes strongly alkaline. If the porous cells be withdrawn, the iron at once oxidises and is precipitated as brown ferric hydroxide.

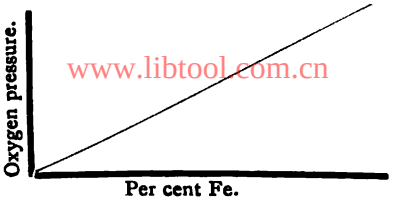
Mr. J. A. Collins, in a thesis presented at the Institute in 1898, noted the fact that if a piece of iron and a piece of magnetic oxide be immersed in water and connected through a voltameter, a very appreciable current would flow through the system with the iron as anode. To determine whether oxygen was a factor in this process the following experiment was performed. In a Jena flask containing hundredth-normal potassium chloride were suspended by fine platinum wires a piece of pure iron and a piece of magnetic oxide. These suspending wires were connected through a silver voltameter. By fitting the flask with a stopper containing gas inlet and outlet tubes, the operation could be carried on in either a vacuum or in any desired atmosphere. When all air and carbon dioxide were expelled by long boiling, and the flask cooled under conditions which preserved the vacuum, no current passed through the voltameter upon closing the switch. When connected through a Lippmann electrometer, however, a difference of potential between the two pieces was apparent. The electromotive force of the system is obviously not sufficient to furnish the "excess voltage" necessary to iberate the hydrogen on the magnetic scale, and while there exists this marked difference of potential, no appreciable current passes. If the concentration of the hydrogen ions be increased, as can be accomplished by saturating the water with carbon dioxide, the electromotive force is then sufficient to overcome this resistance and a measurable current is obtained, the iron passing into solution. If, on the other hand, air free from carbon dioxide be passed into the flask, the cathodic film is depolarised by the oxygen and the iron dissolves. As a secondary reaction, the oxygen oxidises, and the hydroxyl set free at the cathode precipitates the dissolved iron with the deposition of rust; this formation of rust is a factor in corrosion, however, only in so far that the concentration of the iron ions is kept very low, and hence its osmotic pressure is negligible.

The influence of the depolarisation action of oxygen may be conveniently studied by using the ferroxyl indicator. For example, in a beaker may be placed a porous earthenware cell, and the whole filled with ordinary water containing phenolphthalein and a very little ferricyanide. If a piece of iron be placed within the cell and connected by means of an iron wire with a piece of platinum in the outside compartment, immediate action takes place, deep red appearing on the platinum and a coating of blue precipitating on the iron. If, however, the platinum be heated in an alkaline pyrogallate solution, washed in boiling distilled water, and while wet used as the cathode in the cell, no action will take place for a number of hours. Only as the platinum takes up oxygen from the atmosphere does the reaction becomes apparent.

The influence upon the rate of solution of iron which different metals exercise when connected by a metallic conductor with the iron, is also easily shown by this method. Those metals in the electrochemical series more negative than iron influence the action, not in proportion to their relative position in the series, but rather in proportion to some other property, possibly their ability to occlude or condense oxygen. On the other hand, aluminium is much less active in protecting iron than is zinc although it is more electro-positive, while manganese completely reverses the polarity, making the iron the cathode and itself dissolving rapidly with the formation of brown manganese hydroxide.

Another conception of this action which differs only in the point of view from the above, is to consider the metal which acts as a cathode, for example, the platinum, as an oxygen electrode, and that the current flowing through the circuit (on account of which the iron dissolves) is due to the solution of oxygen and the formation of hydroxyl ions charging the solution negatively, and thereby requiring a solution of iron at the other electrode to bring about electrostatic equilibrium. When viewed in either of these two lights, the action should be proportional to the concentration of oxygen in the solution, and hence, according to the laws of Henry and Dalton, to the partial pressure of the oxygen in the atmosphere above the solution. An experiment to test this conclusion was performed as follows :—A number of Jena flasks were partly filled with boiled water and connected by means of a by-pass to a reservoir filled with definite mixtures of oxygen and nitrogen, freed as far as possible from carbon dioxide by being washed through strong potassium hydroxide and stored over barium hydroxide solution. When the water in the flasks was boiling violently, equal weights of pure iron were introduced, and after ten minutes further boiling, the exit tubes were sealed, and by means of the by-passes, each flask as it cooled drew from the reservoir with which it was connected an atmosphere of known composition. Two or three times each day the gas over the solution was changed by passing through the flask a quantity of gas from the reservoir. At the end of a few hours the difference in the rapidity with which the iron was attacked was easily apparent, and after standing for four or five days the wire in each flask was cleaned and weighed. Any oxide which adhered to the wire was reduced in hydrogen and the wire again weighed. The loss of iron was in this way calculated, and the results shown in the

plot. The rate of the reaction is thus seen to be a direct function of the oxygen pressure, and it is to be noted that the curve passes through the zero point. Only that



amount of carbon dioxide which will not be absorbed by strong caustic alkalis could have been present, and this amount must have been constant in each flask. If the presence of carbon dioxide is an important factor in corrosion, it is difficult to understand why the solvent action should be so independent of the amount of carbon dioxide present. Although the same weight of iron was added to each flask, there was not the same area undergoing active corrosion in each case. There were always clearly defined cathodic portions on each wire, which remained perfectly bright, and on which the hydrogen was being deposited and the oxygen absorbed. These differed markedly in the different specimens, but did not seem to bear a definite relation to the pressure of oxygen. When phenolphthalein was present, the bright spots were seen to continue to maintain a red zone in the solution around them. This irregularity in the area of iron actually attacked accounts in some measure for the irregularities in the position of points not falling on the straight line in the plot.

The fact that the acceleration action of increased pressure of oxygen may be looked upon as due to an oxygen electrode, has an interesting bearing upon Dunstan's theory of the intermediate formation of hydrogen peroxide. Richarz and Lonnes (*Zeit. Phys. Chem.*, xx., 145) decomposed water saturated with air by passing through it, between platinum electrodes, a current of low electrode density. They found that at the cathode the hydrogen was to a large extent not liberated as such, but that it combined with the dissolved oxygen to form hydrogen peroxide. These are exactly the conditions which obtain upon the cathodic portions of iron undergoing corrosion, except that here we have iron instead of platinum. The appearance of hydrogen peroxide is therefore to be expected, provided it can exist on an iron surface. Dunstan could detect it when zinc corroded, but failed to get a positive reaction in the case of iron. Dunstan explains the generally recognised inhibiting effect of the alkalis, potassium dichromate, &c., by the fact that they all instantly decompose hydrogen peroxide. If some condition already exists upon the surface of the iron such that hydrogen peroxide cannot exist, and if hydrogen peroxide is a step in the formation of rust, it is difficult to see what influence either for or against corrosion substances can have which also destroy hydrogen peroxide. The peroxide, if formed at all, can be formed only when hydrogen is being oxidised by the dissolved oxygen, and the latter reaction takes place, as we have shown, on points separated from the points at which iron is passing into solution, and where if the water is still, rust patches will not form. The formation of hydrogen peroxide must be considered, therefore, incidental to and not necessary for corrosion.

It is a generally known fact that strong solutions of hydrogen peroxide will entirely protect iron from corrosion. If iron be placed in a solution of pure hydrogen peroxide, oxygen is liberated upon its surface, but no rusting occurs. Moody takes this as a positive proof that oxygen alone cannot occasion corrosion. Assuming that hydrogen peroxide is a cathodic product of the action of iron on water, we would expect the presence of this reagent to inhibit the reaetion, inasmuch as the law of mass action demands that the formation of a substance be limited by the concentration of that already formed.

Another possible explanation of the protective effect of hydrogen peroxide may be found in the formation of a kind of passive condition analogous to that produced by potassium dichromate, already referred to. Although much has been written upon this interesting subject there is as yet no perfectly satisfactory theory of passivity. We have noted that in the action of iron on water, when the concentration of the hydrogen ions is not sufficiently large to overcome the excess voltage of the iron surface, no action takes place unless a depolarising substance such as dissolved oxygen is present, and then the surface divides itself into zones of different polarity. It may be possible that when iron is placed in a dichromate solution or hydrogen peroxide solution, it absorbs or occludes so dense a film of oxygen upon its surface as to render the entire piece of metal so strongly cathodic that no corrosive action can take place (A. S. Cushman, *Bulletin* No. 30, Office of Public Roads, U.S. Dept. of Agriculture).

When bright iron is heated in the air, oxygen attacks the iron directly, forming a closely adhering layer of oxide even if it be of but microscopic thickness. That oxygen does not unite directly with iron in aqueous rusting is shown by the experiment already referred to with the porous cell, and also by the fact that the rust formed is never adherent to the surface of the iron. The slightest rubbing with the hand produces a clean, bright surface of pure iron. Only when this layer of ferric hydroxide dries on the surface of the iron is an adherent scale produced. Moody (*Proc. Chem. Soc.*, xxiii., 84), in a very recent communication, describes an experiment in which he shows that iron does dissolve before being precipitated as rust. He uses this fact as a further proof that carbon dioxide is essential to rusting. We see ample grounds for concluding that carbon dioxide was absent in the experiments already outlined, and yet the iron surely passed into solution before precipitating.

If a piece of chemically pure iron free from mechanical strains and without evident crystallisation be immersed in the ferroxyl indicator, the positive and negative zones will be apparent after a few moments. There appears to be an unequal concentration of oxygen or segregation of oxygen upon the surface, which cannot be explained by discernible differences in the character of the surface. If the ferroxyl indicator be removed, the surface cleaned by rubbing with a dry towel, and the indicator again applied, the same separation into zones is seen, though in an entirely different configuration. The indicator is apparently a very delicate one and susceptible to changes in equilibrium, which up to the present have not been detected by other means.

Since corrosion is manifestly an electrochemical action, it seemed probable that if two specimens of iron were selected, one of which had proven itself in practice as especially resistant to corrosion, and another which had shown itself to be very susceptible to corrosion, certain differences in the electrochemical behaviour should be discernible. Two sets of such specimens were obtained. The first consisted of two pieces of sheet metal which had been used as culverts in road building, one of which had given way in but a short time, while the other was practically intact. The second set consisted of two strands of wire from a piece of ordinary barbed wire fencing, one of which was badly corroded upon an exposure of but six months, while its neighbour was apparently in its original condition. Nothing is known of the history of the two wires; the good piece of sheet was known to be from an open hearth steel ingot containing but a trace of manganese, and in the heating and rolling of which extra precautions had been taken to prevent segregation. The poor piece was known to be from an ingot of ordinary Bessemer steel.

If corrosion be an electrochemical phenomenon depending upon the formation of an anode portion and a cathode portion and the passage of a current between these two, the rate of this corrosion may be assumed to be proportional to the difference of potential between the two

surfaces. In order to determine whether there was any marked difference in the samples of iron above referred to, in regard to variation in potential between points taken at random over the surface of each, the following method was employed :—In the case of the sheet metal, specimens were machined to an area of about three square inches in the form of a rectangle one inch wide by three inches in length. A block of paraffin one-quarter inch thick was cut to have the same surface as the sheet metal. A number of small holes about one-eighth inch in diameter were drilled in the paraffin and the latter pressed upon the sheet after warming the same. A number of small electrically insulated cells were thus formed, the bottom of each being a definite portion of the surface of the metal. The physical condition of the different pieces of metal experimented with was made as uniform as possible before applying the paraffin block, by polishing each upon a fine, dry sandstone. When any electrolyte, for example, hundredth-normal potassium chloride solution, was placed in these cells, a difference of potential between any two could readily be measured by means of Poggendorff's compensation method. The composition of the cell was Pt-KCl-Fe-Fe-KCl-Pt. In many cases a current of sufficient intensity was set up to rapidly polarise the platinum wire electrodes which were used to complete the circuit from the electrolyte in one cell, through the measuring instrument to the electrolyte in the other cell. In order to eliminate any effect which a difference in the surface of the platinum wires might introduce, these were heated in a Bunsen burner before each measurement. By taking a measurement and then interchanging the platinum wires in the respective cells, no difference in the reading was observed, and therefore the potential found was independent of the platinum. A cell for investigating the samples of wire was made in an analogous way, using a long wooden trough in which the wires were inserted, and forming cells by building up partitions of paraffin at intervals along the length of the wire.

The differences in the average variation of any two cells taken at random over the surface of sheet metal in the one case and the two wires in the other, are very marked, a typical set of readings being shown in the following table, the figures representing differences in potential, expressed in millivolts, between various cells :—

Poor Sheet.			*Good Sheet.*		
I.	II.	III.	I.	II.	III.
− 56	−60	+ 47	− 5	− 5	− 8
+ 48	+21	− 86	0	− 8	0
+ 39	+30	− 48	+ 4	0	−20
− 26	−93	− 69	0	0	−20
+ 56	−31	−177	+18	− 8	0
− 30	+ 8	− 58	+ 2	+ 8	0
+ 21	+81	− 32	0	0	− 5
Corroded Wire.			*Good Wire.*		
+161	+13	− 30	0	+ 2	+ 8
+ 93	−24	+ 38	+ 4	+13	0
+ 21	+13	+ 63	+13	0	+ 4
+ 43	−21	+103	0	0	+13
+ 8	−56	+ 26	+17	+ 4	+ 4
+ 30	−64	− 43	− 8	− 5	− 8
+ 55	−43	+ 47	0	+ 9	0
− 16	−52	+119	− 5	0	0
+ 78	−21	+ 8	− 8	+26	− 5

After measuring the difference of potential as above, the paraffin was in each case removed, a fresh surface obtained and the experiment repeated. No two cells ever reacted alike, but there was always the marked difference between the two pieces of metal indicated above.

It is as yet too early to decide that measurements of this kind indicate the tendency of iron to corrode, but by investigating a large number of specimens of known resistance to corrosion we hope to obtain definite information on this point.

Summary.

We have—

1. Proven again that carbon dioxide is not essential for the corrosion of iron ;
2. Substantiated the work of Whitney and shown that iron does dissolve in pure water in the absence of carbon dioxide and oxygen ;
3. Shown that the primary function of oxygen in the corrosion of iron is in depolarising those cathodic portions of the iron upon which hydrogen tends to precipitate, and that a secondary function is the oxidation of the ferrous iron ion to the ferric form, with its subsequent precipitation as ferric hydroxide ;
4. Shown that the rapidity of corrosion in water is a linear function of the partial pressure of the oxygen in the atmosphere above the water ;
5. Shown that an electric current can pass between bright iron and iron covered with scale, (1) if the concentration of the hydrogen ions be increased by the presence of an acid, or (2) if oxygen or some other depolarising substance be present ;
6. Shown that in certain instances, areas having marked difference in potential exist in far greater number upon the surface of a piece of iron prone to corrosion than upon iron which is resistant to corrosion.

This investigation is being continued, and in a subsequent paper the more practical phases of the subject will be dealt with.

REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS, 1908.*

SINCE the preparation of our report for 1907, several important determinations of atomic weights have been published. They are, briefly, as follows :—

Nitrogen.—Richards and Forbes have re-determined the ratio between Ag and NO_3, as shown in the composition of silver nitrate (*Journ. Am. Chem. Soc.*, xxix., 808 ; and *Zeit. Anorg. Chem.*, lv., 34). The ratio found, with all corrections applied, is $Ag : NO_3 = 100 : 57{\cdot}479$. Hence, if $Ag = 107{\cdot}930$, $N = 14{\cdot}037$; and if $N = 14{\cdot}008$, $Ag = 107{\cdot}880$. In short, the higher atomic weight hitherto assigned to silver is inconsistent with the lower value for nitrogen as found in several recent investigations.

Sulphur.—Richards and Jones have measured the ratio between Ag_2SO_4 and AgCl (*Journ. Am. Chem. Soc.*, xxix., 826 ; and *Zeit. Anorg. Chem.*, lv., 72). From the data obtained, if $Ag = 107{\cdot}930$, $S = 32{\cdot}113$, a value much higher than that commonly accepted. If $Ag = 107{\cdot}880$, then $S = 32{\cdot}069$, which is near the figure given in our former tables. Additional evidence relative to this constant is much to be desired, for it influences the determination of many other atomic weights, especially those of the rare-earth metals.

Potassium.—From the ratios Ag : KCl and AgCl : KCl, Richards and Staehler find $K = 39{\cdot}114$, when $Ag = 107{\cdot}930$ and $Cl = 35{\cdot}473$ (*Journ. Am. Chem. Soc.*, xxix., 623 ; and *Ber.*, xxxix., 3611). From the corresponding bromide ratios, with $Br = 79{\cdot}953$, Richards and Mueller find $K = 39{\cdot}1143$ and $39{\cdot}1135$ (*Journ. Am. Chem. Soc.*, xxix., 639 ; and *Zeit. Anorg. Chem.*, liii., 423). The final result of both researches is $K = 39{\cdot}114$, a distinct lowering of the constant in question.

Manganese.—Atomic weight re-determined by Baxter and Hines, from analyses of the chloride and bromide (*Journ. Am. Chem. Soc.*, xxviii., 1560 ; and *Zeit. Anorg. Chem.*, li., 202). The mean of their very concordant determinations is $Mn = 54{\cdot}957$, when $Ag = 107{\cdot}930$.

Cobalt.—From new analyses of the chloride, Baxter and Coffin find $Co = 58{\cdot}997$, or 59 in round numbers (*Journ. Am. Chem. Soc.*, xxviii., 1580 ; and *Zeit. Anorg. Chem.*, li., 171). This confirms the earlier determinations by Richards and Baxter.

* From the *Journal of the American Chemical Society*, xxx., No. 1.

International Atomic Weights. (1908).

Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	75·0
Barium	Ba	137·4
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·96
Cadmium	Cd	112·4
Cæsium	Cs	132·9
Calcium	Ca	40·1
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·45
Chromium	Cr	52·1
Cobalt	Co	59·0
Columbium	Cb	94
Copper	Cu	63·6
Dysprosium	Dy	162·5
Erbium	Er	166
Europium	Eu	152
Fluorine	F	19·0
Gadolinium	Gd	156
Gallium	Ga	70·0
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·0
Hydrogen	H	1·008
Indium	In	115
Iodine	I	126·97
Iridium	Ir	193·0
Iron	Fe	55·9
Krypton	Kr	81·8
Lanthanum	La	138·9
Lead	Pb	206·9
Lithium	Li	7·03
Magnesium	Mg	24·36
Manganese	Mn	55·0
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Neodymium	Nd	143·6
Neon	Ne	20
Nickel	Ni	58·7
Nitrogen	N	14·01
Osmium	Os	191·0
Oxygen	O	16·00
Palladium	Pd	106·5
Phosphorus	P	31·0
Platinum	Pt	194·8
Potassium	K	39·15
Praseodymium	Pr	140·5
Radium	Ra	225
Rhodium	Rh	103·0
Rubidium	Rb	85·5
Ruthenium	Ru	101·7
Samarium	Sa	150·3
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·4
Silver	Ag	107·93
Sodium	Na	23·05
Strontium	Sr	87·6
Sulphur	S	32·06
Tantalum	Ta	181
Tellurium	Te	127·6
Terbium	Tb	159·2
Thallium	Tl	204·1
Thorium	Th	232·5
Thulium	Tm	171
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·2
Xenon	Xe	128
Ytterbium	Yb	173·0
Yttrium	Y	89·0
Zinc	Zn	65·4
Zirconium	Zr	90·6

Indium.—Mathers, from analyses of indium chloride, found In = 114·88 (*Journ. Am. Chem. Soc.*, xxix., 485; and *Ber.*, xl., 1220). From the bromide, In = 114·86. The author recommends the adoption of the rounded-off value, 114·9, when Ag = 107·93, Cl = 35·473, and Br = 79·953.

Tellurium.—Norris, by twelve concordant reductions of the basic nitrate, $2TeO_2 \cdot HNO_3$ to TeO_2, found the atomic weight of tellurium to be 127·48, when N = 14·01 (*Journ. Am. Chem. Soc.*, xxviii., 1675). With N = 14·04, Te = 127·64, which is in better agreement with other recent determinations. The true cause of the difference is not clear.

Neodymium.—Holmberg has re-determined the atomic weight of this element by synthesis of the sulphate from the oxide (*Zeit. Anorg. Chem.*, liii., 83). In mean, when S = 32·06, Nd = 144·08. This is higher by 0·48 than the value given in our table.

Dysprosium.—In two series of determinations, based upon the ignition to oxide of the octohydrated sulphate, Urbain and Demenitroux find for the atomic weight of dysprosium, values ranging between 162·29 and 162·75 (*Comptes Rendus*, cxliii., 598). In mean, Dy = 162·53.

Radium.—Mdme. Curie, in a series of three new determinations, has found a more precise value for the atomic weight of radium (*Comptes Rendus*, cxlv., 422; the atomic weight of radium is also under investigation by Thorpe). Working with material more abundant and pure than that formerly analysed, she found Ra = 226·18 when Ag = 107·8 and Cl = 35·4. With Ag = 107·93 and Cl = 35·45, Ra = 226·45. This number is higher than her earlier determination by more than a unit.

From the data here given, and from those cited in previous reports, it is evident that the entire table of atomic weights is in need of revision. The values assigned to K and Na are too high; those given to Cl and S are too low; and these constants affect the determinations of many others. They depend, however, upon the atomic weight of silver, which is probably, but not certainly, as low as 107·88. It is well known that work upon these fundamental constants is now nearing completion in several laboratories, notably under T. W. Richards, W. A. Noyes, and probably other investigators also. Within a few months it should be possible to enter upon a satisfactory revision of the table, a task which would be unsatisfactory if undertaken now. It is true, as Brauner has suggested (*Chemiker Zeitung*, May 11, 1907), that the present table contains inconsistencies, but they are small in amount, and are due to inconsistencies in the original data from which the values are derived. In our next report we hope to recompute the entire table; but meanwhile, awaiting the completion of the researches which we know to be in progress, we prefer to leave the table practically unchanged. A conservative policy seems to be safer than one of haste, and the delay of another year will do no harm. One exception to the rule may, however, be made. Dysprosium, with the atomic weight 162·5, may now be properly added to the list of the chemical elements, and we recommend its insertion in the table.

It is with the deepest regret that we record the loss, by death, in February last, of our distinguished colleague, Professor Moissan. The Chemical Society of Paris has designated Monsieur G. Urbain as his successor upon this Commission.

(Signed)

F. W. CLARKE,
W. OSTWALD,
T. E. THORPE,
G. URBAIN.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY.

Ordinary Meeting, January 6th, 1908.

Dr. J. LEWKOWITSCH in the Chair.

"*Some Observations on the Keeping Power of Fehling's Solution, together with Notes on the Volumetric Process of Determining Reducing Sugars with it.*" By FRANCIS WATTS, C.M.G., D.Sc., F.I.C., and H. A. TEMPANY, B.Sc., F.I.C. Read by the Honorary Secretary.

The authors point out that, contrary to the commonly expressed ideas, Fehling's solution, or at least Violette's modification of it, is not liable to deteriorate rapidly if kept in the dark, and if access of air is prevented. The solution can thus be kept mixed ready for use for many months, and it is not necessary to keep the stock in the form of two solutions to be mixed as required.

The actual titration is as follows:—Ten cc. of the Violette-Fehling's solution are measured into a small beaker of about 100 to 150 cc. capacity, and to it is added an equal quantity of distilled water. The solution is brought up to boiling-point on a sand-bath, and the reducing sugar solution added from a burette until the blue colour of the liquid is no longer distinctly visible. The end-point of the titration is determined by filtering drops of the solution on a small specially arranged pad of filtering-paper. A sheet of specially toughened filter-paper forms the top layer; this is placed upon two sheets of filter-paper of a rough fairly open type; these layers of filter-paper are then cut into squares of about 1 sq. cm. The liquid to be tested is dropped on the hardened filter-paper and allowed to soak through the three layers; the two upper layers of filter-paper containing all the precipitated cuprous oxide are rejected, and the spot of liquid on the lower one is tested for unreduced copper with ferrocyanide and acetic acid.

As a result of a number of determinations the authors find that, when sucrose is present, each grm. dissolved in 100 cc. of the solution under examination possesses reducing power equal to 0·0033 grm. of invert sugar dissolved in the same volume, and they advocate the use of this factor by way of correction of the amount of invert sugar determined in the presence of known quantities of sucrose. It is shown that in the absence of this correction the amount of invert sugar determined by Fehling's solution, in such cases as that of sugars, may be seriously in error.

"*The Determinations of Small Quantities of Bismuth.*" By HERBERT W. ROWELL.

A series of results by six chemists showing remarkable variations on the same samples justifies the appearance of the paper. The usual methods of separation and the ammonium carbonate methods in particular are unfavourably criticised, and sources of error are pointed out. Methods of separation suitable for ores, copper, and base bullion are given, which eventually precipitate the bismuth together with various impurities which do not affect the subsequent colorimetric estimation, but aid in the collection of the bismuth. The colour test depends upon the solubility of bismuth iodide in excess of potassium iodide producing a yellow colour; iodine is destroyed by sulphurous acid, and the effect of other metals is nullified by the methods given. The test is very delicate, and the amount of bismuth in copper or base bullion may be determined within five hours. A convenient form of colorimeter suitable for this, copper, Nessler, and similar colour tests, is also described.

Solubility of Graphite in Iron.—Georges Charpy.—The author has determined the solubility of graphite in iron, using different methods; for instance, dissolving in iron graphite previously separated by cooling, or slowly cooling liquid pig-iron, and his results show that the solubility decreases regularly with the temperature, and most probably the solubility in pure iron at 1000° is 1 in 100.—*Comptes Rendus*, cxlv., No. 25.

NOTICES OF BOOKS.

Coal. By JAMES TONGE. London: Archibald Constable and Co., Ltd. 1907.

THIS volume belongs to the Westminster series of books upon subjects connected with scientific industries which have a special interest for the public. Town Gas, India-rubber, Electric Power, and Traction have already been treated in different volumes, and Coal might be made quite as interesting as any of these. The author has, however, limited the discussion of his subject in such a way as to reduce rather seriously its attractiveness for the average reader. Thus the paleontology of the coal measures is treated fairly fully, and the chapters on fossil botany are copiously illustrated. At the same time, looking at an illustration of a fossil is a very poor substitute for handling the real thing, and any branch of geology is generally found a dry science unless it is supplemented by a large amount of field work, for which the readers of such a book as this would probably have little opportunity. On the other hand, a description of the working of a coal mine would have been a topic which would surely have interested such readers, but the author has altogether neglected mining practice, although he gives a chapter on the preparation of coal for the market. The chapter on the position and importance of the coal fields of the world is necessarily rather full of statistics, but the early parts of the book on the history and occurrence of coal are well written, and will arouse and stimulate the interest.

The Science Year Book, 1908. London: King, Sell, and Olding.

THE Science Year Book for 1908 is a diary, directory, and scientific summary combined. It contains useful meteorological and astronomical data for every day in the year, and ample room is allowed for recording personal observations and notes. Short summaries are given of the progress made in 1907 in different branches of science, and biographies of British and American scientific men of note are included. The value of the Year Book is increased by the addition of logarithm tables and tables of gradients and speeds.

Guide de Préparations Organiques. ("Handbook of Organic Preparations.") By EMIL FISCHER. Translated by H. DECKER and G. DUNANT. Paris: Gauthier-Villars. 1907.

PROFESSOR Emil Fischer's manual of organic preparations is the outcome of many years' experience of the requirements of students, and is one of the best of its size and scope on the subject. It is divided into two parts, the first of which is intended more especially for the use of chemists, while the second contains the descriptions of the methods of preparation of those compounds which are of more interest and importance for doctors and biologists. An excellent selection of substances has been made, and examples are given of practically all the common methods of synthesis of organic compounds. No theoretical explanations are provided, for the author considers that in the laboratory the student's time is fully occupied with the experimental details, and that therefore, before proceeding to the practical work, he should study the theory of the reactions involved, either in the original publications, to which references are frequently given, or else in standard text-books of organic chemistry. The translation has been made from the latest German edition, and the completeness of the directions given and clearness of language employed together make it particularly suitable for the use of students in large laboratories, where the personal supervision of the teacher is necessarily reduced to a minimum.

Traité de Chimie Analytique Qualitative. "Treatise on Qualitative Analytical Chemistry.") By L. Duparc and Alfred Monnier. Genève: Libraire Kündig. Paris: Félix Alcan. 1908.

This text-book of analytical chemistry is very suitable for the use of senior students. The reactions given for each base and acid in the first part are very numerous, and the general properties of every metal, its oxides, hydroxides, and salts, are included. The systematic separation tables give particularly full explanations, and an ingenious scheme showing the solubility of common salts is likely to be useful. In the second edition an introduction deals with the theoretical knowledge which should be possessed by every student of qualitative analysis. This includes a discussion of the atomic theory and the nomenclature and classification of compounds; there is also a chapter on the theory of solutions and chemical equilibria, and an excellent dissertation on the fundamental principles of qualitative analysis is given. The reactions of some organic acids and alkaloids are considered, and one chapter is devoted to the study of the rare earths.

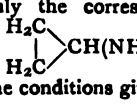
Photographisches Rezept-Taschenbuch. ("Pocket Book of Photographic Recipes.") By P. Hanneke. Berlin: Gustav Schmidt. 1907.

This book is intended both as an instruction book for amateur photographers and a guide for professionals, and gives a short description of most of the best modern methods of preparing negatives and prints. The author has thoroughly tested every recipe given in the book, and hence the beginner may feel confident that he has only to follow implicitly the directions given to get the best possible results with any negative he wishes to develope and print from. The book is issued at a very moderate price, and though it is only of small compass it includes a large number of well-tried recipes. A section on the working up of platinum, silver, and gold residues gives suggestions for such processes as may profitably be applied to these residues on a small scale by the amateur, and general notes on the most suitable preparations and processes to be used for the various operations of developing and fixing, &c., in different cases will be some help to the beginner.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 25, December 16, 1907.

Action of Nitrous Acid upon Allylamine.—Louis Henry.—When subjected to the action of nitrous acid allylamine, $H_2C=CH—CH_2(NH_2)$, unlike propylamine, behaves normally, and gives only the corresponding alcohol. Trimethylene amine,  , the isomer of allylamine, under the same conditions gives allyl alcohol.

Formation of Ozone by the Silent Discharge at a Low Temperature.—E. Briner and E. Durand.—The authors find that cooling the gas increases the yield of ozone. At −78° they obtained 12 grms. of ozone per kilowatt hour. At −194° it is possible to convert the whole of the oxygen into ozone. The most favourable pressure is about 100 mm. of mercury, giving 55 grms. per kilowatt hour. The silent discharge is best for the production of ozone and the spark for nitric oxide.

Certain Relations between the Atomic Weights of Elements.—M. Delauney.—The values of the atomic weights of elements are in the proportion $A^n : n$, where A and n are whole numbers. Thus (O = 16).

Helium	$2^2 : 1$	Beryllium	$8^2 : 7$
Mercury	$20^2 : 2$	Silicon	$16^2 : 9$
Carbon	$6^2 : 3$	Arsenic	$30^2 : 12$
Potassium	$14^2 : 5$	Bromine	$39^2 : 19$
Molybdenum	$24^2 : 6$		

Moreover, allied elements have either equal divisors, or divisors in regular progression:—

Cadmium	$15^2 : 2$	Cæsium	$61^2 : 28$
Mercury	$20^2 : 2$	Beryllium	$8^2 : 7$
Zinc	$14^2 : 3$	Strontium	$35^2 : 14$
Lithium	$13^2 : 24$	Barium	$62^2 : 28$
Rubidium	$47^2 : 26$		

Elements of the same family have divisors which seem to be regular and symmetrical:—

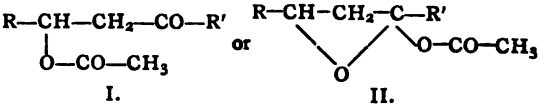
Boron	$11^2 : 11$	Carbon	$12^2 : 12$
Scandium	$23^2 : 12$	Zirconium	$33^2 : 12$
Yttrium	$34^2 : 13$	Silicon	$16^2 : 9$
Lanthanum	$50^2 : 18$	Titanium	$17^2 : 6$
Aluminium	$25^2 : 23$	Cerium	$29^2 : 6$

Fluorine	$19^2 : 19$
Bromine	$39^2 : 19$
Chlorine	$45^2 : 57$
Iodine	$85^2 : 57$

Gases Occluded in Steel.—G. Belloc.—The disengagement of gas is closely connected with the critical points of iron. It is small in the region of α-ferrite, and increases with the temperature. The commencement of the transition of α-into β-ferrite is marked by a copious disengagement which gradually decreases as the transformation proceeds. The disengagement reaches a maximum at the transition of β- into γ-ferrite, and seems to increase with the temperature in the latter region. The gases consist of carbon dioxide and monoxide, hydrogen, and nitrogen. Carbon dioxide is first disengaged and disappears at 550°, when nitrogen appears. From 400° hydrogen and carbon monoxide form the greater part of the gases. The gases were distributed very irregularly throughout the bars of steel investigated.

Extraction of Gases contained in Metals.—O. Boudouard.—The author has performed a series of experiments to study the conditions which allow of the extraction of occluded gases, and he finds that it is extremely difficult to extract all the gases contained in irons and steels. Even when the specimen had previously been twice heated to 1100° the third heating produced a further small quantity of gas, varying from 0·5 per cent of the total volume extracted from the finely-divided metal, to 20 per cent when the metal was in the form of bars and sheets. The quantities of gas extracted are of the order of magnitude of the quantities of sulphur and phosphorus ordinarily found in iron and steel. Incidentally, the author has observed that iron begins to volatilise at 900°.

Constitution of β-Acetoxy-ketones.—E. E. Blaise.—The β-acetoxy-ketones may have either the formula



I. or II.

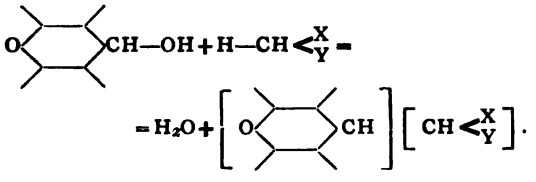
To determine which of these is correct the author found the molecular volume of the ketones, having previously observed that for compounds which contain a closed chain the diminution of molecular volume due to the closing of the chain is very large. The Compound II. would thus have a smaller molecular volume than I. Applying this

method to the ketones he found that the positive or negative variation of volume is of the order of that observed for normal substances with an open chain. Hence these ketones must have the Formula I.

Detection of Tartaric Acid in Cider.—G. A. Le Roy.—The liquid is neutralised, and lead acetate is added in excess. The lead precipitate is washed with cold water and decomposed by sulphuretted hydrogen. The filtered liquid is evaporated and neutralised (after the H_2S has passed off) by means of sodium bicarbonate. It is then evaporated to dryness, and a solution of 1 per cent resorcine in concentrated sulphuric acid is added. On warming, if tartaric acid is present, an intense violet-red coloration is produced. Citric acid gives no coloration; malic and lactic acids give a yellow coloration.

Preparation of Methyl and Ethyl Cyanides.—M. Auger.—Guillemard has recently shown that the formula of potassium cyanide in the solid state is that of the isonitrile. By investigating the action of the aqueous solution of the salt on the neutral sulphates, the acid sulphates, and the iodides of ethyl and methyl, the author has shown that the greater part of the cyanide reacts in the form of K.C:N, but a small part (maximum, 1 per cent) is capable of reacting in the isomeric form and giving carbylamines.

New Reactions of Aromatic Alcohols.—R. Fosse.—The hydroxyl of xanthydrol and of dinaphthopyranol can combine with one atom of the methylenic hydrogen of malonic or cyanacetic acids, β-diketones, β-ketonic esters, and cyanacetic ether, giving one molecule of water and a pyryl methylenic compound.



The hydroxyl of benzhydrol-$p.p$-tetramethyldiamine behaves similarly with the methylenic hydrogen of β-diketones, β-ketonic, and malonic esters. Thus, methylenic tetramethyldiaminobenzhydryl derivatives are obtained. It has never been found possible to replace the hydroxyl in any alcohol by a methylenic residue, $\ldots CH<^{X}_{Y}$. In the aldehydes, on the contrary, the oxygen can easily be replaced by the divalent residue, $:C<^{X}_{Y}$, of malonic, cyanacetic, β-ketonic esters, β-diketones, &c.

No. 26, December 23, 1907.

Influence of Temperature upon the Optical Properties of Dissolved Substances.—C. Chéveneau.—From the results of experiments performed by the author and by Bender, it appears that the variations of the optical constant K for an interval of temperature of about 50° may be calculated from the linear equation $K_t = K_\delta[1+m(t'-\delta)]$, where m is the mean coefficient of cubical expansion of the solution. The general results of the author's investigation are as follows:—1. The index of a dissolved substance varies slightly with the temperature. 2. The variation of the optical constant of a dissolved substance under the influence of the temperature seems to depend upon the change of volume of the solution, and appears to occur in the same sense as the variations in the temperature. 3. The dispersion of the dissolved substance is independent of the temperature to a first approximation.

Determination of Nickel in presence of Cobalt, Iron, and Manganese.—Emm. Pozzi-Escot.—The mineral is treated in such a way that all its metals are dissolved. If metals of the alkaline earths are present they are precipitated by ammonium sulphate. The solution is filtered and concentrated, large excess of a saturated solution of ammonium molybdate is added, and then ammonium chloride solution. The whole is heated to 80° or 90° for some minutes and left to cool for an hour. Thus all the nickel is precipitated as double molybdate of nickel and iron, and nearly all the iron. The solution contains traces of iron, all the manganese, and all the cobalt. It is filtered and the precipitate washed with a saturated solution of ammonium chloride. The precipitate is boiled with water, and ammonium chloride and ammonia are added; thus all the iron is precipitated and all the nickel is left in the filtrate. It may be precipitated by boiling off the ammonia with caustic potash and adding bromine. The oxide is then collected, dissolved in an acid, and the nickel determined by electrolysis.

New Chromium Sulphate.—Paul Nicolardot.—When a solution containing 100 grms. per litre of violet chromium sulphate is boiled, barium carbonate is added, and the liquid filtered, a substance having the formula $(Cr_2O_3)(SO_3)_{2.5}(H_2O)_{7.5}$ is found in the filtrate. This sulphate dissolves easily in water with a slight evolution of heat. The solution is not precipitated by barium chloride nor by sodium phosphate, and thus the substance does not behave either like a sulphate or a salt of chromium. It is precipitated from aqueous solutions by the addition of alcohol or acetone. The aqueous solutions are faintly acid, and are green in colour. As regards the complete repression of the SO_4 ion, this sulphate resembles the green sulphate $(Cr_2O_3)(SO_3)_3(H_2O)_8$ prepared by Recoura.

Influence of Acids and Bases on the Fixation of Acid and Basic Dyes by Wool.—L. Pelet-Jolivet and N. Andersen.—The authors have studied the fixation of crystallised Ponceau and methylene blue by wool in acid, basic, or neutral solution. Their results show that crystallised Ponceau (acid dye) in an acid bath is adsorbed by wool in greater quantities the stronger the acid. In neutral baths only small quantities are fixed, and in alkaline baths none at all. Methylene blue (basic dye) is fixed in smaller quantities the stronger the acid; the fixation is greater in a neutral bath, and at a maximum in an alkaline bath. These facts agree with the colloidal theory of dying. In an acid bath the $\overset{+}{H}$ ions charge the wool positively and increase the fixation of acid ($-ve$) dyes, but decrease that of basic positive dyes. In a neutral bath the wool which is slightly negative fixes more basic than acid dye. In an alkaline bath the $\overset{-}{OH}$ ions charge the wool negatively, and thus the fixation of the positive dye is increased.

Glycide Ethers and Aldehydes in the Naphthalene Series.—Georges Darzens.—α-Naphthylmethyl acetone condenses with ethyl monochloracetate in presence of dry sodium ethylate, giving ethyl-α-naphthylmethyl glycidate, $^{\alpha\text{-}C_{10}H_7}_{CH_3}\!>\!C(O)CH\text{—}CO_2C_2H_5$. This ether saponifies very easily, giving an acid which decomposes when distilled *in vacuo* into carbon dioxide and α-naphthylmethyl acetic aldehyde, $^{\alpha\text{-}C_{10}H_7}_{CH_3}\!>\!CH\text{—}COH$. The β-naphthylmethyl acetone gives the β-isomer of the same glycide ether.

Isosparteïne.—Charles Moureu and Amand Valeur.—Isosparteïne behaves like a ditertiary saturated base; it does not reduce potassium permanganate in acid solution in the cold. When treated with hydriodic acid by Herzig and Meyer's method it behaves like sparteïne and yields no methyl iodide. It is therefore not methylated at the nitrogen. The molecular refraction of isosparteïne is very close to that of sparteïne, and in general properties the two bases are closely allied.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 17, 1907.

Electro-syntheses. — S. M. Losanitsch. — It is a characteristic of the silent electric discharge that it causes the polymerisation or condensation of organic substances, thus synthesising compounds of high molecular weight which probably have a cyclic composition. The products obtained are generally either solid and insoluble, or oily and incapable of being distilled, and hence their purification is a matter of some difficulty. The following results were obtained by the action of the silent discharge :—*Experiments with Sulphur Dioxide.*—$3SO_2 = 2SO_3 + S$, $SO_2 + 2H_2 = 2H_2O + S$, $SO_2 + 2H_2S = 2H_2O + 3S$. *Experiments with Nitric Oxide.* — $4NO = N_2O_4 + N_2$,

$$2NO + 2H_2 = 2H_2O + N_2 = NH_4.NO_2,$$
$$2NO + 2H_2S = 2H_2O + S_2 + 2N,$$
$$2N + 4H_2S = (NH_4)_2S_4.$$

Experiments with Carbon Disulphide.—CS_2 alone gives a brown mass, $(CS_2)_n$. $CS_2 + H$ or H_2S gives an insoluble mass, $3CS_2.2H$. $CS_2 + CO$ gives $3CS_2.2CO$. $CS_2 + C_2H_4$ gives $5CS_2.2C_2H_4$. $CS_2 + C_2H_2$ gives $3CS_2.2C_2H_2$. *Experiments with Acetylene.*—Acetylene condenses and gives two products; one is soluble in alcohol and ether, and remains behind as a thick liquid when its solution is evaporated. The other is a solid, insoluble in all solvents. Analyses of these two products do not agree among themselves, owing to the absorption of the oxygen of the air. Condensed acetylene possesses the property of giving off an emanation which oxidises potassium iodide, liberating iodine, and which acts on the photographic plate through several thicknesses of aluminium or gold foil. It does not ionise the air, and hence is not a radio-active emanation. This action of condensed acetylene is caused by absorbed oxygen, which is bound in a labile state. Acetylene and hydrogen condense, yielding two products of which the one which is soluble has the molecular composition $(C_2H_2.2C_2H_4)_2$, and the same action is observed with acetylene and ethylene, methane, &c. Ethylene by itself and with other organic compounds condenses similarly to substances of high molecular weight.

Amido-group attached to the Nitrogen Atom of Heterocyclic Compounds. — Carl Bülow and Emil Klemann.—The authors have subjected to a thorough examination the N-amido-group of the 1-N-amido-2.5-dimethylpyrrol-3.4-dicarbonic acid ester described by Bülow in 1902. The most important result of their work is the discovery that while the amido-group attached to the ring carbon of carbo- or heterocylic compounds is readily converted into the diazonium group by the action of sodium nitrite in acid solution, the amido attached to the ring nitrogen under the same conditions is split off as nitrous oxide and is replaced by a hydrogen atom. The N-amido-group of this pyrrol derivative is far less reactive than that of a primary C-amine or of a secondary hydrazine.

Use of the Vacuum for Drying Hydrated Salts.—F. Krafft.—There appears to be no essential difference between the so-called water of crystallisation and of constitution in hydrated salts, although water of constitution escapes exceedingly slowly when these salts are subjected to the vacuum of the cathode light. Since sulphuric acid evaporates rapidly in the vacuum of the cathode light it is not suitable for use as a drying agent, barium oxide being preferable. The author gives the figures he obtained when determining the rate of dehydration of the following salts at different temperatures—zinc sulphate, magnesium sulphate, ferrous sulphate, copper sulphate, calcium sulphate, &c.

Auto-reduction of some Metallic Oxides in the Cathode Light Vacuum, and Volatility of the corresponding Sulphides.—F. Damm and F. Krafft.—Many metallic oxides yield the metal in a vacuum, *e.g.*, lead oxide, bismuth and antimony oxides, especially when the experiments are carried out in tubes of quartz glass. Thus lead oxide at 750° gives a metallic mirror, and small quantities of gas are evolved. Bismuth oxide also undergoes auto-reduction when heated for some hours to 650° in a vacuum. At 1050° the auto-reduction of antimony oxide is very great. Possibly the oxide is converted into a higher oxide, and is then partially reduced as shown by the equation $4Sb_4O_6 = 3Sb_4O_8 + 4Sb$. Then the higher oxide gives up oxygen, again yielding the lower oxide. Thus the oxide can be finally completely reduced. The sulphides of these metals are much more volatile than the oxides, and are therefore more stable on heating. Thus cadmium sulphide volatilises at 770—780°, lead sulphide at 600°, bismuth sulphide at 740°, antimony sulphide at 530°, arsenic sulphide at 230°. This great difference in volatility can be used to separate the sulphides almost quantitatively. Mixtures of sulphur, selenium, and tellurium can also be separated similarly.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, January 28, at three o'clock, Prof. F. J. Haverfield delivers the first of two lectures at the Royal Institution, on "Roman Britain"; on Thursday, January 30, Major Martin Hume commences a course of three lectures on "The Story of the Spanish Armada"; and on Saturday, February 1, Mr. Lionel Cust begins a course of two lectures on "Anthony Van Dyck." The Friday Evening Discourse on January 31 will be delivered by Prof. E. Rutherford on "Recent Researches on Radio-activity"; on February 7, by Mr. Humphry Ward, on "Napoleon and the Louvres"; and on February 14, by Dr. C. W. Saleeby, on "Biology and History." The Discourse on March 13 will be delivered by Chevalier G. Marconi, his subject being "Transatlantic Wireless Telegraphy."

Isomerisation of α-Methyl-sparteïne. — Charles Moureu and Amand Valeur.—The di-iodohydrate of α-methyl-sparteïne when heated to 125° with twice its weight of water in sealed tubes yields the mono-iodomethylate, $C_{15}H_{26}N_2.CH_3I$, of a new base, isosparteïne, which is an isomer of sparteïne. Small quantities of the same substance are produced when the di-iodohydrate of α-methyl-sparteïne is decomposed with alkali, while large yields may be obtained by heating α-methyl-sparteïne on a water-bath with a slight excess of normal sulphuric acid. On neutralising the excess of acid with baryta water and treating with barium iodide, the iodohydrate of the iodomethylate of isosparteïne, $C_{15}H_{26}N_2.CH_3I.HI + H_2O$, is obtained. It decomposes with alkalis, giving the iodomethylate of isosparteïne. The iodohydrate of the iodomethylate of isosparteïne decomposes with heat, giving the iodohydrate of isosparteïne, $C_{15}H_{26}N_2.CH_3I.HI = CH_3I + C_{15}H_{26}N_2.HI$. — *Comptes Rendus*, cxlv., No. 24.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8. (Cantor Lecture). "Theory and Practice of Clock Making," by H. H. Cunynghame, C.B.

TUESDAY, 28th.—Royal Institution, 3. "Roman Britain—(*a*) Its Frontiers and Garrison," by Prof. F. J. Haverfield, M.A., LL.D., &c.

—— Society of Arts, 4.30. "The Development of Colonial Self-Government in the Nineteenth Century," by A. Berriedale Keith, M.A., &c.

WEDNESDAY, 29th.—Society of Arts, 8. "The New Patent Act." by John William Gordon.

—— Society of Dyers and Colourists, 8. "Colloidal Dyestuffs," Dr. E. Feilmann. "Notes on the Dyeing of Celluloid," by Dr. J. N. Goldsmith. General Discussion.

THURSDAY, 30th.—Royal Institution, 3. "The Story of the Spanish Armada," by Major Martin Hume.

FRIDAY, 31st.—Royal Institution, 9. "Recent Researches on Radio-activity," by Prof. E. Rutherford, F.R.S., &c.

SATURDAY, Feb. 1st.—Royal Institution, 3. "Anthony Van Dyck," by Lionel Cust, M.V.O., &c.

THE CHEMICAL NEWS.

VOL. XCVII., No. 2514.

THE VARIATIONS OF THE ABSORPTION BANDS OF SALTS OF DIDYMIUM AND ERBIUM IN A MAGNETIC FIELD.

By JEAN BECQUEREL.

IT has been observed that under the influence of a low temperature the absorption bands of solids and of solutions become narrower, or are resolved into components. The examination of the spectra of different salts of didymium and erbium, at the temperature of liquid air, has shown that these substances possess many bands which are variable in a magnetic field.

The salt dissolved in an alcohol, or in a mixture of alcohol and water, is contained in a 3 mm. tube inside another tube filled with liquid air, and surrounded by a vacuum. The solidified solution is traversed, between the poles of an electro-magnet, by a beam of light parallel to the magnetic field. By means of a fluor-spar rhombohedron placed before the slit of the spectroscope, and preceded by a quarter-wave plate, it is possible to obtain in the ocular two contiguous regions and to analyse two circular inverse vibrations at once. When the field is excited, the sensitive bands are displaced in opposite directions in the two regions, and the slight ebb and flow which is seen when the direction of the field is reversed several times running, makes it possible to evaluate the order of magnitude of, if not to measure, the very small displacements.

The bands corresponding to circular vibrations in the same sense are not always displaced to the same side; the effect is of the same order of magnitude as the Zeeman effect, even if it is in the reverse sense to that observed for all vapours.

Neodymium Nitrate.—The results obtained with solutions of neodymium nitrate have been described recently. It was found that the sensitiveness of the bands to the action of a magnetic field is independent of the solvent, and it does not appear to be influenced by the addition of a highly magnetic substance (iron perchloride).

The separation of the bands into two components corresponding to inverse circular vibrations can only be obtained in an isotropic substance, or in a uniaxial crystal, the axis of which is oriented parallel to the field; under these conditions, with undissolved neodymium nitrate, only the asymmetric widening and doubling of the very thin bands of the group situated near 625 $\mu\mu$ are seen.

Didymium Chloride.—Didymium chloride in methyl alcohol possesses several variable bands. The most sensitive is the band 509·6 $\mu\mu$ ($+ve$ electrons, displacement 0·11 $\mu\mu$ per 14000 gauss), and it is interesting to observe that in parisite (carbonate of Ce, La, Di, with Ca and F) the most sensitive band is almost in the same place, and is displaced in the same direction and about twice as much.

In the green there is a group, three bands of which are very clear and intense (520·7 $\mu\mu$; 522 $\mu\mu$; 522·5 $\mu\mu$). The band 520·7 $\mu\mu$ ($-ve$ electrons) gives a displacement estimated at 0·04 $\mu\mu$ per 14000; the neighbouring band ($-ve$) is less displaced, and the band 522·5 $\mu\mu$ does not appear to be sensitive.

In the yellow-green group three variable bands are seen; 576·1 $\mu\mu$ ($+ve$, displacement about 0·04 $\mu\mu$), 578·7 $\mu\mu$ ($-ve$), and 579·6 $\mu\mu$ ($-ve$). Finally two strong bands situated near 680 $\mu\mu$ and corresponding to negative electrons give among their components displacements of 0·06 $\mu\mu$ to 0·07 $\mu\mu$.

All these bands are slightly displaced with ethyl alcohol solutions, or in water containing alcohol. Their displacements in a magnetic field seem invariable.

Mixtures of Didymium Choride and Nitrate.—The additions of small quantities of didymium nitrate to a solution of the chloride very rapidly weakens several of the most intense bands (520·7, 522·5, 572·7, 574·5, 576·1 $\mu\mu$); these bands become very faint or disappear in a mixture of 5 parts of chloride and 5 of nitrate in 100 parts of methyl alcohol.

The band 522 $\mu\mu$ persists in the mixture and in the pure nitrate.

In proportion as the amount of nitrate is increased new bands appear (522·9, 523·5, 577·7, 581·4 $\mu\mu$ in a mixture of 7·5 of nitrate, 2·5 of chloride in 100 of methyl alcohol). The band 522·9 $\mu\mu$ (electrons $-ve$, displacement 0·05) steadily increases, and in the pure nitrate is the most intense band of the green group and the most sensitive to the field; the bands 523·5 $\mu\mu$ (electrons $-ve$) and 581·4 $\mu\mu$ (electrons $+ve$), after having passed through a maximum of intensity, also appear, although very much weakened, in the nitrate.

Finally, the addition of water to the alcoholic solution of the nitrate causes the appearance of some bands of the chloride solution, the band 520 $\mu\mu$ in particular.

Thus each of the bands can be followed through its successive transformations; the displacements in a magnetic field always appear to be independent of these transformations.

Didymium Sulphate.—The sulphate being insoluble in a mixture of water and alcohol, widenings and doublings of the fine bands of the orange group (625 $\mu\mu$) were seen in the solid salt, as before in the case of the nitrate.

Oxalate, Fluoride, and other Insoluble Didymium Salts.—The spectra of these salts may be examined by suspending the powdered material in alcohol and solidifying the mass. No band sensitive to the field appeared; probably the bands are not fine enough for the enlargements to be visible.

Erbium Chloride.—The following bands are displaced in a magnetic field:—487 $\mu\mu$ (electrons $-ve$, displacement about 0·1 per 14,000); 488 $\mu\mu$ ($-ve$); 523·8 $\mu\mu$ ($+ve$, displacement 0·08); 541 $\mu\mu$ ($-ve$).

The principal conclusions drawn from these experiments are as follows:—

I. The variability of absorption bands in a magnetic field, which was first observed in the substance possessing the finest bands, xenotime, and then with more difficulty in tysonite, might appear to be an exceptional phenomenon. By the use of low temperatures the first results have been extended to other crystals (parisite, apatite), and then to other solid or dissolved salts. Thus the phenomenon appeared to be general, and it would doubtless be observed in most substances possessing selective absorption, if it were possible to lower the temperature enough to make the bands fine enough. Thermic disturbance seems to be the principal cause of the perturbation of the movements of the absorbing electrons; hence, in order to study the vibrations of the light bands under the best conditions, it is necessary to endeavour to suppress the other movements.

II. In the experiments actually performed the change of period of the corpuscles producing a band seemed to be independent of the temperature as well as of the conditions which more or less modify the band in question. The magnitude of the displacement of a band in a given field seems to be a characteristic property of the oscillating system.

III. The variability of the direction in which the bands corresponding to circular vibrations in the same direction are displaced is a remarkable and unexpected result. After the first observations I suggested the hypothesis either of an inversion of the direction of the field in the interior of certain atoms, or of the existence of positively charged corpuscles. The inversion hypothesis has been supported by many physicists, but it introduces many difficulties, and the invariability of the displacements does not seem to favour this view. I think that it would be premature either to affirm or to deny the existence of positive electrons; it is, however, interesting to notice

that if the magneto-optical phenomena in crystals and salts of the rare earths had been observed before the discovery of radio-activity and of the Zeeman effect, nobody would have had any hesitation in affirming the simultaneous existence of positive and negative electrons possessing masses of the same order of magnitude, when they came to consider these phenomena of the Hall effect.—*Comptes Rendus*, vol. cxlv., 1412.

VOLUMETRIC ESTIMATION OF IRON IN FERRIC COMPOUNDS.

By M. M. PATTISON MUIR.

THE process of reducing a ferric to a ferrous compound, by warming with zinc and dilute sulphuric acid, occupies a considerable time; not only must all the iron be reduced to a ferrous compound, but also the whole of the zinc must be dissolved before titration with standard potassium permanganate solution. If very little zinc is put into the liquid, the reduction proceeds very slowly: if much zinc is used, the dissolution of the whole of it takes a somewhat long time.

Mr. Charles Bryant, Senior Laboratory Attendant in the Chemical Laboratory of this College, recently noticed that the reaction between zinc and warm dilute sulphuric acid is stopped by adding an aqueous solution of mercuric chloride—mercury is precipitated on the zinc—and then cooling the liquid.

This reaction may be turned to good account in the volumetric estimation of iron in ferric compounds A measured volume of the solution of the ferric compound is placed in a flask fitted with a cork which carries a glass tube narrowed at its upper end; a fair quantity, say, 200 cc., of dilute pure sulphuric acid and about 20 grms. of granulated zinc, free from iron, are added; the liquid is warmed until there is a brisk evolution of hydrogen, and the flask is shaken from time to time until the reduction is completed. About 100 cc. of a nearly saturated aqueous solution of mercuric chloride are now added; the flask is shaken for three or four minutes, and is then placed under running water until cold. A standard solution of potassium permanganate is now run in until a faint pink colour is obtained in the liquid. When one is estimating iron in solutions containing from 0·005 to 0·01 grm. of ferric iron per cc., and is using 25 cc. of such solutions, an estimation is performed in rather less than half-an-hour. The results of many estimations of iron in ferric compounds, made in this laboratory by the modification of the usual method which has been described, were very satisfactory.

Gonville and Caius College Laboratory, Cambridge.
January 16, 1908.

NEW ZEALAND BONED BEEF.

By ALLISTER MACLEAN WRIGHT.

DURING the past three or four years New Zealand has exported considerable quantity of beef, boned and packed in boxes lined with parchment paper, then frozen, and shipped in this condition.

This article of food has been exposed to criticism, both as to its quality and its nutritive properties. As the animals, both before and after slaughter, and while being cut up and packed, are under the most rigid inspection by qualified meat inspectors and veterinians appointed by the New Zealand Government, it is impossible for any but healthy animals to be used for this purpose.

No analyses of this meat have yet been published, and from the following analyses, which are typical, it will be seen that the meat contains equal nutritive value with the ordinary flesh of healthy cattle. For comparison, figures given by Mitchell are quoted ("Flesh Foods," p. 47).

The samples were taken from boxes which had been in cold storage for from six to eight weeks, and represent the product as it reaches the market.

It will thus be seen that, with the exception of the cow beef, the composition is practically identical with the flesh of the average cattle beast.

The cow beef contains considerably more fat than the average, but this is a favourable consideration.

	New Zealand boned beef.										Average (Mitchell).		
	Ox.				Cow.			Veal.			Ox.	Cow.	Veal.
	1.	2.	3.	4.	1.	2.	3.	1.	2.	3.	Medium.	Fat.	Lean.
Water	71·08	72·15	70·32	71·13	67·22	62·31	63·14	76·41	77·12	76·28	72·03	70·96	78·82
Nitrogenous substances	21·94	21·37	21·25	21·76	19·68	19·18	18·92	21·81	21·43	21·93	20·96	19·86	19·86
Fat	6·11	5·66	7·58	6·25	12·27	17·70	17·14	1·06	0·77	1·02	5·41	7·70	0·82
Nitrogen-free extractives	—	—	—	—	—	—	—	—	—	—	0·46	0·41	—
Ash	0·87	0·82	0·85	0·86	0·83	0·81	0·80	0·72	0·68	0·77	1·14	1·07	0·50
Nitrogen	3·51	3·42	3·40	3·48	3·15	3·07	3·03	3·49	3·43	3·51	—	—	—
Calculated to Dryness.													
Nitrogenous substances	75·86	76·73	71·60	75·37	60·04	50·88	51·33	92·45	93·66	92·48	74·94	68·39	93·77
Fat	21·13	20·32	25·54	21·65	37·43	46·97	46·50	4·49	31·36	4·30	19·35	26·51	3·87
Nitrogen-free extractives	—	—	—	—	—	—	—	—	—	—	1·64	1·41	—
Ash	3·01	2·95	2·86	2·98	2·53	2·15	2·17	3·06	2·98	3·22	4·07	3·68	2·36
Nitrogen	12·14	12·28	11·46	12·06	9·61	8·10	8·22	14·79	14·99	14·79	12·00	11·13	15·01

In addition, the flesh was examined by the Stas-Gautier method for ptomaines ("Flesh Foods," p. 298), but none could be isolated.

For permission to publish this paper I have to express my thanks to Mr. W. Murray, Manager of the Christchurch Meat Company, Ltd., in whose laboratory most of the work was carried out.

Niobium Sulphide.—Heinrich Biltz and Ludwig Gonder.—The authors prepared very pure niobium pentoxide from sodium niobate, and ignited it in a current of sulphuretted hydrogen. Thus a brown preparation was obtained; it turned white, and evolved sulphur dioxide when heated. Black preparations were obtained when sulphuretted hydrogen and carbon disulphide were led over niobium pentoxide heated to a bright red heat. When these preparations were analysed it was found that they consisted of niobium and sulphur only. However, no formula could be deduced from the analyses, and in all probability pure niobium sulphide has not yet been obtained, the preparations consisting of an unknown sulphide NbS_2 or Nb_2S_5 mixed with niobium or a lower sulphide. No oxysulphide has been prepared.—*Berichte*, 1907, xl., No. 18.

A PHYSICO-CHEMICAL STUDY OF THE COMPLEX COPPER-GLYCOCOLL SULPHATES.*

By J. T. BARKER, B.Sc.

(Concluded from p. 40).

4. *Conductivity Measurements.*

IN order to throw further light on the complex formations, measurements of the electrical conductivity of the solutions were carried out. It was expected that on continued addition of glycocoll to copper sulphate solutions a fall of conductivity would be observed, owing partly to the formation of slower moving complex cations and partly to the increased viscosity of the solution, although these effects might be to some small extent counterbalanced by an increased ionisation of the complex sulphate. As will be seen the results obtained are extremely interesting, though they cannot be explained in the manner just indicated.

The copper sulphate used had been re-crystallised three times. The glycocoll (Kahlbaum's) was re-crystallised twice from ordinary distilled water and once from conductivity water ($k = 2 \times 10^{-6}$). The specific conductivity of an $n/10$ solution of this purified glycocoll was 6×10^{-6} (temperature, 25°). It was found that the conductivity of a pure glycocoll solution rises rather rapidly when kept in a conductivity vessel in the presence of the electrodes. This effect is probably due to oxidation at the surface of the platinised electrode. It is interesting to note that it does not occur when $CuSO_4$ is present, so that the complex formation appears to protect the glycocoll from oxidation. The results obtained are given in Table VIII.

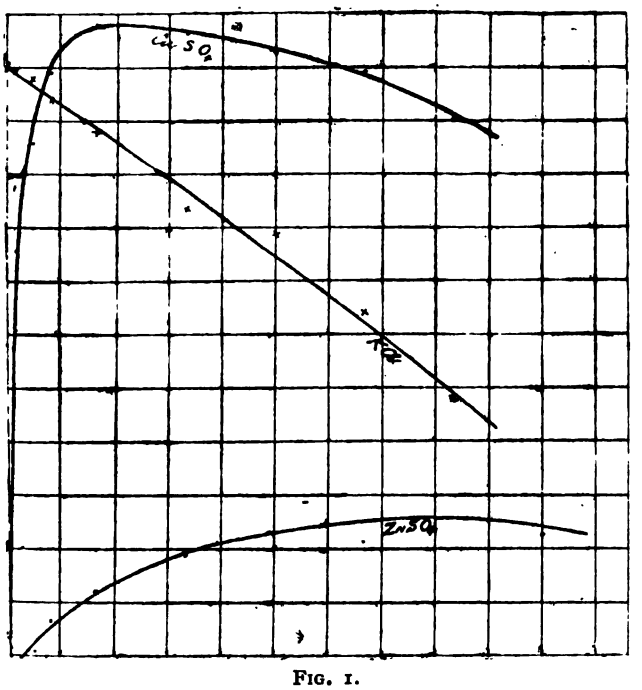


FIG. 1.

The specific conductivities given in Column 2 have been corrected for the specific conductivity of the water (2×10^{-6}).

The curve given in Fig. 1 shows clearly the relationship between conductivity and number of mols. glycocoll present in the solution. In the case of $CuSO_4$ and $ZnSO_4$, the ordinates in the diagram run from 174·7 to 222·7. Contrary to expectation, the first effect of the addition of glycocoll is to increase the conductivity of the solution; thus on the addition of 1 mol. glycocoll the conductivity rises by no less an amount than 16·6 per cent. On the addition of 10 mols. glycocoll per mol. $CuSO_4$ the conductivity attains a maximum (increase of 26·3 per cent), after which further addition of glycocoll produces a gradual decrease of conductivity. The sharp initial rise of conductivity is very marked. In order to see how far this behaviour is to be accounted for by complex formation, the effect of glycocoll on the conductivity of a $ZnSO_4$ solution was studied. The result of these measurements are contained in Table IX.

The zinc sulphate-glycocoll curve, Fig. 1, also shows a maximum, but the effect is not nearly so marked as in the case of $CuSO_4$. Thus on the addition of 1 mol. glycocoll to the $ZnSO_4$ solution the increase of conductivity is only 0·35 per cent, whilst the maximum increase is only 7·3 per cent. With these results may be contrasted the effect of glycocoll on the conductivity of a KCl solution, as shown in Table X.

As will be seen from the curve in Fig. 1, the effect of glycocoll is to diminish the conductivity of the KCl solution by an amount proportional to the concentration of the glycocoll. In the diagram the ordinates for KCl run from 332·52 to 380·52. This diminution is probably due to the increased viscosity of the solution, and is a well known effect of non-electrolytes. This effect will also be present in the cases of $CuSO_4$ and $ZnSO_4$, but there is evidently also present some other cause which tends to *increase* the conductivity, the maxima observed being due to the conflicting action of these two causes. Now both $ZnSO_4$ and $CuSO_4$ are perceptibly hydrolysed in aqueous solution. We may represent the hydrolytic equilibrium by the equation—

$$CuSO_4 + 2H_2O \rightleftarrows Cu(OH)_2 + H_2SO_4$$

or by—

$$Cu^{\cdot\cdot} + 2H_2O \rightleftarrows Cu(OH)_2 + 2H^{\cdot}.$$

Evidently, since glycocoll, being an amphoteric substance, can act both as acid and base, it will disturb this equilibrium. It will tend to remove $Cu(OH)_2$ by the formation of the copper salt of glycocoll, and it may be also supposed to tend to remove $H^{\cdot}$-ions by the formation of glycocoll sulphate. The case of $ZnSO_4$ is similar. Now, it is known that the copper salt of glycocoll is a peculiar salt, which, though the salt of a very weak acid, is preserved from much hydrolysis by an "internal" complex formation (Ley, *Zeit. Elektrochem.*, 1904, x., 954). Hence there may be a considerable formation of this salt from the $Cu(OH)_2$ and the glycocoll, whilst, owing to the fact that glycocoll is a very weak base, there will be only a very small degree of neutralisation of the free acid. The result is that addition of glycocoll to a $CuSO_4$ solution will increase the hydrolysis, producing an increase of $H^{\cdot}$-ions, and hence a considerable increase of conductivity. Somewhat similar considerations will apply to $ZnSO_4$, though in this case, owing to a very much smaller tendency to form complexes, the effect will be much smaller. It is not pretended that these remarks gives a comprehensive analysis of this very interesting equilibrium, though they probably suffice to indicate qualitatively the nature of the reactions occurring. It is necessary, however, to prove that the addition of glycocoll actually *does* increase the $H^{\cdot}$ concentration. Experiments bearing on the point are described in the next section.

* A Paper read before the Faraday Society, December 17, 1907. From the Muspratt Laboratory of Physical and Electro-chemistry, University of Liverpool. Communicated by Dr. F. G. Donnan.

TABLE VIII.—*Conductivity of Glycocoll-copper Sulphate Solutions at 25°. Molar Concentration of* $CuSO_4 = n/80$; *Resistance Capacity of Vessel* = 0·3658.

Resistance (ohms).	Specific conductivity of solution (reciprocal ohms per cm. cube).	Mols. glycocoll per mol. $CuSO_4$.
210·12	174·7 × 10−5	0
179·42	203·7 ,,	1
172·56	211·7 ,,	3
168·44	217·0 ,,	5
165·55	220·7 ,,	10
166·18	219·9 ,,	20
167·25	218·5 ,,	30
168·33	217·1 ,,	40
171·13	213·5 ,,	50

TABLE IX.—*Conductivities of Glycocoll-zinc Sulphate Solutions at 25°. Molar Concentration of* $ZnSO_4 = n/80$; *Resistance Capacity of Vessel* = 0·4226.

Resistance (ohms).	Specific conductivity of solution.	Mols. glycocoll per mol. $ZnSO_4$.
245·40	172·0 × 10-5	0
244·55	172·6 ,,	1
242·89	173·8 ,,	3
239·82	176·0 ,,	5
236·84	178·2 ,,	10
233·30	180·9 ,,	20
232·58	181·5 ,,	30
231·95	182·0 ,,	40
228·66	184·6 ,,	50
231·36	182·5 ,,	60

TABLE X.—*Conductivities of Glycocoll*-KCl *Solutions at 25°. Molar Concentration of* KCl = $n/40$; *Resistance Capacity* = 0·4005.

Resistance.	Specific conductivity of solution.	Mols. glycocoll per double mol. KCl.
106·30	376·52 × 10−5	0
106·37	376·27 ,,	1
106·53	375·70 ,,	3
106·98	374·12 ,,	5
107·66	371·76 ,,	10
109·38	365·91 ,,	20
109·94	364·04 ,,	30
111·74	358·18 ,,	40
113·80	351·68 ,,	50

5. *Effect of Glycocoll on the* H· *Concentration of Aqueous Solutions of* $CuSO_4$ *and* $ZnSO_4$.

In order to test whether addition of glycocoll increased the H· concentration of a $ZnSO_4$ solution, the E.M.F. of the cell—

$$Pd_{H_2} \mid n/80\ ZnSO_4 \mid n/80\ ZnSO_4 + n/8\ \text{glycocoll} \mid Pd_{H_2}$$

was measured at 17°, and found to be 0·0052 volt (current in cell in direction indicated by arrow). The palladium electrodes were charged electrolytically to just visible gas-evolution in dilute H_2SO_4, then washed, and left short-circuited in dilute ($n/200$) HCl overnight. They were found to show a small difference of potential when measured against each other in $n/200$ HCl. This has been deducted in the above result.

The E.M.F. of the above cell shows that the addition of glycocoll produces an appreciable increase in the H· concentration. If we neglect the small liquid potential, and calculate by means of the formula $\pi = 0{\cdot}000198\ T \log \frac{C_1}{C_2}$, we find 1·23 as a roughly approximate value for the ratio of increase of the H· concentration. This method cannot be applied to the copper solutions owing to precipitation of metallic copper by the palladium-hydrogen electrode, so in this case comparative measurements on the rate of inversion of cane-sugar were made. The solutions used were 5 per cent with respect to re-crystallised cane-sugar. The polarimeter readings are ive n in the following table. Temperature 60·5° C.

TABLE XI.—*Inversion of Cane-sugar by Copper-glycocoll Solutions.*

Time (minutes)	$n/80$ $CuSO_4$, 5 per cent sugar.	$n/80$ $CuSO_4$, $n/80$ glycocoll, 5 per cent sugar.
0	179° 40′	179° 41½′
70	179° 41′	
66		179° 42′
147	179° 42′	
148		179° 34′
216	179° 41′	
215		179° 30′

These results, though not pretending to great accuracy, are sufficient to show that the presence of the glycocoll has very appreciably increased the H· concentration of the $CuSO_4$ solution.

6. *Products of Isothermal Crystallisation of Aqueous Solutions containing* $CuSO_4$ *and Glycocoll.*

Solutions containing $CuSO_4$ and glycocoll were allowed to crystallise at room temperature over calcium chloride or concentrated sulphuric acid. The crops of crystals so obtained were drained on the filter-pump, dried on porous plates, and then microscopically examined and analysed. Copper was determined electrolytically or as Cu_2S. Glycocoll was calculated from the percentage of nitrogen found on combustion. Water was determined from the loss of weight on heating to 110—120° *in vacuo*, the substance being contained in a weighed glass tube connected with a gas washing flask containing concentrated sulphuric acid. SO_4 was determined gravimetrically in the usual way.

Experiment 1.

Two solutions were made up, each from 12 grms. glycocoll, 5 grms. $CuSO_4.5H_2O$, and 75 cc. water. The first crop of dark blue crystals from each solution was analysed.

	Crystals from Solution 1. Per cent.	Crystals from Solution 2. Per cent.
Copper	10·6	10·37
Glycocoll (by difference)	65·84	68·81
SO_4	18·75	18·01
H_2O	4·81	3·41

For the crop of crystals from Solution 1 we have $\frac{\text{Mols. glycocoll}}{\text{Mols. Cu}} = 5{\cdot}3$. There is more SO_4 present than would, for the given copper content, correspond to $CuSO_4$ or any complex copper-glycocoll sulphate of the formula $Cu(G)_xSO_4$. The amount of water of crystallisation in the crystals from the second solution corresponds pretty closely to 1 mol. water per mol. copper.

If we calculate, taking the figures in the first column, from the Cu percentage the percentages of glycocoll and SO_4 corresponding to the formula $Cu(4G)SO_4.H_2O$, we get 50 and 16 respectively. The excesses over these, namely, 15·84 and 2·75, are in the molar ratio 1·84 : 1. Assuming these crystal crops to be chiefly heterogeneous mixtures of two phases, it seems possible, therefore, that they might consist chiefly of $Cu(4G)SO_4.H_2O$ and $(NH_2—CH_2.COOH)_2H_2SO_4$ (but see later).

Experiment 2.

Solution made up from 18 grms. glycocoll and 10 grms. $CuSO_4.5H_2O$ in 100 cc. water. The first crop of crystals was dried and extracted with ether in a Soxhlet apparatus. The weight of the substance before extraction was 2·2888 grms., after extraction 2·2700 grms. We may conclude therefore that it contains little, if any, free glycocoll. Analysis of extracted crystals :—

Copper	25·23 per cent
Glycocoll	68·29 ,,
SO_4	2·04 ,,
H_2O (by difference)	4·44 ,,

The result of crystallising from a solution relatively richer in $CuSO_4$ (in comparison with glycocoll) is to more than double the copper percentage, whilst the percentage of SO_4 is reduced to one-ninth of its former value. It is evident that this crop of crystals consist mainly of a compound of copper and glycocoll (see discussion of results of Experiment 3).

Experiment 3.

Original solution the same as in Experiment 2. Successive crops of crystals were obtained, examined, and analysed. The crystals were not extracted with ether.

First Crop.—It consisted of dark blue nodular clumps of crystals.

Analysis.

Copper	27·99 per cent
Glycocoll (by difference) ..	61·88 „
SO_4	2·34 „
Water	7·79 „

Second Crop.—In appearance similar to first crop.

Analysis.

Copper	24·95 per cent
SO_4	3·19 „

Other constituents not determined.

Third Crop.—Evidently heterogeneous. It consisted of dark blue needles mixed with almost colourless crystals.

Analysis.

Copper	9·46 per cent
Glycocoll	66·65 „
SO_4..	19·93 „
Water	2·26 „

Fourth Crop.—Fairly large colourless crystals, with a small amount of dark blue lumpy solid.

The colourless crystals were free from copper, and contained 30·68 per cent H_2SO_4 (calculated from amount of SO_4 found).

Fifth Crop.—Consisted of a mass of dark blue silky needles, with here and there a small dark blue lumpy nodule.

The blue needles contained 28·47 per cent Cu.

During the course of this work a solution containing glycocoll and $CuSO_4$, which had been set aside to crystallise, became accidentally contaminated with HCl. From this solution large very pale blue (monoclinic or triclinic) crystals were deposited. On analysis they yielded the following results:—

Glycocoll	69·57 per cent
H_2SO_4	30·23 „
Copper	0·16 „
Water	0·09 „

Neglecting the copper and water found, these crystals consist to 99·56 per cent of a sulphate of glycocoll of the composition, glycocoll = 69·66 per cent, H_2SO_4 = 30·34 per cent, which corresponds with the known so-called "basic," glycocoll sulphate, whose formula is $(NH_2.CH_2.CO_2H)_3H_2SO_4$ (glycocoll = 69·87 per cent, H_2SO_4 = 30·13 per cent). These crystals corresponded closely in appearance with the colourless crystals observed in the third and fourth crops (Experiment 3), and from the percentage of H_2SO_4 (30·68) found by analysis in the colourless crystals of the fourth crop, there can be little doubt that these colourless crystals were the "basic" glycocoll sulphate. The dark blue needles observed in the fifth crop were separated as far as possible from the rest by means of a mixture of methylene iodide and benzol. In appearance they closely resembled the well known copper salt of glycocoll, $Cu(NH_2.CH_2.CO_2)_2.H_2O$, and contained 28·47 per cent Cu, whilst copper glycocoll contains 27·7 per cent Cu. There can be little doubt that these two substances are identical.

Judging from the microscopical examination, there was now very strong presumption that the third crop consisted chiefly of copper glycocoll and "basic" glycocoll sulphate. This view is confirmed on examining the following figures:

	I.	II.
Copper	9·46	9·46
Glycocoll	67·93	68·73
H_2SO_4	20·35	20·35
Water	2·26	2·68

Column I. gives the composition of the crop as found by analysis. Now, 9·46 parts Cu as copper glycocoll correspond to 22·01 parts glycocoll and to 2·68 parts water, whilst 20·35 parts H_2SO_4 as $(NH_2.CH_2.COOH)_3H_2SO_4$ correspond to 46·72 parts glycocoll. Therefore, had the crop consisted of copper glycocoll and basic glycocoll sulphate, it would have had the composition indicated in Column II., which agrees sufficiently closely with that given in Column I.

It is impossible to say from the experimental results what are the exact constituents of the first crop of crystals obtained in Experiment 3. It appears possible that they consisted of copper glycocoll admixed with a basic complex copper glycocoll sulphate, but as there is not sufficient other evidence to support such a conclusion, it is scarcely worth while to reproduce here the arithmetical details of the numerous calculations made.

In conclusion, it may be stated that the crystals from Solution 2 (Experiment 1) might be looked upon as mainly a mixture of copper glycocoll and the basic glycocoll sulphate, for on analysis the conglomerate yielded 12·84 per cent N, whilst had it consisted of the substances mentioned, a simple calculation from the other analytical data shows that it would have contained 12·44 per cent N.

7. *Conclusions.*

The crystallisation experiments described in Section 6 confirm the conclusions arrived at in Sections 4 and 5 of this paper, namely, that the effect of the first addition of glycocoll to a solution of $CuSO_4$ is to disturb the hydrolytic equilibrium by the formation of undissociated copper glycocoll, with the consequent increase of free H_2SO_4. The maximum increase in the specific conductivity $n/80$ $CuSO_4$, produced by the addition of 10 mols. glycocoll per mol. $CuSO_4$, was 26·3 per cent. If this $CuSO_4$ solution be regarded (to a first approximation) as completely ionised, then, since the ionic conductivities of $2H^{\cdot}$ and $Cu^{\cdot\cdot}$ are about 2×347 and 80 respectively, the replacement of $Cu^{\cdot\cdot}$ by $2H^{\cdot}$ would increase the specific conductivity by 256 per cent. The actually observed increase would correspond, therefore, to a conversion of only about 10 per cent of the $CuSO_4$ present in the $n/80$ solution into copper glycocoll and free sulphuric acid (which at this dilution would combine with very little glycocoll). It is clear, therefore, that this initial action is soon brought to a stop by the increasing $H^{\cdot}$ concentration (which throws back the $Cu(OH)_2$ concentration), and that after this the further addition of glycocoll results mainly in the formation of complex copper glycocoll cations. This second action, therefore, constitutes the main effect in solutions which contain large excesses of glycocoll relatively to $CuSO_4$. The conclusions arrived at in Sections 1, 2, and 3 remain therefore practically undisturbed. The freezing point measurements alone are sufficient to show that in solutions rich in glycocoll the main actions occurring cannot be represented by the equation—

$$CuSO_4 + 2(NH_2.CH_2CO_2H) = Cu(CO_2.CH_2.NH_2)_2 + H_2SO_4$$

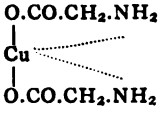
or—

$$CuSO_4 + 4(NH_2.CH_2.CO_2H) = Cu(CO_2.CH_2.(NH_2)_2 + (NH_2.CH_2CO_2H)_2.H_2SO_4;$$

for if so, the addition of 1 mol. of $CuSO_4$ to strong solutions of glycocoll would involve a decided *increase* in the number of "osmotically active" units in the solution, whereas there was always observed a *decrease*. Moreover, the quantitative agreement between the results calculated from

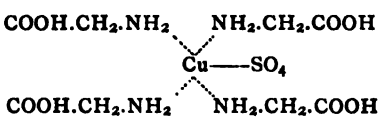
the E.M.F. and freezing point measurements is strong evidence in favour of the theoretical basis on which these results were calculated.

In the complex copper glycocoll sulphates the glycocoll molecules are doubtless related to the copper atom in the same manner as the ammonia molecules in the complex copper ammonia sulphates. In both cases the highest cationic complex appears to contain 4 molecules per 1 atom of copper, and it seems most probable that the glycocoll or ammonia molecules are related to the copper atom through the "subordinate" valencies of the nitrogen atom. The case of copper glycocoll itself has been investigated by Bruni and Fornara (*Rend. d. R. Accad. Lincei*, Roma, xiii., 5*a*, 26), and by Ley (*Zeit. Elektrochem.*, 1904, x., 954). It appears probable that the constitution of this salt must be represented by the formula—



where the secondary or subordinate valencies are indicated by the dotted lines. The deep colour of all these salts is very striking. It is difficult to resist the conclusion that the powerful selective light absorption which they exhibit is intimately connected with the interplay of these secondary or subordinate affinities, and that this phenomenon is a very general one.

The only way in which one can at present represent the constitution of the complex sulphate $Cu(4G)SO_4$ is therefore (in analogy with the above) as follows :—



in which there exist secondary affinity relationships between the copper and nitrogen atoms.

In conclusion, I have great pleasure in expressing my best thanks to Professor Donnan for his kind advice and assistance during the course of this work.

ON THE OXIDATION OF HYDRAZINE.*

By A. W. BROWNE and F. F. SHETTERLY.

In 1902 Tanatar showed that hydronitric acid could be obtained by treating a molecular mixture of hydrazine sulphate and hydroxylamine chloride in acid solution with certain oxidising agents (*Ber.*, xxxv., 1810—1811). Three years later it was demonstrated in this laboratory that the acid could be prepared by the action of hydrogen peroxide upon hydrazine sulphate in the presence of free sulphuric acid (Browne, *Journ. Am. Chem. Soc.*, 1905, xxvii., 551—555). Still later it was found that by the action of several other oxidising agents, respectively, upon hydrazine sulphate in acid solution, varying amounts of hydronitric acid could be produced (Browne, *Science*, N.S., 1905, xxii., 81). In the present article is described a series of experiments performed for the purpose of ascertaining the conditions under which hydronitric acid is formed by the action of ammonium metavanadate in acid solution upon hydrazine sulphate.

Examination of Materials Employed.—In order to test the purity of the hydrazine sulphate (obtained from Kahlbaum, Berlin) used in these experiments, the percentage of sulphur was determined in six different samples of the material. Found: 24·57, 24·60, 24·56, 24·59, 24·58, and 24·54 per cent; theory, 24·64 per cent.

In the ammonium metavanadate (obtained from E. Merck, Darmstadt) the percentage of vanadium was determined by weighing the pentoxide formed by ignition of a weighed quantity of the original material. Found: 43·23, 43·18, 43·19, and 43·17 per cent; theory, 43·67 per cent. The percentage of nitrogen was determined by distilling the ammonia liberated from a weighed amount of the material in alkaline solution into a measured excess of standard hydrochloric acid. Found: 11·84 and 11·85 per cent; theory, 11·95 per cent.

Preparation of Solutions.—Two solutions of hydrazine sulphate were employed: one containing 15 grms. of the salt per litre, and the other 10 grms. The solution of ammonium metavanadate was prepared in each case by dissolving the proper amount of the salt in a certain measured amount of pure concentrated sulphuric acid and diluting with a measured amount of water after the solution had been cooled to room temperature.

General Procedure followed in the Experiments.—A measured volume of the hydrazine sulphate solution was placed in a distilling flask of about one litre capacity. Through a separatory funnel was introduced a measured volume of the ammonium metavanadate solution. A slow current of air was drawn through the flask in order to carry the hydronitric acid through the condenser into the absorption apparatus. This absorption apparatus consisted essentially of an Erlenmeyer flask (150 cc.) and a Muencke gas wash-bottle. The Erlenmeyer flask was provided with a two-hole stopper through which passed the end of an adapter (connected with the condenser) dipping beneath the surface of the absorbing solution. After passing through the flask the gas was led through a second quantity of the same solution in the Muencke gas wash-bottle.

The absorbing solution was prepared by adding 2 cc. of sodium acetate solution (10 grms. in 100 cc.) and 5 cc. of silver nitrate solution (10 grms. in 100 cc.) to 35 cc. of water. Any hydronitric acid evolved from the reacting mixture was precipitated in the form of silver trinitride. The presence of sodium acetate decreases the solubility of the silver trinitride (Dennis and Isham, *Journ. Am. Chem. Soc.*, 1907, xxix., 18). In every experiment complete absorption of the acid was effected in the Erlenmeyer flask. The yield of hydronitric acid was determined by the method of Dennis and Isham (*loc. cit.*).

Results Obtained in the Experiments.—Four series of experiments were performed in order to ascertain the effect upon the yield of hydronitric acid of varying (1) the temperature at which the reaction is permitted to take place, (2) the amount of metavanadate solution used, (3) the method of introducing the metavanadate solution, and (4) the amount of sulphuric acid present. The results of the different series of experiments are given respectively in Tables I. to IV.

In the sixth column is given for each experiment the highest temperature to which the reacting mixture was heated. As this temperature was raised larger yields of hydronitric acid were obtained. This is at least partially attributable to the fact that the acid formed by the reaction is not completely distilled over into the absorption apparatus unless the temperature is raised to 100°. In these experiments the metavanadate was added at once, with the result that the yield of acid even at 100° was not so high as when the solution was added drop by drop under similar conditions (see Experiment 6).

The most satisfactory procedure was found to be as follows :—The reacting mixture was maintained at a temperature of 80° during the addition of the metavanadate solution. The solution was then brought to the boiling-point, and was held at that temperature for a few minutes in order to effect the complete removal of the hydronitric acid from the mixture. This procedure was followed in all the experiments recorded in Tables II., III., and IV.

In Experiments 7, 8, 9, and 10 the amounts of ammonium metavanadate solution employed correspond to 12, 10, 8, and 6 molecules respectively of the salt for every 3 mole-

* From the *Journal of the American Chemical Society*, xxix., No. 9.

TABLE I.

No. of experiment.	$N_2H_4H_2SO_4$ (100 grms. per litre).	NH_4VO_3 solution.			Temperature.	AgCl obtained.	Yield NH_3.
			NH_4VO_3 per 100 cc.	Concentrated H_2SO_4 per 100 cc.			
	Cc.	Cc.	Grms.	Cc.		Grm.	Per cent.
1.	30	100	1·2709	12·8	20°	0·00345	2·09
2.	30	100	1·2709	12·8	60	0·0049	2·97
3.	20 (*a*)	100	1·2709	12·8	60	0·00485	2·94
4.	30	100	1·2709	12·8	100	0·0126	7·62
5.	30	100	1·2709	12·8	100	0·01215	7·35

TABLE II.

No. of experiment.	$N_2H_4H_2SO_4$ (10 grms. per litre).	NH_4VO_3 solution.		Method of adding.	AgCl obtained.	Yield NH_3.
		NH_4VO_3 per 100 cc.	Concentrated H_2SO_4 per 100 cc.			
	Cc.	Grms.	Cc.		Grm.	Per cent.
6.	20 (*a*)	1·2709	12·8		0·0207	12·52
7.	30	1·0811	12·8		0·01735	10·50
8.	30	0·9009	12·8		0·01845	11·16
9.	30	0·7205	12·8		0·0166	10·04
10.	30	0·5405	12·8		0·0135	8·17

TABLE III.

11.	30	100	1·0811	12·8	At once	0·0135	8·17
7.	30	100	1·0811	12·8	Drop by drop	0·01735	10·50
12.	30	100	1·9009	12·8	At once	0·01055	6·38
8.	30	100	1·9009	12·8	Drop by drop	0·01845	11·16
13.	30	100	0·7207	12·8	At once	0·0135	8·17
9.	30	100	0·7207	12·8	Drop by drop	0·0166	10·04

TABLE IV.

14.	30	100	0·9009	6·4	0·0181	10·95
8.	30	100	0·9009	12·8	0·01845	11·16
15.	30	100	0·9009	19·2	0·0224	13·55
16.	30	100	0·9009	19·2	0·0169	10·23
17.	30	100	0·9009	25·6	0·0200	12·10
18.	30	100	0·9009	38·4	0·01285	7·78
19.	30	100	0·9009	76·8	—	—

TABLE V.

No. of experiment.	Total weight NH_3.	NH_3 formed during reaction.	NH_3 formed.
	Grm.	Grm.	Per cent.
1.	0·09353	0·00174	17·7
2.	0·09327	0·00148	15·1
3.	0·09370	0·00191	19·5
4.	0·09388	0·00209	21·3
5.	0·09179	—	—
6.	0·09179	—	—

(*a*) 15 grms. $N_2H_4H_2SO_4$ per litre.

cules of hydrazine sulphate. In all of these experiments the metavanadate solution was added drop by drop after the hydrazine sulphate solution had been heated to 80°. From these experiments it is apparent that as a general rule the formation of hydronitric acid is facilitated, within certain limits, by increasing the amount of ammonium metavanadate.

In Experiment 11, 12, and 13 the entire quantity of ammonium metavanadate solution was added at the outset. It is obvious that when the solution is added drop by drop the yield of hydronitric acid is materially increased.

From these experiments it appears that when the concentration of sulphuric acid is chosen as indicated for Experiment 15, the maximum yield of hydronitric acid is obtained. In Experiment 16 the metavanadate solution was added more rapidly than in the preceding case, with the result that the yield of the acid was considerably reduced. In all other experiments the solution was added slowly drop by drop.

Identification of the Hydronitric Acid Formed.—The properties of the acid and of its silver salt were studied almost exactly in the manner recommended in a previous article (Browne, *Journ. Am. Chem. Soc.*, 1905, xxvii., 551—555). The percentage of silver in the silver salt was determined with the following results:—(1) 0·21635 grm. of the salt gave 0·20605 grm. of silver chloride; (2) 0·21735 grm. of the salt gave 0·20680 grm. of silver chloride. This corresponds to 71·69 and 71·62 per cent silver (theory, 71·97 per cent), or to 3·4 and 3·05 atoms of nitrogen per atom of silver. For all calculations in the present article the atomic weights recommended by the International Committee for 1907 have been employed.

In order to ascertain whether the amount of ammonia present undergoes increase or decrease during the course of the reaction the series of experiments recorded in Table V. was performed. In Experiments 1, 2, 3, and 4, 50 cc. of ammonium metavanadate solution (containing 12·85 grms. of the salt and 128 cc. of pure concentrated

sulphuric acid per litre) were added slowly to 10 cc. of hydrazine sulphate solution (containing 15 grms. per litre) at a temperature of about 80°. The solution was then made alkaline by the addition of a certain excess of sodium hydroxide solution, and the ammonia was distilled, with the usual precautions, into a measured excess of fifth-normal hydrochloric acid. The amount of ammonia was determined by titrating back with fifth-normal sodium hydroxide solution. In the two blank Experiments 5 and 6, 50 cc. of ammonium metavanadate solution were employed, but no hydrazine sulphate solution.

The amount of ammonia formed in the course of the first four experiments was ascertained in each case by subtracting the total weight of ammonia obtained in Experiment 5 (or 6) from the total weight of ammonia obtained in each of the first four experiments. The percentages of ammonia formed were calculated on the basis of the equation suggested in a subsequent paragraph, and used by the authors in calculating the percentage yields of hydronitric acid.

(To be continued).

THE ATOMIC WEIGHT OF HYDROGEN.*

By WILLIAM A. NOYES.

Some years ago the writer carried out a series of determinations of the quantitative composition of water, from which the value 15·896 was calculated for the atomic weight of oxygen on the hydrogen basis (*Am. Chem. Journ.*, 1890, xii., 441). The opinion was expressed in the paper, that the true value was probably within one part in a thousand of this number, and that it was rather below than above the value reported. Several years later Morley published an account of his elaborate determinations of the densities of hydrogen and oxygen, and of the composition of water by weight, which led him to the value 15·879 for oxygen, or 1·00762 for hydrogen (O = 16) ("Smithsonian Contributions to Knowledge," 1895; *Am. Chem. Journ.*, xvii., 267 and 396; *Zeit. Physik. Chem.*, xvii., 87). Meanwhile Richards had shown that copper oxide retains occluded gases obstinately (*Proc. Amer. Acad.*, 1891, xxvi., 276), a fact which was partly known to me at the time of my work, but which was not as carefully considered as it should have been. There was obtained in each of my experiments, at the end, a small amount of gas which was assumed to be nitrogen on the basis of one or two rather imperfect analyses of the earlier samples. The weight of this gas, calculated as nitrogen, was subtracted from the weight of the hydrogen, giving, on the average, a correction of about one part in a thousand. Several years after the publication of Morley's results it occurred to me that this gas came, very probably, from the copper oxide, and that its weight should be subtracted from the weight of the oxygen instead of from that of the hydrogen. On applying the correction in this manner the value 15·879 (or 1·00765) was found.

While this agreement with Morley's value was gratifying, and the fact was stated to a few personal friends, it did not seem proper to publish a statement about the matter until the surmise could be confirmed by new experimental evidence.

In addition to the desire of confirming or refuting the above explanation of my earlier results, several reasons have made it seem worth while to undertake a new determination of this constant. Hitherto our accurate knowledge of the composition of water has rested on Morley's work alone. He secured so high a degree of concordance in his results, and he exercised such an extraordinary degree of care at every point, that the results obtained by all other observers must be considered as having only confirmatory value in comparison. (This is discussed further in the following paper). It seemed worth while, if possible, to secure a similar order of accuracy by a different method.

Richards and Wells (*Journ. Am. Chem. Soc.*, xxvii., 459) have recently given us a very accurate determination of the ratio between silver and chlorine, but the exact value for the atomic weight of chlorine is still in doubt because the ratio between silver and oxygen is not satisfactorily known (Guye and Ter Gazarian, *Comptes Rendus*, cxliii., 411). A determination of the ratio between hydrogen and chlorine has been carried out at the United States Bureau of Standards, and by using hydrogen generated in the same manner for that determination and for the determination of the composition of water, a very direct comparison between oxygen and chlorine has been secured. As the atomic weights of more than forty elements have been determined in their relation to silver or the halogens, or both, the fundamental importance of the ratios of chlorine and silver to oxygen is apparent.

Finally, it seemed possible to so carry out the work as to secure some evidence with regard to the question of change of weight in a chemical reaction in which a large amount of energy is dissipated. This phase of the problem was

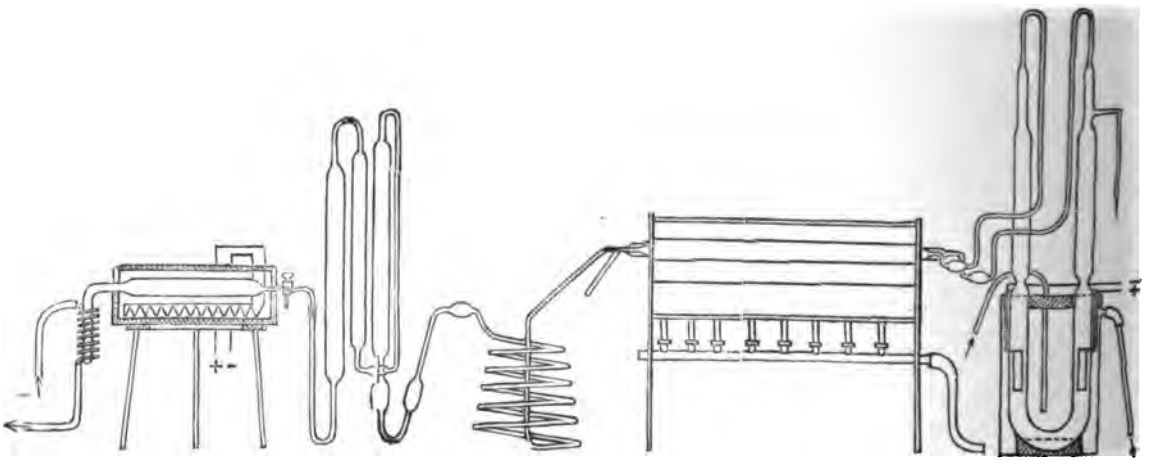


Fig. 1.

* From the *Journal of the American Chemical Society*, xxix., No. 12.

suggested to me while considering the claim made by Prof. S. M. Babcock some years ago that ice loses weight when it melts. He proposed the theory that the loss of weight was intimately connected with the gain of energy by the ice as it melts. If this were true, hydrogen and oxygen should gain weight when they combine to form water. It may be said at once that the results to be given are not conclusive on this point. So far as they have any bearing on the question they indicate a loss rather than a gain in weight when hydrogen is converted into water.

Apparatus.—The apparatus used in the work was, in part, very similar to that used in the previous investigation (*Am. Chem. Journ.*, xii., 441). Five series of determinations have been carried out. In the first four of these the hydrogen and oxygen were obtained by the electrolysis of dilute (15 per cent) sulphuric acid. In the last series the gases were generated by the electrolysis of a 6 to 8 per cent solution of barium hydroxide.

The purifying train will be easily understood from the figure. In the first three series of experiments and in all but the last three determinations of the fourth series, the hydrogen was passed at first through a tube of common glass filled partly with platinised asbestos and partly with copper gauze, and the oxygen was passed through a similar tube filled partly with platinised asbestos, partly with asbestos mixed with lead chromate. These tubes were heated to 300—350°. In the last three experiments of the fourth series hard glass tubes were substituted for the common glass, so that a higher temperature could be used, and in the fifth series hard glass tubes filled with platinised quartz were used. The platinised quartz was prepared by moistening the quartz, which had been heated and quenched in water, with a solution of chlorplatinic acid, and reducing the latter in a current of hydrogen. Each gas then passed through a serpentine tube about 4 metres in length and of 8 mm. internal diameter. These tubes contained a 15 per cent solution of potassium hydroxide, in which was dissolved a small amount of lead oxide. Sulphur compounds present in the hydrogen were reduced to hydrogen sulphide as the mixture passed over the platinised asbestos and copper, and the sulphur of the hydrogen sulphide was retained by the lead as lead sulphide. Only a very small amount of lead sulphide was deposited during the passage of more than 1000 litres of hydrogen through the asbestos. When the barium hydroxide was used as an electrolyte, the serpentine tubes were replaced by bulbs to collect the condensed water, and the solution formed by the deliquescence of the potassium hydroxide. The union between the hard and soft glass was made by grinding the joint and then melting in it a very small amount of Khotinsky cement. Ample evidence is given below that these joints were perfect.

The gases passed next through the tubes containing potassium hydroxide in the form of sticks and then through two or three tubes 15 mm. in diameter and 25 cm. long, filled with phosphorus pentoxide which had been sublimed in a current of oxygen. When not in use these tubes were always sealed, and great care was exercised to avoid the entrance of moist air from the exits where the gases were delivered for use. If the phosphorus pentoxide were to become moist on that side, there would be danger that the gases might carry some of the moisture away with them.

The electrolytic apparatus containing the sulphuric acid or solution of barium hydroxide consisted of a U-tube with platinum electrodes. The limbs of the tube were about 35 mm. in diameter and 55 cm. long. It was filled about two-thirds full at first, and when the solution became too concentrated, water, recently boiled and cooled out of contact with the air, was introduced through the small tube shown on the oxygen side of the apparatus. It was easy to do this without allowing any air to enter, but after each filling a considerable amount of the gases were generated before further use of them for a determination. The water used for preparing the original solution and for subsequent dilutions was purified by re-distilling distilled water with the addition of an alkaline solution of potassium permanganate, and collecting the portion that was free from ammonia.

The resistance of the sulphuric acid in the apparatus was 4 to 5 ohms, while that of the solution of barium hydroxide was considerably greater. It was necessary to cool the electrolytic apparatus with a pretty rapid current of water through the jar containing it. The electrical current used had a pressure of 120 volts, and was reduced by means of a rheostat placed in series with the electrolytic cell. With the sulphuric acid electrolyte a current up to 15 ampéres could be used, giving 6 litres of hydrogen an hour. With the barium hydroxide it was not considered safe to go beyond 4 litres an hour, because of the greater resistance and consequent heating of the solution.

Copper Oxide.—In the first three series of experiments copper oxide was used to convert the hydrogen into water. In the first three experiments copper oxide prepared by precipitating copper sulphate with a hot solution of sodium hydroxide was used. The precipitate was washed by decantation until it became colloidal, and then thoroughly on a Buchner funnel. This oxide retained a trace of sulphate, which was reduced by the hydrogen to sulphur dioxide, and the latter was found in small amount in the water obtained. Only two determinations were made with this oxide. Seven determinations were made with a sample of copper oxide purchased as pure from Kahlbaum. It contained arsenic and other impurities. As these determinations formed a part of the first series, the results of which are rejected for reasons to be given below, they need not be discussed further here. The copper oxide for the remainder of the first, and for the second and third series, was prepared by precipitation of a hot solution of copper sulphate, Rochelle salt, and sodium hydroxide with glucose. The cuprous oxide obtained could be washed indefinitely, and all sulphates were very completely removed. After ignition in a current of oxygen the oxide retained a very small amount of carbon dioxide, but as this appeared as a gas at the end of the experiment, and the amount could be determined, no serious error can have arisen from this source. The same copper oxide was used repeatedly, and after several determinations the carbon dioxide nearly disappeared.

Balance and Weights.—The balance used was made by Ruprecht, of Vienna, and was designed to carry a maximum load of 1 kilogrm. on each pan. The air of the balance case was dried by means of a rapid current of air blown through two wash-bottles containing concentrated sulphuric acid and a little chromic anhydride. The spray of sulphuric acid carried by the current was removed by passing through two tubes, the first containing glass-wool and the second cotton-wool. The current of air was stopped ten to twenty minutes before the weight was determined. During the last series of experiments the balance-case was enclosed in a larger glass case, and the air within the latter was dried by means of large dishes of calcium chloride set on top of the inner case. For determinations in which the weight of the hydrogen was involved, the weight was always determined twice at an interval of one-half hour or more, and with the current of air passing into the case during a part of the interval. In 100 pairs of weights taken from the notebook at random, the average difference was 0·05 mgrm., and the maximum difference 0·12 mgrm.

Weights.—The weights used were carefully calibrated by Mr. Pienkowsky, of the Bureau, at the beginning of the work, a second time after they had been in use for ten months, and a third time at the completion of the investigation, a little more than two years after it was begun. The largest change observed in any of the weights used was 0·04 mgrm.; while none of the platinum weights changed more than 0·01 mgrm. The aluminium rider gained 0·014 mgrm. A re-calculation of the amounts of hydrogen in the last series showed that the use of the new corrections caused no change exceeding 0·14 mgrm. in the weight of the hydrogen for any experiment of that series,

while the algebraic sum of the changes for the five experiments of the series was 0·09 mgrm., or one part in two hundred and fifty thousand of the weight of hydrogen used.

The calibration of the weights was, of course, to a vacuum standard. Since the substances to be weighed were always enclosed in a glass apparatus whose volume remained constant, and which was counterpoised by another glass apparatus of very nearly the same volume and weight, no vacuum correction in the ordinary sense was required. For our present purpose it is most convenient to assume the brass weights in air as standard. If we do this, the platinum weights will appear too heavy because they displace less air in proportion to their weight. This requires a correction of 0·087 mgrm., which must be added for each grm. of platinum weights used. For convenience, a table was prepared which included this correction for the platinum weights with the other corrections as determined in the comparisons of the weights.

(To be continued).

THE CHOICE OF THE MOST PROBABLE VALUE FOR AN ATOMIC WEIGHT: THE ATOMIC WEIGHT OF HYDROGEN.*

By WILLIAM A. NOYES.

A LARGE amount of material has been accumulated from which the atomic weights of the more important elements can be calculated. A very superficial examination of this material reveals the fact that the experimental results on which our knowledge of these constants is based, vary very greatly in their value, and that many of the older determinations have been rendered practically worthless by recent work, which has been more careful and accurate.

As some of these new determinations affect the values for elements of such fundamental importance that a recalculation of the whole table of atomic weights will be necessary in the near future, it seems desirable to formulate some general principles to aid in the elimination of results which have little or no value, and in the combination of the results which remain. Such principles, if they meet with general acceptance, will be of value, not only for the purpose stated, but also as setting a certain standard which must be attained by future workers in this field if their work is to be of permanent value.

The most important general principle which has been proposed for the combination of the results of different observers, is the one based on the mathematical discussion of accidental errors of observation. In accordance with the theory of probabilities, these results, if subject only to accidental errors, should be weighted in inverse proportion to their probable errors (F. W. Clarke, "Constants of Nature," Part V., Edition of 1897, p. 7). A very serious objection to this method of treatment lies in the fact that every determination of this kind is subject to constant errors, and that the amount of these errors is not proportional to their "probable errors" (see Note). Thus Stas obtained 132·8445 ± 0·0008 parts of silver chloride from 100 parts of silver, while Richards and Wells have obtained 132·8670 ± 0·0005 parts (*Journ. Am. Chem. Soc.*, xxvii., 524). The most probable value calculated by the mathematical rule would be 132·8607. If this value is the true one, the real error of the value obtained by Richards and Wells is twelve times its probable error, while the real error of Stas is twenty times the probable error. And, whatever the true value may be, the real error of one of the results, at least, is many times its "probable error." An examination of other cases shows that the relations here found are typical, and it seems evident that the question of constant errors requires some other treatment than the simple mathematical one. The proper treatment, which is an experimental one, has been clearly illustrated in the case which we have under consideration. Richards and Wells studied their method very carefully with especial reference to the elimination of constant errors, and to secure evidence as to the amount of those errors which could not be wholly excluded. They also pointed out certain errors in the work of Stas, and determined, approximately, the magnitude of some of these. It is evident for this reason that very much greater weight attaches to the value found by Richards and Wells than to that found by Stas, and it is proposed as a general principle that when a later observer has pointed out sources of error which are considerable in comparison with the "probable errors," and where the later observer has succeeded in avoiding these sources of error, the earlier work must be looked upon as having only confirmatory value, and the result of the later work should be accepted without modification. It has been objected to this that the later work is also subject to constant errors which may be in the opposite direction from those of the earlier determination, and that if we give a certain weight to the earlier work we may eliminate these errors. But we certainly are not justified in using a value that contains a known error in one direction merely for the chance that we may compensate an unknown error.

(NOTE.—Professor Clarke has, of course, recognised the importance of constant errors, and has often rejected values which he considers subject to such errors. In 1898 (*Amer. Chem. Journ.*, xx., 543) Prof. T. W. Richards pointed out the importance of selecting atomic weights on the basis of the methods employed in their determination and the probable freedom of those methods from constant errors. It is interesting to notice that of the seven values in Professor Richards' table, which differed at that time decidedly from the values given by Professor Clarke, the numbers for four of the atomic weights are nearer to the numbers now given in the International Table than were the values then given by Professor Clarke).

The principle outlined above has been recently proposed, independently, by Professor Guye in his discussion of the selection of the most probable value for the density of a gas (*Arch. Sci. Phys. Nat.*, xxiv., 44). A second principle proposed by Professor Guye is that when the values obtained by two observers agree while that obtained by a third observer is discordant, the values which are in agreement should be given much greater weight. As an extension of this principle, a value of an individual worker which differs materially from the values obtained by several others, should be rejected entirely.

After eliminating the results which are excluded by the application of the foregoing principles, it is proposed to arrange those which remain in the order of their probable errors. Any result with a probable error more than five times that of the smallest probable error may be excluded, as such a result will have only one twenty-fifth the weight, according to the theory of probabilities. In practical effect, this is the same as using the mathematical rule which Professor Clarke has so long employed in weighting the results of different workers. As at least five or six observations are necessary to give a probable error which has any significance, results based on a smaller number of determinations may be excluded unless other evidence warrants the belief that the work is of an unusual degree of accuracy.

The values for any given ratio which remain after the elimination of results which have little value, may well be combined by weighting them inversely as the squares of their probable errors.

For further use, the ratios which are selected in this manner should be weighted, not by the probable error calculated by the mathematical rule, but by the deviation of the results of different observers from the value selected. If the results of only one observer remain after eliminating untrustworthy values (as in the case of the ratio of silver to silver chloride), this result should be weighted in

* Presented in abstract at the N.Y. Meeting of the American Chemical Society, December 28, 1906.

accordance with the average deviation of the results of this observer from his mean. This will, I think, give a much fairer basis than the "probable error" for weighting the value in such cases. Thus the "mean error" of the value of Richards and Wells given above is 0·0018, while the "probable error" is 0·0005. When we consider the certainty that some sources of constant error will always remain, I think every one will agree that the real error is much more likely to correspond to the former than to the latter value.

After selecting the most trustworthy experimental ratios as suggested, we have still to combine them for the calculation of atomic weights. This may usually be done in a variety of ways. In choosing among these, the same general principles as before should be applied. For a given atomic weight, only those ratios should be used for which the uncertainties of the values will affect the atomic weight chosen less than five times as much as any other combination of ratios which might be used. In most cases this will probably lead to the selection of ratios which furnish a direct comparison with oxygen, silver, or one of the halogens rather than of those in which the comparison is more indirect. Densities of gases corrected to the condition of an ideal gas by the method of D. Berthelot (*Comptes Rendus*, cxliv., 76) may be considered as direct comparisons with oxygen, and molecular and atomic weights calculated from these densities should be included with those determined by chemical methods.

The Atomic Weight of Hydrogen.

The following is a summary of the determinations which have been made of the atomic weight of hydrogen by the chemical method :—

	Date.	No. of expts.	Value.	Prob. error.	Real error.	Real error. / Prob. error.
Dulong and Berzelius .	1821	3	1·00667	356	108	0·3
Leduc.. ..	1892	2	1·00749	83	26	0·3
Erdmann and Marchand.	1842	8	1·00160	71	615	8·7
Thomsen ..	1870	8	1·00570	71	205	2·9
Rayleigh ..	1889	5	1·00692	56	85	1·5
Dumas.. ..	1842	19	1·00250	44	525	12·0
Keiser.. ..	1898	8	1·00753	31	22	0·7
Dittmar and Henderson	1890	24	1·00840	29	65	2·2
Noyes (recalculated) ..	1890	24	1·00765	17	10	0·6
Thomsen ..	1895	21	1·00826	14	51	3·6
Cooke and Richards ..	1887	16	1·00826	13	51	3·9
Noyes (original).. ..	1890	24	1·00654	11	121	11·0
Keiser.. ..	1888	10	1·00306	7	469	67·0
Noyes.. ..	1907	48	1·00787	2	12	6·0
Morley.. ..	1895	23	1·00762	2	12	6·0

The probable errors of the table are calculated from those assigned by Professor Clarke ("Constants of Nature," 1897, Part V., p. 24). For the results of Erdmann and Marchand and Leduc, the values are arbitrary. For convenience these errors are given in units corresponding to the last significant figure of the values for the atomic weights.

On applying the principles which have been outlined, we find that the results of Dulong and Berzelius, Erdmann and Marchand, and of Dumas, are excluded because the later work of Dittmar and Henderson by the same method, demonstrates that serious constant errors were involved in the earlier work. Leduc's value is to be rejected because the number of experiments was too small. Keiser's earlier value is to be rejected because it is not in accord with any of the later work, and because he has himself given us a later and better value. My own original value must be rejected because it was subject to a constant error and the recalculated result may be considered as superseded by my later and more careful work. Because the probable errors of all of the other determinations are more than five times as great as those of Morley and myself, they would be excluded by the third principle proposed. The final value, if calculated from these two results, is 1·00775.

It is interesting to notice the relation between the real errors of the various values (assuming this value as true) and the probable errors. *Only in those cases where we now know that there were serious constant errors, is the real error more than six times the probable error.*

Morley calculates a value corresponding to 1·00762 from his determinations of the densities of the gases and their combining volumes. This value has not been considered here, partly because the probable error of the density of hydrogen is about 3 in 100,000, instead of 2 for the chemical method, but chiefly because of the uncertainty of the ratio of the combining volumes (Morley, "Smithsonian Contribution to Knowledge," 1895, No. 980, p. 110).

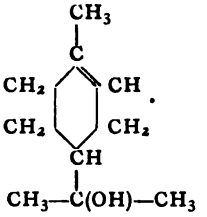
If a value is calculated by Professor Clarke's method, weighting each result in inverse proportion to its probable error, only Keiser's older value and my own original value would affect the value which I have selected by more than about one part in 100,000. Keiser's older value would, however, reduce it by about forty parts, and my own original value by about four parts in 100,000.—*Journal of the American Chemical Society*, vol. xxx., No. 1.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 27, December 30, 1907.

New Method of Hydrating Pinene.—Ph. Barbier and V. Grignard.—Pinene is dissolved in acetic acid and an aqueous solution of monosulphonic benzoic acid is added. After twelve hours water is added, and the part insoluble in water is washed, dried, and subjected to rectification under reduced pressure. The principal product is terpineol (melting-point 35°),—



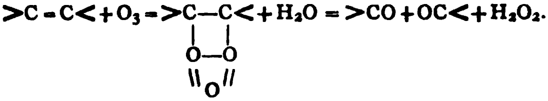
A new hydrocarbon, which the authors are further investigating, is also separated.

Ketone derived from β-Hexahydrocarvacrol.—Leon Brunel.—When β-carvacromenthol, $C_{10}H_{19}OH$, is oxidised by chromic acid in acetic acid solution it is converted into the corresponding ketone, $C_{10}H_{18}O$, carvacromenthone. It is a mobile colourless liquid smelling of cymene. The determination of the physical constants of its derivatives shows that it is identical with the tetrahydrocarvone prepared by Baeyer and Wallach.

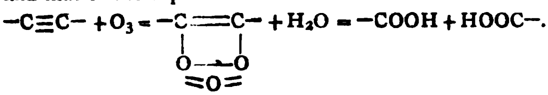
Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 18, 1907.

Action of Ozone upon Substances containing a Triple Bond.—C. Harries.—Molinari has stated that ozone can be used to distinguish aliphatic double bonds from aromatic and triple bonds, since it reacts only with those substances which possess an aliphatic structure.

The author, however, finds that this statement is incorrect, and that stearolic acid, for instance, rapidly absorbs ozone and is converted into a typical ozonide. Phenyl propiolic acid also reacts with ozone violently. The splitting of the double bond by means of ozone may be represented by the following scheme :—



and that of the triple bond thus :—



Rubidium Calcium Sulphates.—J. D'Ans and W. Zeh.—To prepare rubidium syngenite, finely divided gypsum is added to a 30 per cent solution of rubidium sulphate and the mixture allowed to stand in the cold. The salt which separates out is washed with alcohol and ether. Rubidium syngenite crystallises in long needles, and is isomorphous with potassium and ammonium syngenites. A sulphate, $Rb_2Ca_2(SO_4)_3$, separates when 30 per cent rubidium sulphate solution is boiled with gypsum. No rubidium pentacalcium sulphate, $Rb_2Ca_5(SO_4)_6 \cdot H_2O$, has yet been obtained; if it exists its preparation probably requires a lower temperature and a low $RbSO_4$ concentration.

Some Reactions in Ultra-violet Light.—Herm. Thiele.—The author has performed a series of experiments to investigate the effect of ultra-violet light, using a quartz mercury lamp as a source of light and quartz vessels. With water he obtained no reaction with potassium iodide and starch, but a marked reaction on the addition of ferrous sulphate. Formic acid yielded CO_2, O_2, and CO. Mixtures of CO and O_2 and also of CO and H_2O gave some CO_2. No chlorine (or traces only) was formed from hydrochloric acid.

Porous Materials to Replace Cocks in Working with Gases.—Alfred Stock.—The author describes three modifications of Prytz's apparatus for making an air-tight valve. This apparatus consists of a tube or vessel closed by a porous plate, upon which some mercury is poured. Another tube closed with a similar porous plate (without the mercury) is inserted a short distance in the first. If this second tube is connected with an air-pump and the two porous plates are in contact, air passes through them when the pump is in action; when a sufficient degree of exhaustion is reached, on raising the upper tube with the plate the mercury acts as an air-tight stopper to the lower, and thus the space in the lower tube is closed, so that no air can enter. In Pritz apparatus refractory clay was used for the porous material, but the author has found that a more satisfactory stopper is made by burning a mixture of clay with water-glass and rubber. The material thus obtained is not attacked by boiling water or by dilute acids, and, moreover, it can be fused on to glass. Its porosity is comparatively great.

Action of Silver Nitrate and Mercuric Nitrate upon some Inorganic Hydroxides.—Wilhelm Biltz and Friedrich Zimmermann.—When freshly prepared magnesium hydroxide is moistened with a solution of silver nitrate, the hydrogel is coloured yellowish brown owing to the separation of silver oxide. The authors have studied the action of silver nitrate on the hydroxides of the following metals:—Mg, Zn, Cd, Pb, Be, Al, In, Zr, Sn, Sb, Bi, and find that it is only in the case of the first three that there is any coloration. With mercuric nitrate the hydroxides of Be, Mg, Zn, Cd, Al, Pb, and Mn react. Of the rare earths, La and Nd do not react when heated with silver nitrate, but Pr, Y, Sa, Er give a coloration. All of these react with mercuric nitrate, both in the cold and when heated.

MEETINGS FOR THE WEEK.

MONDAY, Feb. 3rd.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Nitro-glycerin and its Manufacture," by Lt.-Col. Sir Frederick Nathan and W. Rintoul.

TUESDAY, 4th.—Royal Institution, 3. "Roman Britain—(*b*) Its Interior Civilisation," by Prof. F. J. Haverfield, M.A., LL.D., &c.

THURSDAY, 6th.—Royal Institution, 3. "The Story of the Spanish Armada," by Major Martin Hume.
—— Chemical, 8.30. "The Metallic Picrates," by O. Silberrad and H. A. Phillips. "Organic Derivatives of Silicon Part V., Benzylethylsilicone, Dibenzylsilicone, and other Benzyl- and Benzylethyl Derivatives of Silicane," by R. Robinson and F. S. Kipping. "Some Physico-chemical Properties of Mixtures of Pyridine and Water," by H. Hartley, N. G. Thomas, and M. P. Applebey. "Constitution of Umbellulone," by F. Tutin. "Residual Affinity of the Coumarins and Thiocoumarins as shown by their Additive Compounds," by A. Clayton. "Influence of Foreign Substances on certain Transition Temperatures and the Determination of Molecular Weights," by H. M. Dawson and C. G. Jackson. "Bromination of *p*-Hydroxydiphenylamine," by Miss A. E. Smith and K. J. P. Orton. "Colour and Constitution of *s*-Methine Compounds," by F. G. Pope. "Decomposition of Ammonium Bichromate by Heat," by W. M. Hooton.

FRIDAY, 7th.—Royal Institution, 9. "Napoleon and the Louvre," by Humphry Ward, M.A.

SATURDAY, 8th.—Royal Institution, 3. "Anthony Van Dyck," by Lionel Cust, M.V.O., &c.

THE CHEMICAL NEWS.

Vol. XCVII., No. 2515.

THE BROMATES OF THE RARE EARTHS.

Part I.—A New Method for the Separation of the Yttrium Earths.

By C. JAMES.

During recent years chemists investigating the rare earths have directed their efforts more towards the cerium group than towards the yttrium earths, with the result that the elements cerium, lanthanum, praseodymium, neodymium, samarium, europium, and gadolinium are fairly well known. On the other hand, the yttrium earths, with the exception of yttrium, ytterbium, and scandium, are still but poorly defined. Many investigators have been of the opinion that "new" erbium is complex, while almost nothing is known about thulium, holmium, dysprosium, and terbium. In addition to the above, victorium, announced by Crookes, is believed by Urbain and some others to be a mixture, although its discoverer still claims that it is a separate and new individual element.

In the case of the cerium group several excellent methods of fractional crystallisation have been developed. On the other hand, no rapid and simple method has been applied to the yttrium earths with the possible exception of the method of Urbain using the ethylsulphates, and some methods employing compounds of a costly nature, such as the acetylacetonates and the metanitrobenzenesulphonates. As one must deal with many kilogrms. of material, expensive compounds are out of the question unless the separation should prove almost quantitative, which is never the case.

Urbain's ethylsulphate method (*Comptes Rendus*, cxxvi., 835; cxxvii., 107; cxxxii., 136) gives good results. He says that yttrium, neo-erbium, and ytterbium accumulate in the most soluble portions, with no trace of the lanthanum group and no earths of the samarium and gadolinium groups. It is very difficult to obtain erbium from fractions rich in holmium by its use, and for separating earths of the same group the method of fusing the nitrates is still the best. Another difficulty is due to the fact that the ethylsulphates are inclined to hydrolyse unless special precautions are taken.

The fractionation of the simple nitrates from concentrated nitric acid proposed by Demarçay (*Comptes Rendus*, cxxii., 728; cxxx., 1020) is very tedious, and the use of a solvent of such a character causes great inconvenience in the laboratory.

The separation obtained by taking advantage of the difference of solubility of the oxalates in a saturated solution of ammonium oxalate developed by Carl Auer von Welsbach (*Monatsh.*, xxvii., 935) gives interesting results. It has drawbacks, however, as it involves the use of two temperatures and requires a large number of operations.

Among the remaining methods only a few need be mentioned:—Fusion of the nitrates and separation of the most easily decomposed portions, by their insolubility in water, separates ytterbium and scandium at one end, and yttrium and terbium at the other. To obtain ytterbium free from erbium and thulium requires about seventy operations. It is also extremely difficult to get yttrium pure by this method, as terbium clings.

Fractional precipitation of the concentrated neutral nitrate solution by means of magnesium oxide (Muthmann and Rolig, *Ber.*, xxxi., 1718), tending to throw down the less basic elements first, gives simllar results.

The precipitation of pure yttria by Muthmann and Böhm's chromate method (*Ber.*, xxxiii., 49, and Chem. News, lxxi., 169) is comparatively simple, but unfortunately it is of no value for separating the other members.

The fractionation obtained by boiling a solution of the oxalates in ammonium carbonate (*Journ. Am. Chem. Soc.*, xxix., 495, and Chem. News, xcv., 181) works well for obtaining erbium free from holmium and dysprosium on the one side, and thulium, ytterbium, and scandium on the other.

Fractional precipitation to be of value must be very rapid. Fractional crystallisation is to be preferred, for it is much easier to carry out a large number of operations. As a rule, in fractional precipitation methods, especially where dilute solutions are employed, a good deal if not most of the material is washed away. It is highly desirable, therefore, that a method consisting of fractional crystallisation of some type of isomorphous compounds with greatly varying solubilities should be found. With this object in view the author has examined the sulphites, xanthates, succinates, double carbonates with sodium, glycollates, methyl sulphates, normal propyl sulphates, camphorates, iodates, sulphocyanides, sulphocyanide double compounds with mercuric cyanide, monochloracetates, monobromsuccinates, oleates, ferrocyanides, bromates, &c., besides nearly every compound proposed in literature for the purpose of fractionation. The bromates are the best suited for the purpose of all those examined up to the present time.

The bromates are easily prepared by using barium bromate, which in turn is formed by mixing boiling solutions containing the required amounts of barium chloride and potassium bromate. As potassium bromate can be prepared cheaply the rare earth bromates are not costly to obtain.

The rare earth material, generally in the form of the oxalates, is mixed into a paste with sulphuric acid, and the temperature raised until the fumes of sulphuric acid cease to be evolved. The residue is then finely powdered, dissolved in ice cold water, and the resulting solution poured over an excess of barium bromate. This operation is best carried out in a large evaporating dish placed on the water-bath, care being taken to keep the mass well stirred.

After a time the precipitate is allowed to settle, and some of the clear liquid taken up by means of a pipette and added to a warm solution of barium bromate; if no precipitate is obtained the liquid is filtered off. Sometimes, however, a precipitate is formed which consists of barium bromate, and therefore it is best to dilute with water and boil. If the precipitate persists either more stirring or more barium bromate is required.

When the double decomposition is complete a little bromine is often liberated, but there is not sufficient to cause any inconvenience in the laboratory. This is evidently due to the fact that a small amount of bromic acid is formed by the action of a trace of free sulphuric acid accompanying the rare earth sulphates. The latter should therefore be well ignited.

The filtered liquid is evaporated until a drop removed on the end of a glass rod just solidifies when stirred on a watch-glass. Under these conditions just about half of the substance in solution crystallises out on cooling. After a little experience there is absolutely no difficulty in judging the most convenient concentration. If the fractionation is carried out in porcelain dishes a little water should be sprayed on the surface so as to prevent the top from solidifying to a crystalline mass.

Casseroles are by far the best utensils to use for this work, especially if small amounts of substances are being separated, as they can be covered by large watch-glasses. This prevents rapid crystallisation and the tendency of the material to creep up the sides of the vessel. Also there is no need to spray any water on the surface after evaporating or dissolving. Very often, but usually when working with small quantities, the liquid refuses to crystallise, or else the crystals separate out as a fine feathery mass, so that it is quite impossible to pour off the mother-liquor. If it does not crystallise the best procedure is to add a trace of the solid, when the whole immediately solidifies, forming the feathery type of crystal as mentioned above. The

mass is then carefully heated so as to dissolve all but a very little, which will start the crystallisation as the liquid cools. An even better plan is to commence the operation by the addition of a crystal while the liquid is still quite hot.

When working on the large scale very fine hexagonal prisms are often obtained, some being more than two inches in length and over a quarter of an inch in thickness.

Even after six series of crystallisations a considerable change is easily apparent, although this is shown more by the spectroscope than by the colour. The most soluble fraction is very pink, and it gives an intense erbium spectrum. The thulium red is also very strong, and the band in the blue has made its appearance, while the bands of holmium and dysprosium have nearly disappeared. The least soluble fraction is still pinkish, and gives intense dysprosium and holmium bands and a weak erbium spectrum. The colour of the oxide of this fraction is orange, showing that terbium accumulates at this end. After the process has been continued until some twenty fractions have been obtained, the least soluble portion forms brilliant colourless crystals which dissolve in water with a tinge of greenish yellow colour seen only in concentrated solution. The absorption spectrum of this fraction shows very faint samarium and holmium bands, while those of dysprosium are much stronger. Practically the whole of this fraction consists of an earth giving a colourless salt, yttrium. And as the oxide is of a brown ochre colour it shows that terbium collects in the least soluble portion. As one goes down the series the fractions become yellower, and the oxides paler. In the fractions that show the strongest yellow, the dysprosium and holmium bands are very intense, and the oxide becomes yellowish. Farther along the series the lines of erbium make their appearance, and even while the erbium absorption is still weak the liquid assumes a pink colour. This increases until it reaches a rosy pink, at which point the spectroscope shows only erbium bands, and the oxide is of a pure rose tint. Further on still the thulium band in the red shows itself, while the solutions become paler and give a very strong thulium spectrum, the erbium bands becoming decidedly weaker. The most soluble fraction is reached when the solution is nearly colourless; the erbium spectrum is faint, while that of thulium, although fainter, is still intense. The oxide of this last fraction is white and dense, and consists largely of ytterbium.

The above series shows that the rare earth bromates arrange themselves in the following order of solubility:—Samarium (europium ?, gadolinium ?), terbium, yttrium, dysprosium, holmium, erbium, thulium, and ytterbium, which is similar to the solubilities of the oxalates in ammonium oxalate, but different from the ethylsulphates; since, according to Urbain, yttrium, erbium, and ytterbium ethylsulphates are found in the most soluble portion.

A fair conclusion can be drawn that the use of the ethylsulphate method would prove valuable in conjunction with the bromate, especially for the separation of yttrium from dysprosium and holmium, and perhaps for the separation of thulium from ytterbium.

Finally, the author would like to point out some of the rapid separations obtained by this method, the most remarkable being the separation of thulium from erbium. And since ytterbium is still more soluble than thulium its removal is even easier. For example, erbium material, supposed to be quite free from thulium, was converted into the bromate and crystallised four times, when the most soluble portion gave the thulium spectrum.

Dysprosium and holmium also separate from erbium with comparative ease, and as yttrium places itself between terbium and dysprosium the latter element can be obtained terbium free. The division between dysprosium and holmium is not so marked.

The absorption spectra and the colours of the various fractions show curious changes which are not altogether understood, and may be simply due to the comparatively small amount of material under examination.

More material (15 kilos.) is at present being fractionated, and in the near future the less basic portion of earths derived from about 100 kilos. of euxenite and 100 kilos. of yttrotitanite, &c., will also be included. The bromate method will be further investigated and also applied to the cerium group, and the results published at an early date.

New Hampshire College, Durham, N.H.,
November 18, 1907.

EXPERIMENTS ON

THE DECOMPOSITION OF PLATINUM BY AN ALTERNATING CURRENT.

By TH. GROSS.

Potassium carbonate was fused and brought to a yellow-red heat in a platinum crucible, and an alternating current of 50 periods per sec., 120 volts, and 1 ampère was passed for several hours through the molten mass by means of electrodes of strong platinum wire, and at the same time small quantities of potassium nitrate were added. The electrodes and the crucible were gradually consumed, and after some time a deposit of small crystalline needles, resembling graphite in colour, was formed at the electrodes. When the current was interrupted a substance which was insoluble in water was found in the melt, and from it, by washing and drying, a brown powder could be separated. If the loss of weight of the crucible and electrodes amounted to, say, 14 grms., the weight of the powder was 6 grms. It was practically free from potassium and carbon. When it was ignited in hydrogen in a magnesium crucible no platinum could be separated from it. When an unglazed porcelain crucible was used it was decomposed into a metallic substance, crystallising in small needles and resembling platinum, and into another substance which fused to a black glaze with the material of the crucible. Before being heated it was soluble in hot hydrochloric acid, but after ignition it was soluble only in aqua regia. With sulphuretted hydrogen the solution gave a precipitate which, when freshly prepared, dissolved almost entirely in hot yellow ammonium sulphide. By evaporating the filtrate from the sulphuretted hydrogen precipitate a new substance was obtained; this was a light red powder, soluble in hydrochloric acid and precipitated from the solution by excess of caustic potash; it lost weight and became insoluble when ignited, and then could be decomposed by alkalis. It was quite free from platinum. The aqua regia solution of the crystalline needles obtained by electrolysis resembled the brown substance in its behaviour towards sulphuretted hydrogen and ammonium sulphide.

These facts cannot be explained on the supposition that platinum remains undecomposed during the experiment. If the behaviour towards ammonium sulphide of the precipitate obtained by sulphuretted hydrogen were to be explained by assuming the existence of a new modification of platinum, which in the author's opinion is an unjustifiable extension of the conception of a "modification," even then the existence of two new substances with the properties of the brown and red powders would be quite inexplicable. The author therefore assumes that platinum can be decomposed chemically by an alternating current, the following process taking place:—During the electrolysis part of a substance is removed from the platinum, oxidised by the fused alkali, and dissolved. From this oxide the hydrate, a red powder, is formed. The remaining substance, which resembles platinum in appearance, but differs from it in its behaviour towards sulphuretted hydrogen and ammonium sulphide and in other reactions, partly crystallises and is partly oxidised, giving the brown substance. Quantitative experiments were performed to test this assumption. The loss of weight of the crucible and electrodes was determined, and the precipitates obtained by sulphuretted hydrogen from all the products of electrolysis were weighed after being heated in hydrogen.

It was then found that their weight was about 15 per cent less than the loss of weight of crucible and electrodes. It must be noted that platinum with normal properties could not be detected in the substances which had taken part in the electrolysis, but only a substance resembling platinum. It must now be determined how much platinum volatilises during the electrolysis. These observations were confirmed by experiments in which the conducting liquid was fused caustic potash, or a mixture of nitric and sulphuric acids. —*Chemiker Zeitung*, 1907, xxxi., 975.

ON THE OXIDATION OF HYDRAZINE.*

By A. W. BROWNE and F. F. SHETTERLY.

(Concluded from p. 56).

On the Use of Ammonium Metavanadate in the Determination of Hydrazine. — Hofmann and Küspert have recommended the use of ammonium metavanadate in the determination of hydrazine (*Ber.*, 1897, xxxi., 64—67). The procedure followed by these investigators consisted in the slow addition of an excess of ammonium metavanadate solution strongly acidified with sulphuric acid to the hydrazine sulphate lotion. When the evolution of nitrogen (which lasts for about twenty minutes) had ceased, the solution was warmed for several minutes to about 60°. The amount of metavanadate that had been reduced was then determined by titration with permanganate solution. In addition to this volumetric method Hofmann and Küspert also suggested the simultaneous measurement of the nitrogen evolved from the mixture. In effecting this operation the reaction was conducted in a current of carbon dioxide by means of which the evolved nitrogen was carried into the measuring apparatus.

In 1899 Rimini, after reviewing several different methods for the determination of hydrazine, made the statement that the above method was undoubtedly the best of those considered (*Gazz. Chim. Ital.*, 1899, (1), xxix., 265).

The reaction was considered by Hofmann and Küspert to proceed in accordance with the following equation:— $N_2H_4.H_2SO_4 + 2O = N_2 + 2H_2O + H_2SO_4$.

In Experiments 1 to 6 (Tables I. and II.) the authors of the present article have used hydrazine sulphate, ammonium metavanadate, and sulphuric acid in the proportions employed in the experiments of Hofmann and Küspert. In each case appreciable amounts of hydronitric acid were obtained. In Experiment 3 the conditions recommended by Hofmann and Küspert have been exactly duplicated; the reacting mixture was allowed to stand at room temperature until the effervescence had ceased, when it was heated to 60° for a few minutes. Even under these conditions, unfavourable as they were to the quantitative removal and absorption of the hydronitric acid formed, a yield of nearly 3 per cent was obtained. In Experiment 2 the conditions were the same as in Experiment 3, except that the hydrazine sulphate solution was more dilute. No very appreciable variation in the yield of acid, however, was observed. In Experiments 4 and 5 the yields of hydronitric acid were considerably higher. In Experiment 6 the method of adding the metavanadate solution was modified and the most favourable temperature conditions were chosen. In this case 12·52 per cent of hydronitric acid were produced.

For the sake of simplicity the percentage yields of hydronitric acid and ammonia have both been calculated on the basis of the equation $2N_2H_4 + 2O = HN_3 + NH_3 + 2H_2O$. From the fact, however, that the yields of ammonia under the most favourable conditions were found to be higher than the yields of hydronitric acid, it is apparent that the secondary reaction does not proceed quantitatively in accordance with this equation.

The magnitude of the error introduced as a result of the secondary reaction indicated by the above equation obviously depends upon the character of the analytical method chosen. If the oxidimetric method is employed, the percentage error will be numerically smaller than the percentage yield of hydronitric acid, while if the gasometric method is employed the percentage loss of nitrogen due to the formation of hydronitric acid should be numerically equal to the percentage yield of the acid.

In the four experiments performed by Hofmann and Küspert it was found that one molecule of hydrazine sulphate required 1·996, 1·964, 1·959, and 1·939 atoms of oxygen (theory, 2 atoms). The mean deficit in consumed oxygen (0·0355 atom oxygen per molecule of hydrazine sulphate, or 1·78 per cent deficit in oxygen), corresponds to a yield of 3·55 per cent of hydronitric acid, provided that the absence of possible errors arising from other sources be assumed.

In order to ascertain experimentally the ratio existing between the errors to which the two methods are respectively subject, a series of determinations has been made of the volume of nitrogen liberated and of the amount of oxygen consumed by the oxidation of a measured amount of hydrazine sulphate. In these experiments a Lunge nitrometer was employed, but the ordinary gas evolution bottle was replaced by a 125 cc. Erlenmeyer flask provided with a small test-tube placed in a slanting position. This flask was immersed in a beaker filled with water for the purpose of avoiding errors due to changes in temperature. The hydrazine sulphate and ammonium metavanadate solutions were identical in composition with those employed by Hofmann and Küspert, and the amount of each solution used was also the same as that employed by these investigators (*i.e.*, 10 cc. of hydrazine sulphate solution containing 15 grms. per litre, and 50 cc. of ammonium metavanadate solution containing 12·85 grms. of the salt and 128 cc. of concentrated sulphuric acid per litre were used). After the flask had been brought to room temperature by immersing it in the beaker of water for some time, the two solutions were mixed in the flask, and with frequent shaking were allowed to remain at room temperature until the greater part of the gas had been evolved. The temperature was then raised to 60° for a few minutes, in order to effect the complete evolution of the gas. After the apparatus had been again brought to room temperature, the volume of gas was carefully measured. Since water was used as the confining liquid, corrections for the tension of aqueous vapour were introduced. The amount of oxygen consumed was in each case determined by titration of the residual solution (after diluting to 250 cc.) with a solution of potassium permanganate containing 7·0274 grms. of the salt per litre. Owing to the difficulty in observing the exact end-point of the reaction, a slight excess of permanganate was in each case unavoidably introduced, for which no correction could be satisfactorily made. For this reason the error inherent in the oxidimetric method is to some extent reduced by the compensating error due to the presence of a slight excess of permanganate. The results obtained are given in Table VI.

From the above experiments it is apparent that when the reaction between hydrazine sulphate and ammonium metavanadate in sulphuric acid solution takes place in a Lunge nitrometer, the error due to the formation of hydronitric acid averages about 4·5 per cent in case the gasometric method is employed, or about 1 per cent when the oxidimetric method is used.

Summary.—When hydrazine sulphate and ammonium metavanadate are brought together under favourable conditions in the presence of sulphuric acid, a secondary reaction takes place (to an extent depending on the conditions chosen) which results in the formation of hydronitric acid and ammonia. Under the most favourable conditions studied by the authors the yield of hydronitric acid, as calculated from the equation $2N_2H_4 + 2O = HN_3 + NH_3 + 2H_2O$, amounted to 13·55 per cent of the theory. The highest yield of ammonia

* From the *Journal of the American Chemical Society*, xxix., No. 9.

TABLE VI.

No. of experiment.	Nitrogen evolved (0° 760 mm.).	Deficit in nitrogen.	Permanganate solution.	Oxygen consumed.	Atoms of oxygen per molecule hydrazine.	Deficit in oxygen.
	Cc.	Per cent.	Cc.	Grm.		Per cent.
1.	24·65	4·57	20·4	0·03626	1·966	1·70
2.	24·17	6·43	20·45	0·03635	1·971	1·45
3.	24·61	4·72	20·5	0·03644	1·976	1·20
4.	24·86	3·76	20·7	0·03679	1·995	0·25
5.	24·78	4·07	20·6	0·03661	1·985	0·75
6.	25·02	3·14	20·65	0·03670	1·990	0·50
Average ..	—	4·45	—	—	—	0·975

amounted to 21·3 per cent on the basis of the same equation. The use of ammonium metavanadate in the determination of hydrazine, as recommended by Hofmann and Küspert, is theoretically subject to a percentage error numerically equivalent to the percentage yield of hydronitric acid when the nitrometric method is employed, and to a smaller error when the oxidimetric method is chosen. By the use of a Lunge nitrometer the error was found to be about 4·5 per cent for the nitrometric method and about 1 per cent for the oxidimetric method.

THE ATOMIC WEIGHT OF HYDROGEN.*

By WILLIAM A. NOYES.

(Continued from p. 58).

Purity of the Gases Used.

As with all atomic weight determinations, the value of the present investigation depends in very large measure upon the purity of the substances weighed—in this case, hydrogen, oxygen, and water. The impurities which might be present were :—In the hydrogen, nitrogen, oxygen, water, phosphorus pentoxide, and compounds of sulphur ; in the oxygen, there might be the same impurities with hydrogen in place of oxygen ; in the water, sulphur dioxide or carbon dioxide.

Nitrogen.—In the former series of determinations there was obtained at the end of each experiment a small amount of gas which, when calculated as nitrogen, corresponded to about one one-thousandth of the weight of hydrogen used. It was found quite early in the present investigation that when the water is removed from the apparatus containing reduced copper it carries with it a small quantity of hydrogen, probably hydrogen which has been occluded by the copper. The gases were analysed in a narrow eudiometer of such length that when the amount of gas was small, the column of mercury in the eudiometer was 600 to 650 mm. in length, so that the gas was under a pressure of only about one-seventh of an atmosphere. In this way quantities of nitrogen as small as 0·02 mgrm. could be measured.

As will be seen below, it was possible to secure copper oxide so pure that only very small amounts of nitrogen were found at the close of experiments in which it was used. But the best evidence of the freedom of the hydrogen from nitrogen was obtained in the last series. From 22·6 grms. of hydrogen and the equivalent amount of oxygen there was obtained only 0·59 mgrm. of nitrogen. This includes all of the nitrogen in the oxygen as well, and all of the leakage of the stopcock during seven weeks. If we assume that two-thirds of this nitrogen came from the hydrogen, it is only 1 part in 57,000 by weight, or 1 part in 800,000 by volume. On the basis of this evidence it is assumed that all of the hydrogen used was free from nitrogen, and no correction has been made for the small quantities found in each experiment. It is not believed that the error from this source can be so great as 1 part in 20,000.

Incidentally, these experiments have demonstrated the possibility of using, without leakage, ordinary well-ground and carefully lubricated stopcocks under such conditions that they are subjected to atmospheric pressure with a vacuum inside of the apparatus for days together. The well known rubber lubricant was used. It was made by heating a mixture of 16 parts of vaseline, 8 parts of pure rubber, and 1 part of paraffin to a temperature of 350—400° for several hours until it was thoroughly homogeneous. For warm weather, or for a stopcock liable to become warm, a little more paraffin was added.

Oxygen.—After the investigation had progressed so far that it was evident that the results differed from Morley's by a much larger amount than can be accounted for by accidental errors, it was feared that the hydrogen contained a trace of oxygen which escaped conversion into water as the gas passed over the platinised asbestos and copper gauze, especially as the latter were heated to only about 350°. To test this possibility the purified and dried hydrogen was passed through a hard glass tube containing platinised asbestos heated to dull redness, and then through a phosphorus pentoxide tube, The latter was closed with stopcocks, and was weighed each time filled with hydrogen and with the use of a counterpoise. The earlier experiments gave appreciable amounts of water (1 mgrm. from 1 grm. of hydrogen), which was in part, at least, from the asbestos, and even after the asbestos had been heated almost daily for six weeks some water was still obtained (1·1 mgrm. from 2·74 grms. of hydrogen).

(It seems possible that this water may have passed through the walls of the red-hot tube during the five hours of the experiment. It seems not improbable that glass, as a viscous liquid, may dissolve a small amount of water, and that such dissolved water might slowly diffuse through to the inner surface. This question is worthy of further study).

But when some of the same hydrogen was passed over strips of palladium heated to 360° in an electrical air-bath, 3·78 grms. of hydrogen gave a change of weight of −0·08 mgrm. It still seemed possible that a trace of oxygen mixed with *dry* hydrogen might pass the palladium without change. To test this a small T-tube was introduced between the hydrogen generator and the palladium tube in such a manner that the lower arm could be filled with dry oxygen. This would then find its way into the hydrogen by slow diffusion. The amount of oxygen retained in the arm of the T-tube was found in two experiments to be 1·68 and 1·94 mgrms. respectively, while in three experiments in which similar amounts of oxygen were allowed to diffuse into the hydrogen before it entered the palladium tube, there were found 2·29, 2·21, and 2·58 mgrms. of water. While the conditions were such that an exact quantitative agreement could not be expected, the experiments demonstrated that minute quantities of oxygen can be readily detected by this method.

After the close of the last series of experiments the hydrogen was tested by passing it through the tube containing strips of palladium heated to 360°, and then through the pentoxide tube. In these experiments there were passed 2·74, 2·92, and 2·92 grms. of hydrogen respectively, while the changes in weight of the phos-

* From the *Journal of the American Chemical Society*, xxix., No. 1

phorus pentoxide tubes were −0·44, +0·14, and +0·04 mgrms., quantities scarcely beyond the errors of weighing and insignificant in proportion to the weight of the hydrogen.

Water.—The experiments just described demonstrate the absence of water in the hydrogen used in the last series. After the close of the third series, hydrogen from the apparatus was passed through the phosphorus pentoxide tube at the rate of 6 litres an hour for five successive days, 12·6 grms. of hydrogen in all. The changes in weight of the pentoxide tube were −0·01, +0·63, −1·06, −0·33, −0·14 mgrms.; in all a net loss of 0·76 mgrm., or 1 part in 17,000. At the close of the fourth series 3·78 grms. of hydrogen were passed through the pentoxide tube at the rate of 6 litres an hour with a change in weight of −0·04 mgrm., and a similar amount passed through the tubes containing heated palladium gave a change of weight of −0·08 mgrm.

It seems, therefore, that the phosphorus pentoxide used to dry the hydrogen retained its efficiency to the end. The first of these tubes showed considerable deliquescence, caused by the water still remaining in the hydrogen after it passed the sticks of caustic potash, but the last tube showed no sign that it was affected by the moisture.

Phosphorus Pentoxide.—Morley has shown that 1 litre of a gas at ordinary temperatures carries with it only 0·00002 mgrm. of vapour of phosphorus pentoxide (*Journ. Am. Chem. Soc.*, xxvi., 1171). This would correspond to 0·0002 mgrm. in 1 grm. of hydrogen, an amount without any significance in comparison with the degree of accuracy now possible in determinations of atomic weights. It is believed that the crystalline phosphorus pentoxide obtained by sublimation, adhering as it did closely to the walls or the tube and fibres of glass-wool, on which it was deposited, was much less likely to be carried on mechanically by the current of gas than the finely pulverulent pentoxide in its usual form would have been.

Compounds of Sulphur.—After the close of the third series a careful test for compounds of sulphur was made by bringing together the hydrogen and oxygen, delivered by the apparatus, in such a manner that they could be burned and the water collected. The hydrogen was evolved at the rate of 6 litres an hour, the most rapid rate used in the atomic determinations. The water obtained weighed 112·4 grms. A little bromine water and 0·1 grm. of sodium carbonate were added to it, and it was evaporated to dryness in a platinum dish on an electric plate. The residue was acidified with hydrochloric acid, filtered from silica which came from the glass apparatus in which the gases were burned, and the filtrate was tested with a solution of barium chloride. A trifling turbidity appeared slowly, estimated to be less than that occasioned by 0·1 mgrm. of sulphuric acid in a solution of similar volume and character. This would correspond to 1 part of sulphur dioxide, by weight, in 250,000 parts of the hydrogen.

Purity of the Oxygen.—The experiment just described demonstrates the practical absence of sulphur in the oxygen. Tests for moisture also showed that no amount which could be of significance was present.

Purity of the Water.—In the two experiments referred to above in which copper oxide prepared by the precipitation of copper sulphate with sodium hydroxide was used, some sulphur dioxide was found. When pure copper oxide was used no evidence of its presence was ever obtained. In all experiments in which the sulphuric acid electrolyte was used the water was tested with a dilute solution of potassium permanganate (1 cc. = 0·05 mgrm. available O) and with N/10 barium or sodium hydroxide, with phenolphthalein as an indicator. The amounts required never exceeded 0·1 cc. of the permanganate and 0·03 cc. of the N/10 alkali, to produce a colouration in from 20 to 40 cc. of the water. The water of the last two series, especially, was frequently tested for hydrogen peroxide, but none was found.

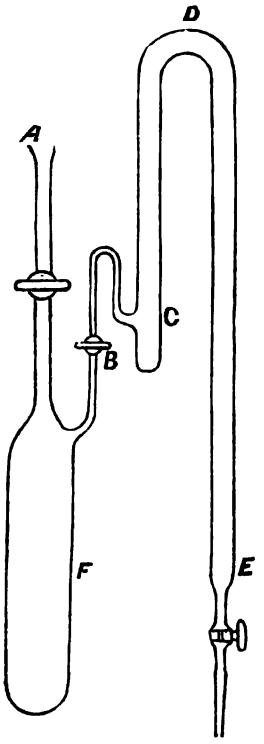


FIG. 2.

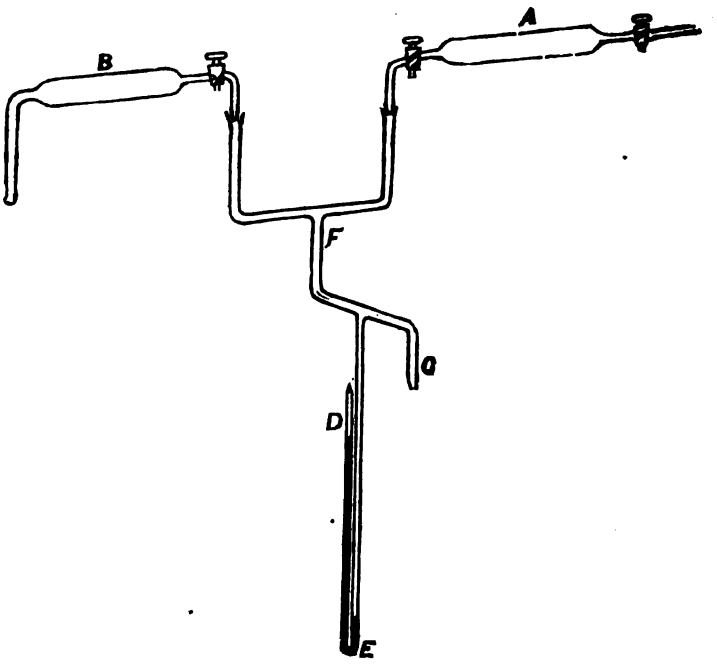


FIG. 3.

First Series.

This series consisted of twenty experiments. In the earlier experiments the weight of the hydrogen was determined by the gain in weight of a piece of apparatus containing copper oxide, the water formed by the oxidation of hydrogen being condensed within the same apparatus. The method used will be clear from Fig. 1. About 160 grms. of copper oxide were placed in the part of the apparatus represented as lying in the electrical air-bath. After sealing the apparatus at the end designed to collect the water, its volume was determined by hydrostatic weighing, and a tube of almost the same volume and weight was prepared. The apparatus was then placed in the air-bath, and heated to 400°, while it was connected with a Sprengel air-pump and exhausted. A phosphorus pentoxide tube, sealed to the pump, was interposed between the pump and the apparatus, and also a small McLeod gauge. The exhaustion was carried to the hundred thousandth of an atmosphere or further, and the heating continued for some time.

(The bulb of the gauge had a capacity of about 16·5 cc. To avoid contaminating the mercury by contact with india-rubber, the gauge was sealed below to an upright glass tube about 12 mm. in diameter. In this was a light, loosely fitting glass plunger. By pressing the plunger down the mercury could be easily forced up into the gauge for the measurement).

For connection with the pump and for other similar connections used throughout the work, the end of the apparatus was drawn out to fit a glass socket connected with the pump. The joint was completed by melting a little Khotinsky cement between the parts in contact. Such a joint, if properly made, will hold for an indefinite length of time against atmospheric pressure, without any leakage that can be measured. The parts are easily separated by gentle warming, and cleaned by warming and wiping with cotton, followed by a cloth moistened with alcohol.

After cooling, the apparatus was rinsed with distilled water, wiped with a clean cloth, and placed on the balance. The tare and weights were placed on the other pan, the current of dry air started through the balance case, and the weighing completed, with the use of the rider, on the following day.

The apparatus was then connected with the source of hydrogen, the copper oxide heated to 300—350°, and hydrogen passed in for four to six hours. A coil of small tin pipe conveying cold water was placed around the part of the apparatus outside of the air-bath to condense the water. By means of the rheostat connected with the electrolytic apparatus it was easy to regulate the supply of hydrogen to correspond with the rate at which it was oxidised by the copper oxide. The operation was always stopped before the copper oxide was all reduced, and by heating for a short time after closing the stopcock, the conversion of the last of the hydrogen to water was completed.

After cooling and standing over night, as before, the weight of the hydrogen, which had been introduced, was determined. The apparatus was then connected at A with the apparatus shown in Fig. 2, the other end, E, of the apparatus being connected with the Sprengel pump. This apparatus was filled with phosphorus pentoxide from C to E. The end at C is designed to collect the phosphoric acid resulting from the deliquescence of the pentoxide, while it is quite necessary that the part C D should be directed up and not down, as otherwise the syrupy phosphoric acid runs down into the unchanged phosphorus pentoxide and seals the tube. The apparatus was, of course, previously exhausted and weighed, using a glass counterpoise of nearly the same volume and weight.

After exhausting the connecting tubes by means of the pump, the bulb F was placed in a freezing mixture of ice and sulphuric acid, the stopcock B was closed, and the stopcock of the copper oxide apparatus opened. By passing hot water through the coil of tin pipe surrounding the part of the apparatus containing the water, the latter was easily distilled into F in the course of two to four hours. By opening B occasionally any permanent gas brought over with the water vapour was allowed to pass on to the pump, and transferred by means of the latter to the eudiometer in which the gas was analysed. When permanent gases were allowed to accumulate in F the passage of the water vapour was checked, and condensation occurred in the connecting tubes. This difficulty occurred especially in the last two series, when considerable hydrogen was present, but was rarely experienced in the first three series. After the water had been transferred to F and the bulb containing the copper had been heated to 400° for a short time, the apparatus containing the water was removed and replaced by a tube containing phosphorus pentoxide, and the heating of the apparatus continued for some time longer. Only a few mgrms. of water were obtained in this manner. The apparatus containing the reduced copper was then cooled and weighed next morning, the loss of weight as compared with the original weight giving the weight of the main portion of the oxygen.

The reduced copper still retains, however, at 400°, either water or hydrogen which cannot be removed by the process described. To obtain this the apparatus was again placed in the electrical air-bath, heated to 400°, and the copper oxidised as far as possible by means of oxygen from the electrical apparatus. The water formed was then removed by connection with a phosphorus pentoxide tube, and heating as before. After cooling and weighing, the apparatus was now ready for a second experiment.

In seven determinations of this series the hydrogen was absorbed in palladium, and its weight was determined twice, first by the loss in weight of the palladium tube, and second by the gain in weight of the copper oxide tube. The palladium tube was given the form shown at A in Fig. 3. The palladium foil was furnished by Heraeus. It was 0·05 mm. in thickness. 360 grms. of it were cut into strips 4 cm. wide, and these were wound in three rolls which were placed in the tube A. Before use the rolls were placed in a hard glass tube, and heated to redness in a current of oxygen. After placing it in A it was heated for some time in a current of hydrogen till thoroughly dry. It was then cooled and charged with hydrogen, and when saturated a current of hydrogen was passed through the tube for a short time. The tube was weighed with a counterpoise, and after standing over night, in the same manner as described for the copper oxide tube.

The arrangement employed for the transfer of the hydrogen to the copper oxide tube is shown in Fig. 3. For greater simplicity the air-baths in which A and B were placed and supported are not shown. The tube C was connected with the Sprengel pump. After exhaustion of the connecting tubes the connection with the pump was cut off by means of a stopcock situated close to the connection with C. The palladium tube was then slowly heated while the copper oxide tube was heated to 350°. The pressure in the system could be easily followed by means of the shortened manometer D E. This contained a small amount of air at D, but not enough to carry the mercury beyond the bend at E when the pressure in F fell to zero. The heating of A was so regulated that the pressure was usually a little below that of the atmosphere, the reaction in B proceeding most rapidly under slightly reduced pressure. The 360 grms. of palladium absorbed 2·3 grms. of hydrogen, and of this 2 grms. could be easily expelled at 150—160°. This amount could be transferred from A to B in three to five hours. The rate of transfer could be followed by the amount of water condensed in B. When enough water had collected, the stopcock of the copper oxide tube was closed, and the palladium was allowed to cool till most of the hydrogen in the connecting tubes had been re-absorbed. The stopcock of the palladium tube was then closed, and the hydrogen in the connecting tubes pumped out into a eudiometer and measured. This

hydrogen varied from 0·02 to 0·14 mgrms. according to the time allowed for the palladium to cool.

The twenty experiments of the first series gave for the atomic weight of hydrogen as calculated from the weight of the hydrogen and the weight of the oxygen, 1·00819 ± 0·00010, and from the weight of the hydrogen and water, 1·00821 ± 0·00010. This is a smaller probable error than has been obtained by any previous observer except Keiser and Morley, but it was found at the close of the series that it is subject to a constant error which is, apparently, about three times the "probable error."

It was known at the beginning of the investigation that copper oxide at 400° would retain a small amount of water. It was hoped, however, that this might be made very small, and also that by making the end of one experiment the beginning of the next the total amount of water retained would be so nearly constant that it would not affect, appreciably, the result of any experiment in the series after the first. At the close of the last experiment of this series it was thought wise to test this point by transferring the copper oxide to a hard glass tube, and heating it in a current of oxygen. To my surprise there was obtained 37·7 mgrms. of water, although the previous oxidation and heating at 400° had given only 3·3 mgrms. If we assume this water to have come from the last six experiments of the series, which formed a continuous set in which the end of one experiment was the beginning of the next, the value for the six determinations becomes 1·00782 as calculated from the hydrogen and oxygen, or 1·00791 as calculated from the hydrogen and water. It was at once decided to reject the determinations thus far made, and which had taken about a year's time, and to begin a new series in which this source of error should be eliminated, if possible.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 16th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

MESSRS. F. Buckney, J. E. L. Moore, W. H. Nuttall, and D. Willott were formally admitted Fellows of the Society.

The PRESIDENT announced that the Council had recommended the following gentlemen as Honorary and Foreign Members to be balloted for at the next meeting of the Society:—Messrs. J. A. Le Bel, H. L. Le Chatelier, A. E. J. Gautier, A. Haller, J. W. Hittorf, T. W. Richards, and O. Wallach.

Certificates were read for the first time in favour of Messrs. Robert Barton, jun., 48, Wellclose Mount, Leeds; Harry James Brown, Pembrey Lead Works, Burry Port; Hans Thacher Clarke, Gayton Corner, Harrow; Arnold Merrick, 66, Rothbury Terrace, Newcastle-on-Tyne; Arthur Stead, B.Sc., 113a, Kellner Street, Bloemfontein, O.R.C.; Thomas Marshall Tyson, 2, Osborne Road, Forest Gate, E.; David Thomas Williams, 9, Calvert Terrace, Swansea; Francis Charles Benjamin Wood, Deurne, nr. Antwerp, Belgium.

A certificate was authorised by the Council under By-law I. (3) in favour of Joseph Valentine Francies, Engineering College, Sibpur, Calcutta.

The Council has ordered the following letter and report to be printed in the *Journal* and *Proceedings* of the Society:—

Government Laboratory,
Clement's Inn Passage, Strand, London, W.C.
November 13th, 1907,

GENTLEMEN,—I have the honour to forward you, for presentation to the Council of the Chemical Society, the Report of the International Committee on Atomic Weights, 1908, to which I have appended, as desired by them, the names of Professors Ostwald and Urbain.

It will be seen that since our last Report a number of important re-determinations of atomic weights have been published, and the existing table in consequence reveals a number of small inconsistencies due to the original data from which the values are derived. We think it is inopportune at present to attempt to re-calculate these values as the work known to be in progress on certain fundamental constants, to which reference was made in our last Report, has not yet been published. We have good reason to believe, however, that it will soon make its appearance, and we hope to be able to present an amended table with our Report for next year.—I am, Gentlemen, your obedient Servant, T. E. THORPE.

(The Report was inserted in the CHEMICAL NEWS, January 24th, p. 43).

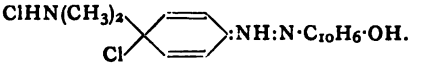
Of the following papers, those marked * were read:—

*1. "*Colour and Constitution of Azo-compounds.* Part II. *The Salts of* p-*Hydroxyazo-compounds with Mineral Acids.*" By JOHN JACOB FOX and JOHN THEODORE HEWITT.

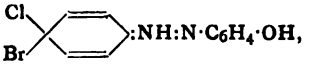
In several communications of one of the present authors, the view has been advanced that, whilst *p*-hydroxyazobenzene has a constitution which is correctly expressed by its name, the salts which it forms with mineral acids are derived from the tautomeric quinonehydrazone. W. B. Tuck (*Trans.*, 1907, xci., 449), from a consideration of the absorption spectra of benzeneazophenol and its ethyl ether in alcoholic and concentrated hydrochloric acid solutions, concludes that the hydrochlorides of both compounds "have similar structures, and consequently the hydrochlorides of the free hydroxyl substances have an azo-structure."

From an examination of benzeneazo-*α*-naphthol and its ethyl ether, the present authors agree with Tuck's statement as to similarity of structure, but deny that this structure is of azo-type, as the reactions of hydroxyazo-compounds in concentrated acid solution negative this view.

F. Baker's attempt (*Trans.*, 1907, xci., 1490) to formulate these compounds as carbonium salts is unsatisfactory; it requires quinquivalent nitrogen in a hitherto unobserved form, whilst the dihydrochloride of dimethylaminobenzeneazo-*α*-naphthol (prepared by the authors) would have to be written—



The most conclusive evidence is given by the fact that the hydrochloride of *p*-bromobenzeneazophenol and the hydrobromide of *p*-chlorobenzeneazophenol, which, according to Baker, should both have the constitution—



are actually different substances, yielding the components from which they are respectively derived when decomposed by alkali.

The present authors suggest, instead of the formulæ hitherto proposed, the constitution of oxonium salts for these compounds; for example,—

$$C_6H_5\cdot NH\cdot N:C_6H_4:O(H \text{ or } C_2H_5)Cl.$$

The formulation of the salts of the ethers and parent substances is thus the same, whilst the reactions in concentrated sulphuric acid solution are easily explained.

DISCUSSION.

Mr. TUCK said that the absorption spectra of the hydrochlorides of the free *p*-hydroxyazo-compounds and their ethers were the same, and this fact showed that their constitutions therefore were identical. If this was so, then

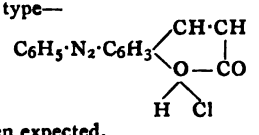
Dr. Hewitt's conclusion (*Ber.*, 1897, xxx., 1625), that hydrochloric acid converted the *p*-hydroxyazo-compounds into quinonehydrazones, must be incorrect. This was now accepted by Dr. Hewitt.

As the absorption spectra of these hydrochlorides agreed with that of azobenzene hydrochloride, one must conclude that the acid was combined in precisely the same manner in each case; that is, the hydrochlorides were true azo-derivatives.

The objection to Dr. Hewitt's formula for the hydrochlorides lay in the fact that it was impossible to assign the same structure to azo-benzene hydrochloride as he did to hydroxyazo-hydrochlorides.

Mr. BALY pointed out that Dr. Hewitt's explanation seemed to fail in two respects. In the first place, it could not account for the formation of the deeply coloured hydrochloride of azobenzene where, of course, the oxonium structure was excluded. Moreover, the change of colour on adding hydrochloric acid to a neutral solution of azobenzene was precisely of the same character as Dr. Hewitt had shown in the case of the hydroxyazo-compounds. In the second place, the addition of the acid molecule to the oxygen atom with the formation of the oxonium salt would undoubtedly decrease the colour of the compound in the sense that the absorption band would shift towards the *blue*. In the hydrochlorides of the hydroxyazo-compounds, the absorption band had shifted towards the *red*, causing the salt to be bluer than the parent substance. This decrease in colour would be caused by the decrease in the residual affinity of the system, due to the oxygen becoming quadrivalent.

Mr. H. V. MITCHELL drew attention to the fact that he had been unable to prepare a hydrochloride of benzeneazocoumarin (*Trans.*, 1905, lxxxvii., 1231), whereas if the view put forward by the authors were correct, a hydrochloride of the type—



might have been expected.

Dr. HEWITT, in reply, pointed out that Mr. Tuck stated definitely in his paper, "the hydrochlorides of the free hydroxyl substances have an azo-structure," whilst Mr. Baly's arguments derived from the properties of benzeneazo-*p*-cresol and its derivatives depended for their validity on this substance being a quinonehydrazone. Since this point was still disputed and the bulk of the evidence seemed to be in favour of a hydroxylic structure for the free *o*-azo-compounds, the arguments lost in weight.

No surprise need be occasioned by Mr. Mitchell's inability to obtain a hydrochloride from benzeneazocoumarin, for the lactonic oxygen atom would scarcely have pronounced basic properties, whilst Professor Armstrong's arguments against the formula depended on supposed basicity of the benzene nucleus and non-existence of oxonium salts. Basicity of the benzene nucleus scarcely accorded with the feeble acidity of phenol and the diminishing basicity observed in amines by introduction of benzene nuclei, whilst the possibility of oxonium salt formation was recognised by all who had made a comparative study of the xanthhydrol and acridinium groups.

*2. "*A New Method of Determining Vapour Densities.*" (Part I.). By PHILIP BLACKMAN.

*3. "*Studies in the Camphane Series.* Part XXV. *Action of Diazomethane on the Two Modifications of* iso-*Nitrosocamphor.*" By MARTIN ONSLOW FORSTER and HENRY HOLMES.

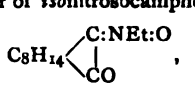
When diazomethane acts on the stable *iso*nitrosocamphor (m. p. 152°) dissolved in ether the N-methyl ether is produced, whilst the unstable modification (m. p. 114°), treated with a deficit from one molecular proportion of the agent, merely undergoes isomeric change to the less fusible variety; in view of this observation, some caution will be necessary in drawing conclusions regarding the structure of a compound based on its behaviour towards diazomethane. The benzaldoximes do not behave in the same way, benz*anti*-aldoxime (m. p. 35°) yielding the O-methyl ether, whilst the *syn*-aldoxime (m. p. 128°) remains unchanged.

By the action of *p*-nitrobenzyl chloride on an alcoholic solution of *iso*nitrosocamphor in presence of sodium ethoxide, three products arise. The *compound*, $C_{17}H_{20}O_4N_2$, having the composition of a nitrobenzyl ether of *iso*nitrosocamphor, crystallising in pale brown prisms, melting at 175°, and having $[\alpha]_D$ 123·0°; the *compound*, $C_{17}H_{18}O_3N_2$, forming lustrous, transparent, yellow plates, melting at 214°, with $[\alpha]_D$ −65·3°, and an *oil*, which is characterised by developing an intense blue coloration when caustic alkali is added to a solution in methyl, ethyl, or *iso*butyl alcohol. If silver oxide is substituted for sodium ethoxide as a condensing agent, and *p*-nitrobenzyl chloride is replaced by the bromide, an isomeric *compound*, $C_{17}H_{20}O_4N_2$, is produced, crystallising in colourless prisms, melting at 114°, and having $[\alpha]_D$ 138·0°.

On mixing an ethereal solution of iminocamphor with formaldehyde, no change occurs until a trace of acid is added, when the product, dissolved in alcohol, develops an intense magenta-red coloration with caustic alkali; ether precipitates from this solution an unstable solid, having the appearance of indigo, and yielding camphorquinone, formaldehyde, and ammonia with dilute sulphuric acid.

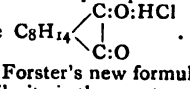
Camphorquinone is rapidly oxidised by an aqueous solution of hydrogen peroxide to camphoric anhydride.

The N-*ethyl* ether of *iso*nitrosocamphor,—



produced in association with the O-ethyl ether when ethyl iodide acts on *iso*nitrosocamphor in presence of sodium ethoxide, melts at 57°, and has $[\alpha]_D$ 248·1°; it is readily hydrolysed by acids, yielding camphorquinone and ethylhydroxylamine.

DISCUSSION.

Mr. BALY said that the formulæ for the two forms of *iso*nitrosocamphor which Dr. Forster referred to as being given by Baly, Marsden, and Stewart had resulted from the adverse criticism their paper received when it was read. When their paper was first written, they had inclined to the nitroso-formula, and it was therefore extremely interesting to find that Dr. Forster's experiments seemed to support this view. As regards the new formula which Dr. Forster had given to the N-ethers of *iso*nitrosocamphor, he (Mr. Baly) spoke strongly in favour of it from the point of view of the absorption spectra of these substances. They exhibited a very marked absorption band, exactly the same as that which might be described as the middle band of *p*-benzoquinone. The latter substance in aqueous solution exhibited three absorption bands, the middle one of which was absent from the spectrum of an alcoholic solution. It had occurred to him that the middle band might be explained by the formation of a hydrate of quinone, and so the absorption spectrum was examined of an alcoholic solution of *p*-benzoquinone to which a little alcoholic solution of hydrogen chloride had been added. The absorption spectrum then showed only the middle band, and was, indeed, the same as that of the N-ethyl ethers of *iso*-nitrosocamphor. Seeing that exactly the same was observed with camphorquinone, it did not seem unreasonable that the hydrogen chloride molecule combined by virtue of the quadrivalency of one of the oxygen atoms, and that in the case of camphorquinone a compound was formed of the type  . The analogy between this and Dr. Forster's new formula was sufficient to account for the similarity in the spectra of camphorquinone dissolved in alcohol containing some hydrogen chloride

and the N-alkyl ethers of *iso*nitrosocamphor. There was no doubt that the absorption spectra offered striking evidence against either of the varieties of *iso*nitrosocamphor having the formula $C_8H_{14}\begin{cases}C{:}NH{:}O\\ |\\ C{:}O\end{cases}$, for there was no resemblance between the spectra of the *iso*nitroso-compounds and the N-alkyl ethers.

Dr. HEWITT asked Mr. Baly if he had convinced himself that the colourless additive product of benzoquinone and hydrochloric acid was not really chloroquinol.

4. "*The Oxidation of Aromatic Hydrazines by Metallic Oxides, Permanganates, and Chromates.*" By FREDERICK DANIEL CHATTAWAY.

Primary aromatic hydrazines are readily attacked by most substances capable of giving up oxygen at all easily. The products are in the main the same as those which are formed by free oxygen.

The chief action, which results in the replacement of the hydrazino-group by hydrogen and the liberation of nitrogen, is generally accompanied by secondary ones which take place to a relatively very small extent. By these secondary actions, hydrocarbons of the diphenyl group or azo-derivatives are formed. Diazo-compounds are only obtained in presence of acids; in presence of alkalis, they are not formed.

Potassium chromate oxidises primary aromatic hydrazines very easily, and gives a theoretical yield of nitrogen and hydrocarbon. This reaction affords the most convenient method yet described for replacing an aromatic amino-group by hydrogen, the diazonium group yielded by it being first reduced to the hydrazino-group, and this then replaced by hydrogen through oxidation with potassium chromate.

All the evidence obtained shows that the explanation of the behaviour of primary aromatic hydrazines on oxidation recently put forward by the author is correct (*Trans.*, 1907, xci., 1324), namely, that an unstable hydroxyhydrazine is first produced, which, in presence of caustic alkali, immediately breaks down into hydrocarbon, nitrogen, and water:—

$$\begin{matrix}R{\cdot}N{\cdot}H\\ |\\ H{\cdot}N{\cdot}OH\end{matrix} \rightarrow \begin{matrix}R\\ |\\ H\end{matrix} + \begin{matrix}N\\ \|\\ N\end{matrix} + \begin{matrix}H\\ |\\ OH\end{matrix}.$$

Copper oxide easily gives up its oxygen to phenylhydrazine, and if the reduction is conducted under suitable conditions the metal can be deposited on glass in the form of a fine mirror. The film of metal thus laid down is as brilliant as a similar deposit of silver, and shows the beautiful red colour of polished copper.

5. "*Studies in Fermentation.* Part II. *The Mechanism of Alcoholic Fermentation.*" By ARTHUR SLATOR.

The velocity of the conversion of dextrose, lævulose, galactose, and mannose into alcohol and carbon dioxide by the action of living yeast has been measured in the manner already described (*Trans.*, 1906, lxxxix., 128). The main results are as follows:—

1. The rate of fermentation of dextrose, lævulose, galactose, and mannose is approximately independent of the concentration of the sugar between the concentrations 1 grm. to 10 grms. per 100 cc.

2. The fermentation of dextrose and lævulose under all conditions proceeds with approximately equal velocities.

3. The temperature-coefficient is almost the same in the case of the fermentation of dextrose, lævulose, and mannose, but is somewhat less in the case of the fermentation of galactose.

4. Many yeasts (very probably all yeasts) are unable to ferment galactose unless the yeast has been grown in the presence of this sugar.

5. The ratio of the rate of fermentation of dextrose to mannose varies greatly, depending on the treatment the yeast has undergone.

6. When two sugars are fermented simultaneously in the same solution, interference takes place between the reactions.

7. The velocity of fermentation by living yeast can be easily lessened by the addition of certain inhibiting agents, but cannot be appreciably raised.

8. In all probability the fermentation of sugars by preparation from yeast proceeds on the same lines as that by living yeast, but the reaction is much complicated by secondary changes.

The supposition that the reaction which has the main control of the velocity of fermentation is the decomposition of a stable compound between the enzyme and the sugar can be made to explain these results. Possibly three enzymes are present in yeast which will ferment the four sugars:—Glucozymase which ferments dextrose and lævulose, galactozymase which ferments galactose, and mannozymase which ferments mannose.

6. "*Organic Derivatives of Silicon.* Part IV. *The Sulphonation of Benzylethylpropylsilicyl Oxide and of Benzylethyldipropylsilicane.*" By HERBERT MARSDEN and FREDERIC STANLEY KIPPING.

Although the optically-active silicon compounds described recently (Kipping, *Trans.*, 1907, xci., 212) were actually prepared from the product of the sulphonation of benzylethylpropylsilicol, their investigation indicated that they were sulphonic derivatives of benzylethylpropylsilicyl oxide. As this view of their constitution seemed to need some confirmation, the authors have prepared benzylethylpropylsilicyl oxide itself and sulphonated it with sulphuric and with chlorosulphonic acid; in both cases there was formed an acid having the composition of a derivative of the oxide, and identical with the compound which has been resolved; any uncertainty regarding the composition of the optically-active compounds is thus removed.

The sulphonation of phenylbenzylethylpropylsilicane with chlorosulphonic acid gave results similar to those obtained with sulphuric acid; that is to say, the phenyl group was eliminated and the product was a sulphonic derivative of benzylethylpropylsilicyl oxide identical with that previously described.

Benzylethyldipropylsilicane, $BzEtPr_2Si$, has been prepared and converted into *benzylethyldipropylsilicanesulphonic acid*, $EtPr_2Si{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H$, with the aid of chlorosulphonic acid; the *l-menthylamine*, *cinchonidine*, and *quinine* salts of this acid resemble very closely the corresponding salts of *dl*-benzylmethylethylpropylsilicanesulphonic acid (*loc. cit.*, p. 717), a fact which indicates that the latter are mere mixtures of their optically-isomeric components.

Diphenylethylsilicyl chloride, $Ph_2EtSiCl$, a colourless liquid boiling at 206—208° (50 mm.), *diphenylethylsilicyl oxide*, $(Ph_2EtSi)_2O$ (m. p. 65·5.), *triphenylethylsilicane*, Ph_3EtSi (m. p. 76°), and *triphenylmethylsilicane*, Ph_3MeSi (m. p. 67—67·5°) were also described.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, January 24th, 1908.

Prof. J. PEERY, F.R.S., President, in the Chair.

MR. R. S. SMITH and Mr. J. G. Howarth were elected Fellows of the Society. Mr. W. C. Campling was elected a Student member of the Society.

A paper by Mr. W. ROSENHAIN on "*Observations on Recalescence Curves*" was read by Dr. R. T. GLAZEBROOK.

Referring to the importance of the accurate study of recalescence phenomena in metals and alloys, the author describes the two principal methods employed for obtaining recalescence curves. These are known as the "Inverse Rate" and "Differential" methods respectively. In the former method the time occupied by successive equal decrements of temperature are observed and plotted against the temperature of the cooling body, thus giving a

curve whose ordinates are temperature (t) and dT/dt (T = time) respectively. In the differential method the difference of temperature between the body under observation and a neutral or "blank" body cooling under approximately the same conditions is observed and plotted against the temperature of the body. The physical interpretation, in terms of quantity of heat evolved and of rate of evolution of heat of these two kinds of curves, are discussed by reference to the fundamental curve representing the time-temperature relations of one or two cooling bodies. On both types of curve, recalescences are indicated by peaks, and it is shown that in the case of an inverse-rate curve the area of a peak when taken between proper limits is roughly proportional to the quantity of heat evolved divided by the rate of cooling. Serious errors affecting this proportionality in practical cases are, however, pointed out. The differential curves are first discussed for the ideal case in which the neutral body cools at the same average rate as the body under observation, but it is pointed out that this case cannot be readily attained in practice. The effect of differences in the rates of cooling of the two bodies is shown to be the production of a general slope in the differential curve, upon which peaks due to recalescences are superposed. The author suggests the elimination of this general slope by plotting a "derived differential curve" in which the movements of the differential galvanometer during the process of cooling through successive intervals of temperature are plotted against the temperature of the cooling body. This curve represents the differential coefficient of the ordinary differential curve. Peaks representing recalescences on these curves are shown to have exactly the same physical meaning as peaks on the inverse-rate curves, and the conclusion is arrived at that the two methods lead to identical results, the choice between them being thus reduced to a question of experimental expediency. The experimental requirements of the two methods are then described, and it is shown that to arrive at the same degree of accuracy in the curves, the means of measuring temperature used for the inverse-rate method must be very much more sensitive than those required for the differential method. This necessity arises from the fact that in the inverse-rate method the actual temperature of the cooling body must be determined to the same degree of accuracy as the difference of temperature between the two bodies in the differential method, and while the latter difference rarely exceeds 40° C., the former frequently attains 800° C. The fact that accurate autographic methods appear to be more readily attainable with the differential method is also an argument in its favour, as is also the fact that it is less subject to accidental error from external disturbing causes.

The theoretical views advanced in this discussion are then illustrated by a series of actual recalescence curves, chiefly of steel, taken by both methods. These illustrate the advantages of plotting the results in the form of the derived differential curves. This is particularly apparent in the case of three recalescence curves taken of samples of the same steel, in which the rate of cooling was varied from one and three-quarter hours to twelve minutes. With the more rapid cooling, the ordinary differential curves become very oblique and unintelligible, but the derived differential curves are quite definite in character and are in good agreement with one another. The author, however, advocates the determination of recalescence curves by observations on gradual cooling rather than on the rapid cooling sometimes adopted. A recalescence curve obtained by a modification of the differential method in which the cooling of two pieces of the same steel is utilised, is also shown; in this curve a recalescence is indicated by a forward swing of the galvanometer followed by an equal and opposite swing.

Finally, the author describes a recalescence first observed to occur somewhat mysteriously in the body of certain furnaces at a temperature of 580° C. This was ultimately traced to a transformation occurring in crystalline silica, whether free or in admixture with porcelain or fire-clay. Heating- and cooling curves of quartz-sand are given, showing this recalescence vigorously. The author points out that this recalescence in crystalline silica coincides with certain points in the iron-carbon diagram of Roberts-Austen and of Carpenter and Keeling, and suggests that the recalescences observed by those workers may have arisen from silica in their furnaces.

Mr. F. J. SELBY remarked on the skill with which the author, by direct reasoning from certain approximate assumptions, had arrived at his interesting results as to the points of importance in connection with recalescence curves. Mr. Rosenhain had shown, very clearly and graphically, that from the theoretical point of view all the methods of representing the cooling-curves must give identical information, and that therefore the decision as to method to be adopted depended simply on the experimental accuracy attainable; while, in this respect, he had brought forward very strong evidence in favour of the Roberts-Austen differential method. Mr. Selby suggested that it might be worth while to draw out theoretical cooling-curves based on certain simple assumptions as to the conditions of cooling. He showed how this might be done for the parts of the curve preceding and following the recalescence; and that by making a suitable supposition as to the variation in the rate of evolution of heat during the recalescence, such as $dQ/dT = (a - bT)^n e^{cT}$, a complete theoretical curve might be drawn by the comparison of which with the experimental curve the constants might be determined, and all the quantities of importance in connection with the recalescence estimated with greater accuracy. In particular, and without any assumption as to the form of dQ/dT, some of the results in the paper could be verified; it could be shown that the evolution of heat was not completed at the peak on the derived differential curve (the point of inflection on the Roberts-Austen curve), and the point of maximum evolution of heat on the experimental curve could be fixed. The value of the derived differential curve advocated by the author becomes apparent from such calculations.

Mr. A. CAMPBELL remarked that the end of the paper was the part which would most likely be of interest to physicists. It was most interesting to find that the author has shown (by the cooling-curve method) a change-point in silica near 580° C. Quite a number of years ago Le Chatelier showed that between 460° and 500° C. the coefficient of expansion of quartz showed a quick increase, and he predicted that a change-point should occur at 270° C. Randall's experiments in 1905 on quartz showed a similar result so far as the expansion is concerned. Experiments which he (Mr. Campbell) had made with nickel showed no abnormality in coefficient of expansion at temperatures which gave strongly marked thermo-electric change-points. For the direct reading of rates of cooling, Dejean not long ago devised an ingenious arrangement in which the thermocouple is connected to one coil of a differential moving-coil galvanometer whose other coil is connected to a second galvanometer: the readings of the latter will be a function of the rate of cooling. It occurred to the speaker that a transformer would give a simpler method of obtaining di/dt, but the slowness of change of i makes it too insensitive. The assumptions made in the paper that the specific heat, the thermal conductivity, and the emissivity of any material remain approximately constant even over a small range of temperature near recalescence, seem somewhat uncertain to the physicist, and must be regarded merely as working conventions by the metallurgist.

Mr. S. W. J. SMITH expressed his interest, from the consideration of magnetic data, in the author's opinion that there is no critical point near 580° C. in the cooling-curves of iron and steel. It was curious that in the paper in which Roberts-Austen describes the critical point found at about 580° C., he cites the magnetic experiments of Morris in support of the fact that a change occurs in iron at that temperature. Morris puts the temperature of the magnetic change at about 550° in one specimen, but at

about 500° in another; while in a third the effect was scarcely observable. Even in the specimen most studied, the magnitude of the effect seemed to depend upon the annealing temperature. In some experiments on permeability-temperature variation in nearly pure iron (0·06 per cent C., 0·1 per cent Mn) annealed at about 850° C., Mr. Satterly and the speaker found a distinct change in the slope of the $\mu-\theta$ curve (H=0·43) slightly below 500° during cooling, and a distinct minimum value of μ near 250° during heating. But with the field-strength used there was no apparent break in the slope of the $\mu-\theta$ curve near 580° C. There was thus apparently no conclusive evidence from magnetic data of a critical point at 580° C. The effect observed at 580° by Roberts-Austen was very feeble compared with another effect which began near 500° and continued over a considerable range. This effect was obvious as a more or less pronounced "hump," of which the maximum lies near 400° on practically all the permeability-curves. It was even traceable in the curves of Hopkinson, although his observations below 500° were very few in number. Their own magnetic experiments agreed with those of Morris and with the Roberts-Austen cooling curve in showing another critical point near 250°, although in their case the effect was only detected during heating.

A paper by Mr. W. C. M. Lewis entitled "*An Experimental Examination of Gibbs' Theory of Surface Concentration regarded as the Basis of Adsorption, and an Application to the Theory of Dyeing*" was postponed.

ROYAL INSTITUTION.

General Monthly Meeting, February 3rd, 1908.

Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair.

Lord Ellenborough and Mr. Alfred Moseley, C.M.G., were elected Members. The Honorary Secretary reported the decease of the Right Hon. Lord Kelvin, O.M, G.C.V.O., P.C., D.C.L., LLD., D.Sc., F.R.S., Grand Officer of the Legion of Honour, Chancellor of the University of Glasgow, on the 17th of December, 1907, and the following Resolution was passed.

Resolved, That the Managers of the Royal Institution of Great Britain desire to record at this, their first meeting subsequent to his death, their sense of the great loss sustained by the Institution and by Science in the decease of Lord Kelvin.

Lord Kelvin became a Member of the Royal Institution in 1886. He gave his first lecture at the Royal Institution at the time when Faraday was engaged in his epoch-making researches on Electricity and Magnetism; and between the years 1856 and 1900 Lord Kelvin delivered a Course of Lectures on The Electric Telegraph in 1863, and no less than nine Friday Evening Discourses on the following subjects:—"The Origin and Transformations of Motive Power" (1856), "Atmospheric Electricity" (1860), "Tides" (1875), "Effects of Stress on Magnetisation of Iron, Nickel, and Cobalt" (1878), "The Sorting Demon of Maxwell" (1879), "Elasticity viewed as possibly a Mode of Motion" (1881), "Isoperimetrical Problems" (1893), "Contact Electricity of Metals" (1897), "Nineteenth Century Clouds over the Dynamical Theory of Heat and Light" (1900).

On the occasion of the celebration of the Jubilee of his appointment to the Chair of Natural Philosophy in the University of Glasgow, an address of congratulation was presented to Lord Kelvin on behalf of the Members of the Royal Institution, expressing their high appreciation of the conspicuous services rendered by him in the extension and diffusion of scientific knowledge.

When Lord Kelvin resigned his Professorship and came to reside in London he took much interest in the Royal Institution, and became a Manager in 1892.

The Managers desire to offer on behalf of the Members of the Royal Institution the expression of the most sincere sympathy with Lady Kelvin and the family in their bereavement.

The Special Thanks of the Members were returned to Dr. W. J. Russell, F.R.S., for his donation of £100 to the General Fund; and to Mr. Charles Hawksley for his donation of £100 (in commemoration of the 100th anniversary of the birth, on July 12th, 1807, of Thomas Hawksley, F.R.S., Civil Engineer), to the Fund for the Promotion of Experimental Research at Low Temperatures.

Letters were read from Prof. A. Haller, Prof. L. Troost, and Prof. W. Spring acknowledging their election as Honorary Members of the Royal Institution.

The Chairman announced that the Managers had appointed Dr. Kenneth Robert Hay, M.B. (Cambridge), Medical Officer to the Royal Institution in succession to the late Dr. Woodhouse Braine, who held the appointment for thirty-six years.

NOTICES OF BOOKS.

A Text-book of Organic Chemistry. By A. F. Holleman, Ph.D., F.R.A.Amst. Translated by A. Jamieson Walker, Ph.D. (Heidelberg), A.A., assisted by Owen E. Mott, Ph. D. (Heidelberg). Second English Edition. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1907.

The original Dutch edition of this work proved a valuable and in some respects unique text-book of organic chemistry for the beginner, and the translations into English, German, Italian, and Russian have been equally well received. The great advantage of its use to the student is the special prominence given to theory, and in particular to the structure of the compounds considered. The empirical facts enumerated are reduced to the minimum which is compatible with a thorough elementary knowledge of organic chemistry, while the attention of the student is concentrated upon general reactions and principles. The book is well up to date, and gives full accounts of the application of physico-chemical methods to organic substances, and brief notes are added upon some important technical processes. In the second English edition the text has been completely re-written, Prof. Holleman himself having given the translators valuable assistance in the selection and arrangement of the new material.

Traité Complet d'Analyse Chimique Appliquée aux Essais Industriels. ("Complete Treatise of Technical Chemical Analysis.") By J. Post and B. Neumann. Second French Edition, edited by Dr. L. Gautier. Vol. II., Part I. Paris: H. Hermann. 1908.

Part I. of Volume II. of this comprehensive treatise deals with chalk, mortar and cements, the ceramic industry, and glass making. The choice of analytical methods is above criticism, and in every respect it is clear that thoroughness has been the special aim of the compilers. The translator, Dr. L. Gautier, has made many additions to the text, and has taken every care to make the French edition as valuable and trustworthy as the German.

Royal Institution.—On Tuesday next, February 11, at 3 o'clock, Prof. Stirling begins a course of six lectures at the Royal Institution on "Membranes—Their Structure, Uses, and Products"; and on Saturday, February 15, at the same hour, Mr. Selwyn Brinton commences a course of three lectures on "The Art of Florence." The Friday Evening Discourse on February 14 will be delivered by Dr. C. W. Saleeby on "Biology and History," and on February 21 by Sir Oliver Lodge on "The Ether of Space."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 1, January 6, 1908.

New Homologues of Diglycollic Acid.—E. Jungfleisch and M. Godchot.—*a*-Ethyl a_1-methyl diglycollic acid on distillation *in vacuo* at 140—150° gives up water and is partially transformed into anhydride. It is completely dehydrated by the action of boiling acetyl chloride, and on distillation *a*-ethyl a_1-methyl diglycollic anhydride,—

$$CH_3-CH_2-\overset{(a)}{CH}-CO \quad O \quad CH_3-\overset{(a_1)}{CH}-CO$$

is isolated. The diethyl derivative of *a*-ethyl a_1-methyl diglycollic acid yields the corresponding diamide with alcoholic ammonia,—

$$NH_2-CO-CH(CH_2-CH_3)-O-CH(CH_3)-CO-NH_2.$$

aa-Dimethyl a_1-methyl diglycollic acid,—

$$COOH-\underset{(a)}{C(CH_3)_2}-O-\underset{(a_1)}{CH(CH_3)}-COOH,$$

is prepared by the action of ethyl *a*-bromoisobutyrate on sodium ethyl lactate. The diethyl ether of *a*-isopropyl a_1-methyl diglycollic acid,—

$$COOH-\underset{(a)}{CH}[CH=(CH_3)_2]-O-\underset{(a_1)}{CH}(CH_3)-COOH,$$

is formed when ethyl bromo-isovalerianate is substituted for ethyl bromo-isobutyrate in the above reaction.

Mechanism of Phenyl Transpositions in Iodohydrines and Aromatic Glycols.—Marc Tiffeneau.—The author has shown that the *a*-glycols, *a*-chlorhydrines, and tetra-substituted oxides of ethylene, poly-substituted aromatic glycols of general formulæ $Ar-CHOH-COH<\begin{matrix}R\\R'\end{matrix}$ and $Ar-CHOH-CHOH-Ar'$, and aromatic halogen hydrines of general formulæ $Ar(R)=C(OH)-CHX-R'$ and $Ar-CHOH-CX=RR'$, are capable of undergoing molecular transpositions when converted into aldehydes or ketones. Thus certain reagents convert the halogen hydrines, $Ar-CHOH-CHX-R$, into ethylene oxides without any transposition,—

$$Ar-CHOH-CHX-CH_3 \xrightarrow{-HX} Ar-\underset{O}{CH}-CH-CH_3,$$

while others act as follows:—

$$Ar-CHOH-CHX-CH_3 \xrightarrow{-HX} Ar-CH<\begin{matrix}CHO\\CH_3\end{matrix}.$$

The same differences are observed with the corresponding ether oxides, $Ar-CH(OR)-CHX-R$. The author has shown that a mono-ether, such as $C_6H_5-CH(OCH_3)-C(OH)(CH_3)_2$, does not undergo the following change, giving a methoxystyrolene compound,—

$$C_6H_5-CH(OCH_3)-C(OH)(CH_3)_2 \xrightarrow{-H_2O} C_6H_5-C(OCH_3)=C(CH_3)_2,$$

but yields dimethylphenylacetaldehyde,—

$$C_6H_5-CH(OCH_3)-C(OH)(CH_3)_2 \xrightarrow{-CH_3OH} CHO-C<\begin{matrix}C_6H_5\\(CH_3)_2\end{matrix}.$$

MISCELLANEOUS.

South-Western Polytechnic, Chelsea.—The Lord Alverstone, G.C.M.G., Lord Chief Justice of England, presents Prizes and Certificates to Students of Evening Classes and Day College on March 13 at 8 o'clock p.m.

Acid Properties of Ozone.—W. Manchot and W. Kampschulte.—With ammonia at the ordinary temperature ozone forms dense mists, which do not contain nitric oxide. Similar phenomena are observed with organic bases such as methylamine, trimethylamine, piperidine, &c., and with strong bases it is more marked than with weak. Ozone forms compounds with the caustic alkalis, and the stability of the compound decreases as the atomic weight of the metal falls; thus the cæsium derivative is the most stable, and the lithium derivative the least. Mg, Ca, Sr, and Ba oxides destroy ozone rapidly at the temperature of the room, and heat is evolved by the reaction. The compounds formed are decomposed by water. The acid properties of ozone are also shown by the fact that blue litmus is coloured distinctly red, and other indicators give a decidedly acid reaction with it. It makes water conduct an electric current. The acid properties of ozone seem to belong partly to a decomposition product which appears to be the decomposition product of a hydrate of ozone. The mist formed with ammonia must contain this product.—*Berichte*, xl., No. 18.

Institute of Chemistry.—*January Examinations*, 1908.—Of twenty-three candidates who presented themselves for the Intermediate Examination, the following fourteen passed:—W. Cameron; F. Challenger, B.Sc. (Lond.); P. W. Copeland, B.Sc. (Lond.); G. A. M. Cunningham; H. Davies; J. G. Hay; A. Hepburn; H. R. Jensen, B.Sc. (Liverpool); C. H. Kirkaldy; F. W. Linch; W. A. Riley; V. J. Tilley; R. Unwin; and C. H. Warner. In the Final Examination for the Associateship, of four candidates who presented themselves in the branch of Mineral Chemistry, the following three passed:—S. L. Archbutt; C. P. Matthews, B.Sc. (Lond.); and L. A. Levy, B.A. (Cantab.), B.Sc. (Lond.). One candidate presented himself in Physical Chemistry, and passed:—N. P. Campbell, B.A. (Oxon.). Of six in Organic Chemistry, three passed:—T. P. Hilditch, B.Sc. (Lond.); B. D. Porritt, B.Sc. (Lond.); and H. E. Watson, B.Sc. (Lond.). Eight candidates presented themselves in the Chemistry of Food and Drugs, of whom the following seven passed:—A. P. Davson, Assoc.R.C.Sc. (Lond.); A. G. Harrington; H. Mansfield, B.Sc. (Lond.); R. D. Masson; P. Murphy; B. F. Sawbridge, B.A. (Oxon.); and J. M. Wilkie, B.Sc. (Lond.). W. P. Hayworth, A.I.C., also passed this examination in order to obtain the special certificate recognised by the Local Government Boards. Four candidates presented themselves for examination for the Fellowship, and the following three passed:—W. Barbour, M.A., B.Sc. (St. Andrews), in the Branch of Organic Chemistry; P. V. Dupré, A.C.G.I., in Mineral Chemistry; and A. C. Franklin, in Metallurgical Chemistry.

MEETINGS FOR THE WEEK.

Monday, 10th.—Society of Arts, 8. (Cantor Lecture). "Theory and Practice of Clock Making," by H. H. Cunynghame, C.B.

Tuesday, 11th.—Royal Institution, 3. "Membranes—Their Structure, Uses, and Products," by Prof. William Stirling, M.A., LL.D., D.Sc., &c.

Wednesday, 12th.—Society of Arts, 8. "The Application of Science to Foundry Work," by R. Buchanan.

Thursday, 13th.—Society of Arts, 4.30. "The New Imperial Gazetteer of India," by Richard Burn, I.C.S.

—— Royal Institution, 3. "The Story of the Spanish Armada," by Major Martin Hume.

Friday, 14th.—Royal Institution, 9. "Biology and History," by Dr. C. W. Saleeby.

—— Physical, 8. Annual General Meeting. President's Address.

Saturday, 15th.—Royal Institution, 3. "The Art of Florence," by Selwyn Brinton, M.A.

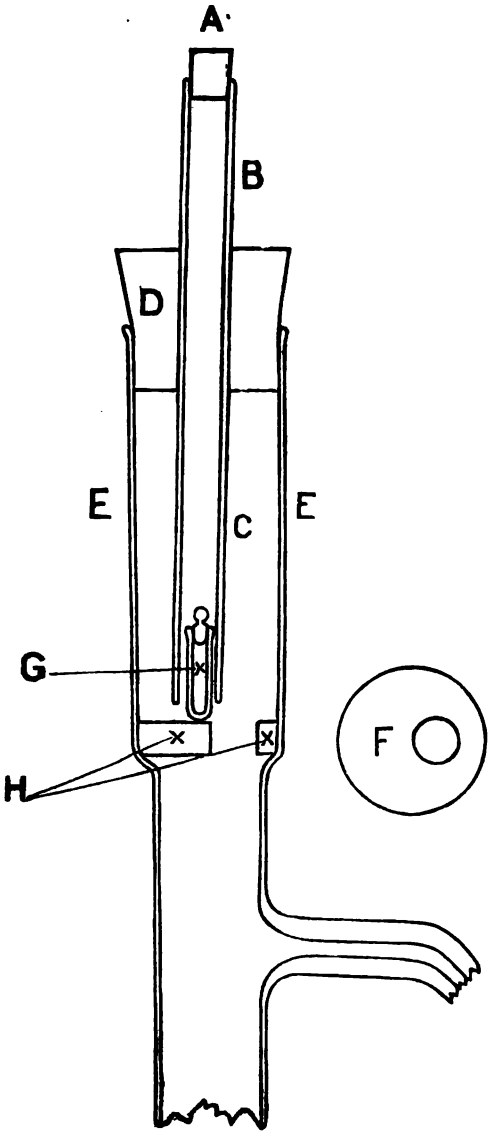
THE CHEMICAL NEWS.

Vol. XCVII., No. 2516.

A SIMPLE FORM OF RELEASE FOR VICTOR MEYER'S VAPOUR-DENSITY APPARATUS.

By T. S. PATTERSON.

The following simple release may be found convenient for fitting to the ordinary type of Victor Meyer's vapour-density apparatus, and it may be found to present advantages over other forms of release presently in use.



The figure shows the upper part of the neck of an ordinary Victor Meyer apparatus. A narrow slice, F—about a quarter of an inch in thickness—is cut from a cork which just fits into the wide part, E, of the neck, and excentrically in this slice is bored a small hole a quarter of an inch in diameter. The slice of cork is then placed fairly firmly in position, as shown (in section) at H. The open end of E is fitted with a rubber stopper, D, through which a hole is bored *in a slanting direction* to take the glass tube, B C, of about a quarter inch bore. This tube is closed by the small rubber stopper A. (The apparatus should be so arranged that a line drawn lengthwise through the centre would stand vertical).

When, in the course of a determination, the bulb of the apparatus has been heated so long that no further expulsion of air takes place, the stopper, A, is removed, and the little Hofmann tube, G, containing a weighed quantity of the substance to be investigated is dropped into the position shown in the figure, after which the stopper, A, is firmly replaced. In order to drop the Hofmann tube into the bulb at the desired time, the tube, B C, is moved by hand (the elasticity of the rubber stopper D permitting of this without any leak), so as to bring its lower end just over the hole in the cork, H, when the tube, G, drops into the bulb of the apparatus.

An advantage of this arrangement is that the little tube is kept always in a vertical position and no leakage can occur until the hot region of the bulb is reached.

Organic Chemistry Laboratory,
Glasgow University.

NOTE ON THE CUTTING OF SODIUM.

By D. P. McDONALD, M.A.

In cutting sodium by means of the Gattermann knife considerable difficulty constantly arises from the fact that the metal, becoming slightly warmed by the hand and by the friction of cutting it, softens, and is very apt to stick to the blade of the knife.

This difficulty may readily be overcome if, from time to time when signs of softening occur, the lump of sodium is dipped in anhydrous ether for a moment or two. The metal is chilled by the immersion, and further cooled by the evaporation of the liquid left on the surface after removal from the ether, and can then be cut with great ease. The cut slices are generally dropped into a basin containing ether, and the same ether of course serves for cooling the stick which is being cut.

Organic Chemistry Laboratory,
Glasgow University.

MODE OF VALUING RAW RUBBER.

By CLAYTON BEADLE and HENRY P. STEVENS.

In a previous paper entitled "The So-called 'Nerve' of Rubber" (Chemical News, 1907, xcvi., 247) we have given details of mechanical tests on raw rubbers both before and after mechanical treatment and exposure to low temperatures. The results of these tests show clearly that the tensile strength and resiliency of a rubber are enormously influenced by the conditions to which the test piece is subjected. We do not claim to have brought forward anything especially novel in this communication, as the principle which we have sought to demonstrate has long been recognised by manufacturers.

In spite, however, of all this, we find in recent published researches on the subject a general tendency to overestimate the importance to be attached to the properties of raw rubbers, and to pay little or no attention to the properties of the vulcanised product.

We find tables of figures giving the tensile strength and other physical properties of raw rubbers, without any explanation of the methods employed in getting the test

pieces in suitable form for applying the tests or of the temperature to which the samples have been exposed.

To consider only the latter point. In the paper above referred to, we gave results obtained with the same rubbers before and after exposure to a low temperature; a sample of masticated rubber may have its tensile strength increased several fold by freezing or even cooling at a winter's temperature. It is therefore obvious that a sample tested after it has lain a few days in a cold room in winter will give a higher tensile strength than a sample which in summer would not have been exposed to these conditions.

If, then, figures for the physical properties are to be of value and capable of comparison with one another, the rubbers must all be treated under carefully specified conditions, probably from the time of coagulation onwards. But it must readily be seen that such a procedure is entirely out of the question.

In attempting to ensure such normal treatment, it would probably be best to take as a guide the process employed in the manufacture of cut sheet. The dry rubber should first be masticated between rolls at a uniform speed, at a fixed distance apart and for a definite length of time. To get uniform results rolls of the same dimensions should always be used, and the same quantity of rubber taken for mastication. The temperature would have to be maintained at a constant figure for all samples, and a given number of foot-pounds of work would have to be applied to each sample. When the mastication is finished, the rubber should be rolled to a uniform sheet of, say, 1 mm. in thickness for cutting test pieces. The sample may then be tested straight away, a portion being set aside and cooled to 0° C. in an ice-chest for a definite period—say, one week—and again tested.

This is a rough outline of what may be suggested as a possibly reliable method for obtaining uniform results.

Even then the results may not be found to be of any very extraordinary value, but a number of tests on these lines would be of great interest, and if the rubbers were also vulcanised under uniform conditions and tested, it would be of great interest to note in how far there exists a correlation in properties between the raw and vulcanised rubbers.

To correlate the properties of rubbers before and after vulcanisation would involve an immense amount of research, and at the end of it all it is highly doubtful whether there exists any relationship of a useful order. On the other hand, random tests carried out on crude rubbers under conditions anything but uniform can be of no practical value, but must inevitably mislead.

Such a procedure is, however, far more laborious and complex than performing on each sample, as we do, a series of vulcanisations until the right conditions of vulcanisation are discovered, and then comparing the results so obtained by physical tests with similar tests performed on some well-known brand after proper vulcanisation, such, for instance as hard-cure para.

We have on previous occasions urged the advantages of vulcanising rubber under uniform conditions, and testing the vulcanised as against the testing of crude rubbers, for the simple reason alone that practically all rubber is vulcanised in the course of manufacture. It is obvious that it would entail too much work for the method to be applied to the valuation of rubber for purposes of buying and selling; on the other hand, it would be of importance for any plantation company turning out a uniform product, as they are all striving to do, to have a means of ascertaining at first hand how their product compares in practical utility with the products of other estates and with the products of wild rubbers.

The importance of vulcanisation as a means of testing was brought out recently at the discussion of the Society of Chemical Industry on Messrs. Schidrowitz's paper on "The Influence of Formaldehyde on the Properties of the Latex of Funtumia Elastica" (*Journ. Soc. Chem. Industry*, xxvi., No. 24). The tensile strength of the coagulated product is shown to be enormously increased, but if the physical properties of the vulcanised rubber are not similarly enhanced the method has no value except perhaps, as ingeniously suggested by one of the speakers, it should turn out to be a new method of vulcanisation. Even then the paramount importance of the keeping qualities of the rubber so produced require to be investigated, for, as is well known, it is the easiest thing in the world to obtain strength and resiliency in vulcanisation at the expense of keeping qualities, and manufacturers of high-class rubbers will require the properties to be preserved unchanged for at least three years.

After all we do not see that in assessing the value of any new kind of rubber that the methods employed by the most progressive rubber manufacturers in their laboratories have in any way been improved upon by any recently published paper upon the subject. The proof of the pudding is in the eating, and the proof of the rubber is in the vulcanised product.

NITROGLYCERIN AND ITS MANUFACTURE.*

By Lieut.-Col. Sir FREDERIC L. NATHAN, R.A.,
and
WILLIAM RINTOUL, F.I.C.

NITROGLYCERIN was discovered by A. Sobrero in 1847 at Turin. He recognised its explosive properties, but it was not until 1863 that A. Nobel introduced it as a blasting agent in Norway. Owing to several serious accidents in its manufacture and use, its application did not become general until Nobel in 1867 succeeded in absorbing it with kieselguhr, in which form it is known as dynamite. Blasting gelatin, in which soluble nitrocellulose is the absorbent, produced by Nobel in 1875, marked another step in the employment of nitroglycerin as a disruptive explosive, and finally it forms a constituent of ballistite and cordite, both propulsive explosives.

Nitroglycerin is produced by adding glycerin to a mixture of sulphuric and nitric acids. After nitration the nitroglycerin formed separates out from the waste acid, and is submitted to a thorough washing with water and soda solution to remove all traces of acid and unstable bodies. In the early days of its manufacture, the plant was on a very small scale and of simple construction. With the introduction of dynamite, nitroglycerin was made in much larger quantities and the plant was on a bigger scale. Lead vessels were adopted for nitrating and washing, the nitrating apparatus was provided with lead coils through which cold water circulated; compressed air agitation was introduced, and many minor improvements in both plant and process gradually followed. The plant erected at the Royal Gunpowder Factory in 1903 differs in some essential particulars from the plants previously used. Instead of running by gravity the mixture of nitroglycerin and waste acid on the completion of nitration into a separating tank below the nitrating vessel, allowing the separation of the nitroglycerin from the waste acid to take place in this tank, and then running the nitroglycerin again by gravity into a washing tank, the separation is allowed to take place in the nitrator itself, and as the nitroglycerin separates out it is displaced by waste acid admitted at the bottom of the nitrator, down a gutter attached to the top of the nitrator into the pre-wash tank, placed so that its top is very slightly lower than the top of the nitrator. This arrangement much simplifies the plant and obviates the dangers incidental to the use of earthenware cocks. Advantage is taken of the fact that the addition of a small percentage of water to the waste acid after the nitroglycerin has separated out, prevents the formation of further small quantities of nitroglycerin on allowing the waste acid to stand, to do away with the tedious and expensive operation known as "after-separating." Water

* Read before the London Section of the Society of Chemical Industry, February 3rd, 1908.

is added to the waste acid in the nitrator separator, and the acid sent away at once for recovery.

A further improvement, now very general in all modern plants, is the substitution of rubber pipes for earthenware cocks for running off nitroglycerin.

The proportions of sulphuric to nitric acid and of glycerin to the nitrating acid mixture have been varied from time to time. In the early days of manufacture two parts of sulphuric to one of nitric was used, and the proportion of glycerin to mixed acid varied from one-sixth to one-eighth. The more modern practice is to use a mixture of three parts by weight of nitric acid of 1·3 sp. gr. and five parts by weight of sulphuric acid of 1·842 sp. gr., and to nitrate one part by weight of glycerin in every eight parts by weight of the mixture.

The early yield of nitroglycerin varied round 200 per cent; in more modern factories yields averaged about 210 per cent, but an average yield of over 214 per cent was obtained at the Royal Gunpowder Factory over a series of eight years previous to the introduction of the improved plant referred to above; with the introduction of this plant the yield increased to just over 220 per cent. Similar results have also been obtained at other factories using this plant.

Nitrating acid of the composition referred to above contains about forty-seven parts of water which perform no useful function, appearing again in the waste acid. By using an anhydrous nitrating acid of altered composition this water is eliminated, and a much smaller quantity of nitrating acid for a given charge of glycerin can be used, resulting in the production of a smaller quantity of waste acid, the composition of the latter remaining the same as before. As nitroglycerin is absorbed to a certain extent by waste acid (3·7 per cent in one of normal composition) the less the quantity of waste acid the better should be the yield of nitroglycerin. By using Nordhausen acid, an anhydrous acid can be produced, and manufacturing experience has proved that with practically such an acid a yield of 230 per cent of nitroglycerin is obtainable. The absorption of nitroglycerin by waste acid is not merely a case of solution. A secondary reaction also takes place between the sulphuric acid and the nitroglycerin with the production of sulphoglycerin and nitric acid. This reversible reaction speedily attains an equilibrium, so that with a normal waste acid of the total nitroglycerin absorbed, one-half exists as sulphoglycerin and the remainder as nitroglycerin in true solution.

NOTE ON IONIUM.

By W. MARCKWALD and B. KEETMAN.

WE have for some time been occupied with experiments to determine the proportion in which radium and actinium are contained in the ores of uranium, and we have thus come upon a hitherto unknown radio-active constituent of these ores, which is obviously identical with the substance, allied to thorium, recently discovered by B. B. Boltwood (*Am. Journ. Sci.*, 1907, [4], xxiv., 370) and O. Hahn (*Ber.*, 1907, xl., 4415). Boltwood proposed the name "ionium" for this substance.

When a uranium ore—we used Joachimsthal pitchblende, crystallised pitchblende from German East Africa, and autunite—is dissolved in nitric acid, the nitrate is converted into sulphate, and filtered from insoluble sulphates (lead, barium, radium), a very strongly active precipitate is separated from the solution by the addition of hydrofluoric acid. It consists chiefly of fluorides of the cerium and yttrium earths, and of thorium. If these fluorides are again brought into solution by evaporating with concentrated sulphuric acid, and then oxalic acid is added to the strongly acid solution, almost all the activity separates with the thorium oxalate. Boltwood precipitated the same substance with thorium by means of thiosulphate.

Boltwood found that the α-radiation of his ionium was much more easily absorbed than that of polonium. Our precipitate also showed this characteristic property. More than two-thirds of its α-radiation is absorbed by aluminium foil of thickness 0·007 mm., while only half of that of polonium is absorbed.

Boltwood found that the ionising power of the substance was to that of the radium separated from the same amount of ore as 8 : 10, while we obtained an average of 7 : 10. The substance does not give an emanation.

There can be no doubt about the identity of the two substances. We have not yet succeeded in separating ionium from thorium. Like thorium oxalate it is dissolved by ammonium oxalate, and again precipitated from the solution by acids. Both thorium and ionium carbonates are soluble in ammonium carbonate.

This last property explains why a substance with such a high emanation power has hitherto escaped discovery. On a large scale only the residues of the Joachimsthal uranium manufacture have been treated for the separation of radio-active substances. But, as our experiments show, these residues are comparatively poor in ionium. Clearly the greater part of the substance goes into solution with the uranium during the process, if to separate it from impurities soda solution is added to the sulphate solution. Therefore the ionium must be looked for, not in the residues, but in the mother-liquor of the manufacture of uranium.

According to the interesting observations of Boltwood and Hahn, ionium seems to be the long-sought intermediate product between uranium or uranium X and radium. We do not intend to go further into this question, which the authors mentioned above have begun to study before us. But we consider that we are justified in continuing our research, the most important results of which we had deduced long before any publication by the above authors had appeared.

We take this opportunity of reporting a surprising circumstance which we observed during the investigation of autunite. This mineral, which is calcium uranium phosphate, and occurs in beautiful crystals, was found to be free from lead when 10 grms. of it were investigated, or at any rate this quantity does not contain one-tenth of a mgrm. of lead. This result, which will be further examined, is of importance because lead is supposed to be the end product of the radio-active transformation of uranium.—*Berichte*, xli., 49.

SOME COMPOUNDS OF TERBIUM AND DYSPROSIUM.

By G. URBAIN and G. JANTSCH.

WE have begun a study of the elements of the yttrium group recently isolated by one of us in order to find out what relations exist between the different members of the series, and what differences can be employed to form the basis of processes of separation of these substances, which will be less tedious than those which have been employed to prepare them.

It seemed best to begin this research by studying the simplest compounds, the oxides, chlorides, nitrates, and sulphates. In this article we shall limit ourselves to the description of our first experiments with terbium and dysprosium.

Terbium Peroxide, Tb_4O_7.—Terbium peroxide, which is formed by igniting salts of terbium the acid radicle of which can be eliminated by heat, corresponds exactly to the formula Tb_4O_7, if care is taken to avoid too high a temperature.

At a white heat the oxide, Tb_4O_7, loses oxygen, all of which it does not re-absorb on cooling. For this reason the oxide, which results on igniting the sulphate at 1600°, has a variable composition; the determination of oxygen generally gives numbers which are lower than those required by the formula Tb_4O_7.

If terbium oxalate or hydroxide is heated in a muffle a peroxide is obtained, the percentages of oxygen in which correspond exactly to the above formula.

We convinced ourselves of this by employing a method of determining oxygen which is less liable to error than reduction by hydrogen at a red heat, or the iodometric method previously employed. This method consists in dissolving terbium peroxide by warming it with a titrated solution of ammoniacal ferrous sulphate containing free sulphuric acid in an atmosphere of coal-gas. The excess of Mohr's salt is then titrated by potassium permanganate. The numbers found by this method agree with the theoretical number 2·13 to within 1/100 to 2/100.

The establishment of this formula is of great importance for the analysis of compounds of terbium; terbium can be determined as peroxide, Tb_4O_7, if the precautions which have just been described are observed.

Terbium Nitrate, $Tb(NO_3)_3.6H_2O$.—Terbium peroxide is difficultly soluble in nitric acid in the cold. When warmed it dissolves with evolution of oxygen. On evaporating the solution on a water-bath only a syrup is obtained, which on cooling forms a white radiating mass. From nitric acid, containing one-eighth of its volume of water and not used in excess, the nitrate, $Tb(NO_3)_3.6H_2O$, is obtained in the form of colourless monoclinic crystalline needles. This salt is soluble in alcohol. Its aqueous solution is neutral to litmus. In a sealed tube it melts in its water of crystallisation at 89·3°.

Terbium Sulphate, $Tb_2(SO_4)_3.8H_2O$.—The preparation and properties of this salt, which was used for the determination of the atomic weight of terbium, have already been described (G. Urbain, *Comptes Rendus*, 1905, cxli., 521).

The same hydrate is obtained when an aqueous solution containing terbium and sulphuric acid is precipitated with alcohol. It then forms a crystalline powder composed of micaceous lamellæ, insoluble in alcohol and difficultly soluble in water.

Terbium Chloride, $TbCl_3.6H_2O$.—Terbium peroxide dissolves on warming with hydrochloric acid, chlorine being evolved. After the solution has been concentrated until it contains 40 to 45 parts of anhydrous salt in 100 parts of solvent, about one and a-half times its volume of hydrochloric acid is added, and it is left in a sulphuric acid desiccator. The chloride readily gives supersaturated solutions. It is best to induce crystallisation by rubbing the sides of the vessel with a glass rod. The salt thus obtained has the formula $TbCl_3.6H_2O$. It forms colourless transparent prismatic crystals. It is extremely hygroscopic, is soluble in alcohol, and its aqueous solution is neutral to litmus.

Dysprosium does not form a peroxide. Its oxide, Dy_2O_3, does not change in weight when it is heated either in an oxidising or in a reducing atmosphere. Its salts are light yellowish green in colour.

Dysprosium Nitrate, $DyNO_3.5H_2O$.—Under conditions in which terbium nitrate with 6 molecules of water is formed we have always obtained a penta-hydrated dysprosium nitrate.

This nitrate resembles the corresponding bismuth nitrate in every respect, and is almost the same colour. It loses water in a dry atmosphere, and rapidly becomes opaque. It is soluble in alcohol, very soluble in water, and less soluble in water containing nitric acid than in pure water. Its aqueous solution is neutral to litmus. It melts in its water of crystallisation at 88·6°.

Dysprosium Sulphate, $Dy_2(SO_4)_3.8H_2O$. — This salt, which was used for the determination of the atomic weight of dysprosium, has already been described (G. Urbain and Demenitroux, *Comptes Rendus*, cxliii., 598). It resembles very closely the corresponding compound of terbium.

Dysprosium Chloride, $DyCl_3.6H_2O$.—This compound is prepared in the same way as the corresponding chloride of terbium, which it resembles in most of its properties, being, however, less hygroscopic. Its aqueous solution is neutral o litmus.—*Comptes Rendus*, 1908, cxlvi., 127.

THE ATOMIC WEIGHT OF HYDROGEN.*

By WILLIAM A. NOYES.

(Concluded from p. 67).

SECOND SERIES.—*Hydrogen from Sulphuric Acid, Weighed Twice.*

In this series the hydrogen was weighed in palladium, and also after transfer to the copper oxide tube as described above. In order to increase the quantity of hydrogen and reduce the error, after the water had been removed and the copper re-oxidised, a second quantity, and in one case a third quantity, of hydrogen was introduced, and the water removed. Finally, the reduced copper was transferred to a hard glass tube, and oxidised in a current of oxygen, and the amount of water formed was determined. The oxygen used was partly from the S. S. White Dental Manufacturing Company, and was purified by passing it over red-hot copper oxide and through wash-bottles containing a solution of sodium hydroxide, and over phosphorous pentoxide. In some of the experiments electrolytic oxygen was used.

Several experiments were made to determine the amount of water taken up by the copper oxide in the transfer to the hard glass tube. In a similar manipulation with dry copper oxide there were obtained 2·63, 1·30, 5·32, and 2·45 mgrms. of water. This would correspond to an average error of about one part in 10,000. It has not been thought best to apply any correction for this error, partly because of the uncertainty in its amount, but chiefly because it is probably balanced by small errors in the opposite direction, due to the retention of water by the copper oxide even after several hours at a red heat in a current of oxygen, and to the retention of a trace of water by the walls or lubricant of the copper oxide apparatus. There is good reason, however, for believing that the error from each of these sources is very small.

Weights of Hydrogen (Second Series).

	Grms. H.		Mgrms. H.		Corrected H.		Average H.
	CuO tube.	Pd tube.	In T tube	From Cu.	CuO.	Pd.	
1.	3·72469	3·72689	0·15	0·07	3·72462	3·72667	3·72565
2.	3·80383	3·80280	0·17	0·05	3·80378	3·80258	3·80318
3.	3·75898	3·75886	0·18	0·10	3·75888	3·75858	3·75873
4.	2·96309	2·96357	0·05	0·03	2·96306	2·96349	2·96328
5.	2·11437	2·11366	0·08	0·03	2·11434	2·11355	2·11395
6.	3·53126	3·53173	0·19	0·04	3·53122	3·53150	3·53136
7.	3·53963	3·53982	0·19	0·04	3·53959	3·53959	3·53959

Weights of Oxygen and Water (Second Series).

	O from loss of CuO.	N.	CO_2.	Water by re-oxidation.	O corrected.	Water.
	Grms.	Mgrm.	Mgrm.	Mgrms.	Grms.	Grms.
1.	29·56469	0·76	0·28	15·26	29·57891	33·30408
2.	30·16645	0·37	2·33	20·25	30·18400	33·98748
3.	29·81141	0·32	0·79	23·28	29·83358	33·59127
4.	23·49099	0·13	0·60	29·61	23·51987	26·48379
5.	—	0·20	1·16	27·65	—	18·89214
6.	27·99401	0·38	0·89	36·36	28·02910	31·56024
7.	28·05652	0·24	0·22	40·13	28·09619	31·63554

Atomic Weight of Hydrogen (Second Series).

	From H : O.	From H : H_2O.
1.	1·00765	1·00767
2.	1·00800	1·00799
3.	1·00792	1·00795
4.	1·00792	1·00790
5.	—	1·00795
6.	1·00791	1·00792
7.	1·00785	1·00786
Mean ..	1·00787	1·00789
	± 0·00003	± 0·00003

Mean of all .. 1·00788 ± 0·00002

* From the *Journal of the American Chemical Society*, xxix., No. 12.

Seven determinations were made in this series, but in one of them the weight of the oxygen was lost. The results are given above.

THIRD SERIES.—*Hydrogen from Sulphuric Acid Weighed after Conversion to Water by Copper Oxide.*

In this series hydrogen directly from the electrolytic apparatus was passed into the copper oxide bulb and converted into water. The purpose of the series was more especially to determine whether the purity of the hydrogen had been increased by absorption in the palladium. The results of the series are not as concordant as those of the second, but they indicate that the hydrogen directly from the electrolytic apparatus is, if anything, a little lighter and presumably a little more pure than after it has been absorbed in palladium. The results were as follows:—

Weights of Hydrogen and Oxygen (Third Series).

	H by gain of CuO.	H from Cu.	H corrected.	O by loss of CuO.	N.	CO_2.	Water by re-oxidation.
	Grms.		Grms.	Grms.	Mgrm.	Mgrm.	Mgrms.
1.	2·44282	0·03	2·44279	19·34104	0·16	0·10	56·79
2.	2·18741	0·02	2·18739	17·33722	0·10	0·05	25·98
3.	2·75132	0·03	2·75129	21·80908	0·18	0·05	34·60
4.	4·00068	0·06	4·00062	—	—	—	62·31
5.	4·04061	0·04	4·04057	32·04471	0·17	0·06	32·41

Atomic Weight of Hydrogen (Third Series).

	O corrected. Grms.	Water. Grms.	Atomic weight. From H : O.	Atomic weight. From H : H_2O.
1.	19·39757	21·84042	1·00746	1·00746
2.	17·36305	19·55117	1·00784	1·00780
3.	21·84345	24·59389	1·00764	1·00768
4.	—	35·75073	—	1·00803
5.	32·07689	36·11762	1·00772	1·00772
		Mean . ..	1·00767 ± 0·00006	1·00774 ± 0·00006
		Mean of all	1·00771 ± 0·00004	

It will be noticed that the amounts of carbon dioxide found are much smaller, owing to the fact that the copper oxide has been freed from it by repeated use. The amount of nitrogen was also smaller, perhaps because of the simpler manipulations involved.

FOURTH SERIES.—*Hydrogen and Oxygen from Sulphuric Acid combined by means of Palladium.*

With the best manipulation which it has been possible thus far to secure, the use of copper oxide involves several sources of small constant errors. It is hoped that these errors do not, in the aggregate, exceed one part in 10,000, but it seemed very desirable to find some radically different method which should avoid the use of copper oxide. Such a method consists in absorbing hydrogen in palladium and converting it into water by means of oxygen. This method has already been used by Keiser (*Am. Chem. Journ.*, xx., 733), but his method of manipulation compelled him to use comparatively small amounts of hydrogen, and the degree of concordance which he was able to secure was not such that his value for the atomic weight of hydrogen can be used to decide between Morley's value and that found here.

The problem seemed at first a very simple one, but several months were spent in fruitless experiments before a satisfactory method of manipulation was found.

The 360 grms. of palladium foil previously used were placed in a somewhat wider tube and were kept from direct contact with the glass by means of small glass beads strung on platinum wires. The stopcock at one end of the tube was replaced by a tube having a capacity of about 50 cc. At the beginning the palladium tube was heated and charged with hydrogen and partially exhausted several times to remove moisture. It was then heated to 380°—400° and exhausted until the hydrogen showed a residual pressure of 0·50 to 0·70 mm. as measured by the McLeod gauge. At this pressure and temperature 360 grms. of palladium retain only 2—3 mgrms. of hydrogen, and the amounts of hydrogen given out for small changes of pressure are as follows:—

0·40 to 0·50 mm.	0·11 mgrm. H
0·50 „ 0·60 „	0·10 „
0·60 „ 0·70 „	0·094 „
0·70 „ 0·80 „	0·087 „
0·80 „ 0·90 „	0·080 „
0·90 „ 1·00 „	0·073 „
3·90 „ 4·00 „	0·044 „
16·90 „ 17·00 „	0·020 „

A change of temperature of 10° for pressures less than 1 mm. corresponds to a change of 0·03 mgrm. in the amount of hydrogen retained. At the end of an experiment it was easy to bring the apparatus to a condition of temperature and pressure closely approximating that at the beginning, and by means of the table a correction of sufficient accuracy could be applied.

After exhausting, and measuring the temperature and pressure as described, the apparatus was allowed to cool, rinsed with distilled water, wiped, placed on the balance, and on the following morning it was weighed. It was then charged with hydrogen (about 2·3 grms.) and weighed again on the morning of the third day. The apparatus was then connected with the oxygen side of the electrolytic generator. The palladium tube was inclined so that the water formed ran down into the receptacle at the end. The oxygen entered rapidly for a few minutes, but the heat generated soon caused the pressure of the hydrogen to increase and check the current. The oxygen then continued to enter slowly, with the stopcock partly closed, for two or three hours. After that the rate at which the oxygen was taken changed quite suddenly, so suddenly that the first time the experiment was tried the electrolyte was drawn over and the electrolytic apparatus was broken. From this time to the end the entrance of the oxygen was regulated by the stopcock and was allowed to enter as rapidly as it was thought desirable to run the generator. More than enough oxygen to combine with the hydrogen present was easily introduced. On the fourth day, after weighing, the apparatus was charged again with hydrogen.

On the fifth day the manipulation varied. In some cases oxygen was admitted in excess as on the third day. In other cases, as the end of the oxidation of the hydrogen approached, the apparatus was weighed roughly at intervals and the admission of the oxygen was stopped while 5—10 mgrms. of hydrogen remained unoxidised. By this method of manipulation a day was saved. On the sixth day, or, when an excess of oxygen was admitted, on the fifth, a small excess of hydrogen was admitted. It was necessary to wait till the following day before weighing.

On the sixth or seventh day, according to the method of manipulation chosen, the water and excess of hydrogen were removed and the apparatus brought back to a condition for the beginning of a new experiment. A receptacle similar to that described on p. 66 was used for the water. On account of the hydrogen which accumulated rapidly in the bulb with the water and stopped the current of water vapour, it was found desirable to give the bulb a capacity of about 100 cc. Any nitrogen present was, of course, carried over with the first portions of the water vapour and hydrogen, and this part of the gas was collected and analysed separately. At the close of the removal of the water, the receptacle for the water was replaced by a phosphorous pentoxide tube, which permitted of a free connection between the palladium tube and the pump for the measurement of the residual pressure. It was necessary to heat the palladium tube at least two hours in the electrical air-bath to secure constant conditions for the measurement of the residual pressure. This was not understood

in the earlier determinations of this series, and may be one reason why some of the results are not very satisfactory.

In the results which follow, the amounts of nitrogen and carbon dioxide are given as an indication of the magnitude of the errors which may have been occasioned by traces of these gases or by leakages, but no correction for these gases has been applied.

Theoretically, the weight of the apparatus at the end of an experiment should be the same as at the beginning. Practically, it was almost always heavier because of the retention of a small amount of water. When the hydrogen was allowed to accumulate in the receptacle for water the moisture would condense in the connecting tubes and stopcocks, and if allowed to remain for a short time in contact with the lubricant of the stopcock, could not be entirely removed. In some cases minute drops of water could be seen within the bore of the stopcock, and these would not evaporate during any reasonable length of time. The gain in weight of the apparatus during the experiment was, accordingly, assumed to be due to water which had been retained and was added to the weight of water found directly. In cases where condensation was avoided this amount of water was very small or even became negative. (See the following series.)

Weights of Hydrogen and Oxygen (Fourth Series).

	H.	Corrected for changes of *t* and P.	H recovered.	H corrected.	N.	CO_2.	O.
	Grms.	Mgrm.	Mgrms.	Grm.	Mgrm.	Mgrm.	Grms.
1.	2·31840	−0·05	39·19	2·27916	0·48	0·02	18·08455
2.	4·13630	−0·06	8·90	4·12734	0·50	—	32·76527
3.	4·18248	+0·24	7·16	4·17556	0·52	0·02	33·13449
4.	4·19599	−0·51	2·02	4·19346	0·15	0·16	33·27384
5.	2·31593	−0·01	8·46	2·30746	—	—	18·30863
6.	4·60148	−0·23	4·33	4·59692	0·11	0·08	36·48543
7.	4·63931	+0·14	3·20	4·63625	0·07	0·07	36·79354
8.	4·57292	+0·18	0·36	4·57274	0·02	0·28	36·28696

Weights of Water and Atomic Weight of Hydrogen.

	Water. Grms.	Water retained. Mgrms.	Water corrected. Grms.	Atomic weight. From H : O.	Atomic weight. From H : H_2O.
1.	20·29807	63·21	20·36128	1·00823	1·00830
2.	36·87182	18·61	36·89043	1·00774	1·00780
3.	37·30667	1·20	37·30787	1·00818	1·00821
4.	37·46202	2·51	37·46453	1·00822	1·00831
5.	20·61671	−3·14	20·61357	1·00825	1·00839
6.	41·07653	5·09	41·08162	1·00795	1·00797
7.	41·41452	14·53	41·42905	1·00806	1·00808
8.	40·85460	3·74	41·85834	1·00813	1·00817
		Mean		1·00809 ± 0·00004	1·00815 ± 0·00005

Mean of all .. .. 1·00812 ± 0·00003

FIFTH SERIES.—*Hydrogen and Oxygen from Barium Hydroxide, combined by Means of Palladium.*

The manipulation in this series was essentially the same as in the fourth series. The series has much greater value than the former one, partly as shown by the concordance of the results, partly because the processes of manipulation had been more thoroughly mastered, and partly because the electrolyte used gives a greater probability of purity for the hydrogen. In those experiments in which oxygen was introduced last, a small quantity was left in the bore of the three-way stopcock and was usually found in the subsequent analysis of the first portions of gas removed. In one experiment of this series only one-half the quantity of hydrogen was used, and too much oxygen was admitted by mistake. This so complicated the manipulation that the experiment was unsatisfactory and it has been omitted from the table. It gave the values 1·00814 and 1·00823.

Weights of Hydrogen and Oxygen (Fifth Series).

	H.	Corrected for changes of *t*° and P.	H recovered.	H corrected.	N.	CO_2.	O.	O.
	Grms.	Mgrm.	Mgrms.	Grms.	Mgrm.	Mgrm.	Mgrm.	Grms.
1.	4·61443	−0·07	2·56	4·61180	0·11	0·17	—	36·60909
2.	4·62877	0·00	5·19	4·62358	0·08	0·03	0·13	36·69575
3.	4·60386	−0·02	5·31	4·59853	0·22	0·00	1·31	36·50484
4.	4·56300	+0·04	4·72	4·55832	0·06	0·00	0·29	36·17887
5.	4·21188	−0·04	7·85	4·20399	0·11	0·00	0·11	33·37000

Weights of Water and Atomic Weight of Hydrogen,

	Water. Grms.	Water retained.	Water corrected. Grms.	Atomic weight. From H : O.	Atomic weight. From H : H_2O.
1.	41·21934	1·71	41·22105	1·00779	1·00779
2.	41·30740	9·07	41·31647	1·00798	1·00806
3.	41·09872	3·40	41·10212	1·00776	1·00780
4.	40·74186	−2·82	40·73904	1·00795	1·00790
5.	37·57132	6·04	37·57336	1·00782	1·00786
		Mean		1·00786 ± 0·00003	1·00788 ± 0·00003

Mean of all .. .. 1·00787 ± 0·00002

The mean of the four series, giving them equal weight, is 1·00787 from the hydrogen and oxygen, and 1·00791 from the hydrogen and water. The second and fifth series have, however, much greater weight than the third and fourth, and when we consider, further, that there was probably a trifling loss of water, especially in the third series, the value 1·00787 seems to be the most probable result which can be calculated from the work.

(The mean of the results of the twenty-three determinations in which the hydrogen and oxygen were weighed is 1·00791 and the mean of the twenty-five determinations in which the hydrogen and water were weighed is 1·00794. The mean of all, considered as a single series of forty-eight determinations, is 1·00793 ± 0·00002).

It has seemed of interest to recalculate Morley's results on the oxygen basis for comparison with the result here given.

Atomic Weight of Hydrogen (Morley's Results).

1.	1·00765	1·00778
2.	1·00751	1·00766
3.	1·00768	1·00774
4.	1·00755	—
5.	1·00773	1·00750
6.	1·00773	1·00778
7.	1·00777	1·00786
8.	1·00764	1·00761
9.	1·00759	1·00752
10.	1·00752	1·00737
11.	1·00746	1·00734
12.	1·00744	1·00771
Mean ..	1·00761 ± 0·00002	1·00763 ± 0·00003

Mean of all .. 1·00762 ± 0·00002

The difference between this result and that given above is greater than can be accounted for on the basis of accidental errors. While the average of the results of the best determinations by either observers approaches more nearly to the result of this investigation than to Morley's value, it does not seem justifiable to calculate a mean on such a basis. For reasons which will be given in a later paper the most probable value which we can get at the present time seems to be the average between Morley's value and that here given. That average is *1·00775*. Morley's value and my own each differ from this by one part in 8000.

Change in Weight of the Hydrogen when Converted into Water.

As was stated in the introduction, one purpose of this investigation was to secure, if possible, some evidence of a change of weight which might occur in a reaction in which a large amount of energy is dissipated. In twenty-five experiments the same hydrogen was weighed, first, as absorbed in palladium and, second, after conversion into water by means of the copper oxide. The results were as follows :—

Gain of CuO.	Loss of Pd.	Difference (mgrm.).
1·04216	1·04295	+0·79
1·46493	1·46642	+1·49
0·96114	0·96231	+1·17
1·51279	1·51296	+0·17
1·17961	1·17973	+0·12
1·22273	1·22268	−0·05
1·13563	1·13541	−0·22
1·30184	1·30150	−0·34
1·22851	1·22699	−1·52
0·99563	0·99600	+0·37
1·24243	1·24270	+0·27
1·24639	1·24754	+1·15
1·52682	1·52706	+0·24
0·95151	0·95207	+0·56
1·98130	1·98053	−0·77
1·82248	1·82205	−0·43
2·04840	2·04816	−0·24
1·71042	1·71042	−0·06
1·96621	1·96648	+0·22
0·99685	0·99707	+0·22
2·11434	2·11335	−0·79
2·20439	2·20472	+0·33
1·32683	1·32678	−0·05
2·07207	2·07281	+0·74
1·46752	1·46678	−0·74
36·72299	36·72562	+2·63

An examination of these results shows that in fourteen experiments the hydrogen as weighed in the palladium appeared heavier, while in eleven experiments the hydrogen after conversion into water appeared heavier. The average difference between the two weights of a given quantity of hydrogen was 0·52 mgrm. or one part in 3000, while the average amount by which the hydrogen as weighed in the palladium appeared heavier was 0·11 mgrm., or one part in 14,000. It is clear that these results do not justify any conclusion either way with regard to a change in weight of the hydrogen during the reaction other than that if any change of weight occurs it must be very small. It seems scarcely possible that a change of so much as one part in 10,000 of the weight of the hydrogen takes place. It is possibly of interest to note that, so far as the results furnish any indication whatever, they point toward a trifling loss of weight, a result which would agree with Landolt's elaborate study of the question (*Zeit. Physik. Chem.*, lv., 589). It is hoped that this problem may be taken up again by a method capable of giving more accurate results.

Lothar Meyer Memorial. — The Council of the Chemical Society has decided to make a donation of £10 to the Lothar Meyer Memorial Fund. Many old pupils and admirers of the author of "Die Modernen Theorien der Chemie" may be desirous of contributing to this Memorial, and the Treasurer will be glad to receive, at an early date, subscriptions from Fellows and others to the Fund. Cheques, &c., should be made payable to Dr. Alexander Scott, crossed "Lother Meyer Memorial Fund A/c," and sent to the Treasurer, Chemical Society, Burlington House, W.

THE INFLUENCE OF LIGHT AND OF COPPER ON FERMENTATION.*

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and
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THE action of light on various species of Saccharomyces has been studied by different observers, and amongst these the researches of Kny and Lohmann are of some importance (Duclaux, "Traité de Microbiologie," iii., p. 289; Kny, *Ber. d. Botan. Gesells*, 1894, Heft 3; Lohmann, "Inaug. Dissertation," Rostock, 1896).

The former placed the yeast in culture solutions in flat dishes, and exposed a part to the light of five gas flames, whilst the other part was in the dark, the heat rays being removed by filtering the light through water. His conclusion was that the *budding* of *S. Cerevisiæ* took place in moderate light with the same activity as in darkness.

Lohmann studied the action of both sunlight and the arc. He seeded cultures of *S. Cerevisiæ* on wort gelatin on glass slips, and exposed them to the action of a powerful arc lamp for eight hours. Above a temperature of 18° C. he found that the budding was retarded in the cultures subjected to the light. The same yeast was seeded on agar-agar plates, and exposed to the action of sunlight, when the yeast was killed after several hours. He also noticed that even diffused daylight had a retarding influence on the budding of the cultures, but that this only occurred after prolonged exposure to the light.

The influence of light and various spectral colours on the sporulation of Saccharomyces has been studied by Purvis and Warwick (*Proc. Camb. Phil. Soc.*, xiv., Part 1, p. 30). They observed that the red rays accelerated the formation of spores more quickly than white light and more quickly than when the development took place in the dark: that the green rays retarded the development: that the blue and violet rays retarded the sporulation still more: and that the ultra-violet rays were still more effective, and that they influenced the vitality of the cells detrimentally when the latter were exposed to the influence for some time.

It appeared to be of some interest to study the effect of light during a normal fermentation of hopped wort and other fermentable solutions, and the following notes describe the results of a comparative study of the influence of light and of various spectral colours upon fermentation when conducted in (*a*) unsterilised copper vessels, (*b*) sterilised glass vessels, and (*c*) in unsterilised glass and copper vessels. The effects of the influences were traced in determinations of the optical activity, the copper oxide reducing power, the nitrogen content, the acidity, and the specific gravity of the distilled fermented solution (and therefore the amount of alcohol produced). The temperature of the fermenting wort was noted from time to time.

Description of the Apparatus.

In the first series of experiments there were four copper vessels, and one side of three of these was replaced (1) by ordinary glass, (2) by red glass, (3) by an ammoniacal solution of copper sulphate; whilst, for the experiments in the dark, a copper vessel of the same size and volume as the first three was used. As regards the first three vessels they were arranged with the glass sides facing a fairly large incandescent light, the red glass copper vessel a little further away than the other three, and they were covered with loosely fitting lids. The four vessels, and the central light, were covered with thick black cloth so as to exclude any external light. The time during which the fermentation was allowed to proceed varied from four to seven days.

The nitrogen determinations were by Kjeldahl's method; the specific gravities by a specific gravity bottle; the optical activity by a three shadow polariscope; the copper

* *Proceedings of the Cambridge Philosophical Society*, xiv., Part 4.

oxide by reduction of the oxide by hydrogen in small glass tubes and weighing the copper produced. In determinations of the acidity, 50 cc. of one of the fermented solutions were made up to a definite volume, 4 cc. of litmus solution added, and N/10 alkali until, as far as could be roughly judged, neutralisation was complete; 50 cc. of this solution was then placed in a Nessler cylinder. Fifty cc. of the other solutions made up to the same volume as before were then neutralised until, on taking out 50 cc., the same tint was observed as the original 50 cc. The method was also used in the nitrogen determinations, and it gave most satisfactory results.

As regards the temperature observations, we only give the details in the second series of experiments, and merely note the average temperatures in the others. In the determination of the other constituents we give the mean of two separate experiments.

Sterilised hopped wort was used in the series of Experiments A and C: whilst a specially prepared fermentable solution was used in the series of Experiments B.

Details of the Experiments.

A.

I. Equal volumes of hopped wort were placed in the four vessels and allowed to ferment under the influence of ordinary English yeast. The analysis of the unfermented wort gave: copper oxide reducing power of 20 cc. of a 5 per cent solution = 0·189 grm. Cu. The optical activity at 15° C. for 100 per cent wort = +17·68°.

The N. content; 50 cc. of N/10 H_2SO_4 were used, and 42·7 cc. of N/10 NaHO were required to neutralise excess after Kjeldahling 10 cc. of the wort.

The temperature on starting the fermentation was 15·5° C., and the average temperatures between April 24 at 2 p.m. and April 27 at 9.30 a.m were :—

Dark	=22·6° C.	Red	=22·9° C.
White	=23·2	Blue	=22·4

After the fermentation the following results were obtained.

1. Optical activity for 100 per cent solution at 15° C.:—

Dark	= +14·10°	Red	= +8·08
White	= +7·98	Blue	= +7·86

The number for the dark is high and comparable with that of the original wort. It may be the result of the action of acidifying organisms growing very rapidly; and at the rather low starting temperature the resultant acid dissolving a little copper of the vessel, and thereby influencing detrimentally the growth of the yeast. In the remaining experiments the wort was previously warmed to a temperature higher than 15° C.

2. Copper oxide reducing power—20 cc. of a 5 per cent solution gave :—

Dark ..	=0·1580 grm. Cu.	Red ..	=0·1930 grm. Cu.
White..	=0·1345	Blue..	=0·1895

It is noticeable that the copper oxide reducing power is comparable with the optical activity, with the exception of the white light. The discrepancy is not quite explicable, for in the remaining experiments, the white light ones are quite normal and comparable.

3. Specific gravity :—

Dark.	=999·49	Red..	=992·52
White	=992·22	Blue	=993·99

The specific gravities show differences which are not so marked as in the later experiments; and this may be due to the rise in temperature in the red being much more rapid than in the blue and the dark, owing to the absorption of the red rays; the bacteria have then much less chance of active development in the blue and in the dark than in the red.

The acidities and the nitrogen contents were not determined.

II. The following is the analysis of the unfermented wort :—

The optical activity for 100 per cent solution = +24·34°.

The copper oxide reducing power of 20 cc. of a 5 per cent solution = 0·222 grm. Cu.

The nitrogen content; 25 cc. N/10 H_2SO_4 were used, and 13·7 cc. of N/10 NaHO were required to neutralise the excess after Kjeldahling 10 cc. of the wort.

The wort was pitched on April 30 at 4 p.m., and as an example of the changes in temperature during the fermentation, the following table gives details of the readings in °C. :—

	Dark.	White.	Red.	Blue.
May 1, 10 a.m... ..	22·25	22·25	22·75	22·00
,, 2 p.m... ..	26·75	26·00	27·25	26·00
May 2, 10.30 a.m. ..	23·25	22·75	23·50	23·25
,, 4 p.m-.. ..	24·75	23·50	23·75	24·25
May 3, 11 a.m... ..	23·00	23·00	23·75	23·50
,, 3 p.m... ..	23·60	24·00	24·75	24·10
May 4, 9 a.m... ..	22·75	22·25	23·50	23·00

The average temperatures throughout the fermentation were :—

Dark	=23·8° C.	Red	=24·2° C.
White	=23·4°	Blue	=23·7°

The higher temperature is the red as compared with the others is to be noted.

The fermentations were stopped on May 4 at 9.30 a.m. The one in the red and the dark had marked ethereal odours. The white was less so, and the blue hardly at all. The following results after the fermentations were obtained :—

1. The optical activity for 100 per cent solutions at 15° C.

Dark	= +7·86°	Red	= +7·32
White.. ..	= +6·94	Blue	= +6·54

2. The copper oxide reducing power in 20 cc. of a 20 per cent solution gave :—

Dark..	=0·1170 grm. Cu	Red ..	=0·1015 grm. Cu
White.	=0·0980	Blue..	=0·0860

3. The specific gravity gave :—

Dark	=987·40	Red	=987·11
White	=987·39	Blue..	=987·13

4. The nitrogen content; 10 cc. of each of the fermentations were used in the Kjeldahl method and 25 cc. N/10 acid used to neutralise the NH_3 distilled. The number of cc. of N/10 acid required to neutralise the NH_3 were :—

Dark	=7·95 cc.	Red	=7·85 cc.
White	=8·00	Blue	=7·95

These numbers appear to prove that there is little or no effect upon the nitrogen assimilation or solution.

5. The acidity. The following numbers represent the number of cc. of N/10 alkali used in the neutralisation.

Dark	=13·6 cc.	Red	=15·1 cc.
White	=13·8	Blue	=13·7

III. The following is the analysis of the unfermented wort :—

Optical activity for 100 per cent solution = +6·96°.

The copper oxide reducing power for 20 cc. of a 20 per cent solution = 0·197 Cu.

The nitrogen content; 25 cc. of N/10 H_2SO_4 were used and 21 cc. of N/10 NaHO were required to neutralise the excess after Kjeldahling 10 cc. of the wort.

The wort was pitched on May 6, and the average

temperatures between May 7 at 10 a.m. and May 11 at 9 a.m. were :—

Dark .. .. = 23·8° C. Blue .. .. = 23·9° C.
White .. .. = 24·0

The fermentation in the red was not continued owing to an accident.

The following numbers give the results of the analysis of the various fermentations :—

1. Optical activity for 100 per cent solutions at 15° C.

Dark . .. .. = +2·10° Blue.. .. .. = +2·31°
White .. .. = +2·37

2. Copper oxide reducing power in 20 cc. of 50 per cent solutions :—

Dark.. = 0·0725 grm. Cu. Blue . = 0·0660 grm. Cu.
White. = 0·0970

3. Specific gravity :—

Dark.. .. .. = 997·88 Blue.. .. .. = 997·94
White. .. .. = 998·23

4. The nitrogen content ; 10 cc. of each fermentation was Kjeldahled, and the NH_3 distilled into 25 cc. of N/10 acid. The following numbers represent the amount of N/10 alkali used to neutralise excess of acid :—

Dark .. .. = 22·95 cc. Blue .. .. = 23·37 cc.
White .. .. = 23·60

5. The acidity. The following numbers represent the amounts of N/10 alkali required to neutralise 50 cc. of each of the various fermentations :—

Dark .. .. = 7·77 cc. Blue. .. .. = 6·20 cc.
White .. .. = 12·47

The small development of acidity in the dark and blue is very marked.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 16th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

(Concluded from p. 69).

7. "*The Formation and Reactions of Imino-compounds.* Part VI. *The Formation of Derivatives of Hydrindene from o-Phenylenediacetonitrile.*" By CHARLES WATSON MOORE and JOCELYN FIELD THORPE.

When *o*-phenylenediacetonitrile (I.) is warmed in alcoholic solution containing a trace of sodium ethoxide, it is completely converted into *α-cyano-β-iminohydrindene* (II.), which can be hydrolysed to *α-cyano-β-hydrindone* (III.).

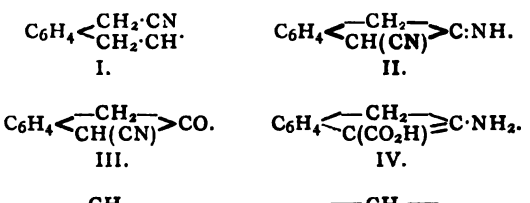
α-Cyano-*β*-iminohydrindene (II.) is a neutral imino-compound, which is hydrolysed by dilute acids, and does not evolve nitrogen with nitrous acid. If, however, the nitrile group is replaced by carboxyl, carboethoxyl, or the carboxylamino-group, the compounds formed are true bases. Thus, *2-aminoindene-3-carboxylic acid* (IV.), *ethyl 2-aminoindene-3-carboxylate* (V.), and *2-aminoindene-carboxyl amide* (VI.) are all bases, which are not hydrolysed by dilute acids, and evolve free nitrogen when treated with nitrous acid. There is no evidence that these compounds are capable of reacting in the imino-form.

α-Cyano-*β*-hydrindone (III.) gives a well-defined *phenylhydrazone*, and on methylation yields *α-cyano-α-methyl-β-hydrindone* (VII.), which gives *phenyleneaceticpropionic acid* (VIII.) on hydrolysis. When, however, the ketone is treated with sodium ethoxide and ethyl iodide, the O-ethyl derivative, *3-cyano-2-ethoxyindene* (IX.), is alone produced.

α-Cyano-*β*-hydrindone (III.) reacts also as a phenol, since it can be readily alkylated by alkyl sulphates, yielding, with methyl sulphate, *3-cyano-2-methoxyindene* (X.) and with ethyl alcohol and sulphuric acid, 3-cyano-2-ethoxyindene (IX.), identical with the compound prepared by the alkylation of the ketone with sodium ethoxide and ethyl iodide. The constitution of these salts is shown by their hydrolysis with dilute acids to *α*-cyano-*β*-keto-hydrindene.

It is therefore probable that groups greater than Me and CN cannot attach themselves to the *α*-carbon atom of *β*-hydrindone or *β*-iminohydrindene, and it is suggested that the term "stearic inhibition" should be applied to this phenomenon rather than "stearic hindrance."

β-Hydrindone (XI.) can be prepared by distilling with steam a solution of 2-aminoindene-3-carboxylic acid (IV.) in dilute sulphuric acid. This substance is quite stable when pure, and does not show any tendency to pass into a brown resin as stated in the literature.



8. "*Valency.*" By JOHN ALBERT NEWTON FRIEND.

The author suggested a new theory of valency by means of which many reactions receive explanations not forthcoming from the usually accepted theory. The theory was also considered in its relation to that of Werner.

9. "*The Esterification Constants of the Normal Fatty Acids.*" By JOHN JOSEPH SUDBOROUGH and JAMES MYLAM GITTINS.

The esterification constants of some sixteen of the more common normal fatty acids, from formic to stearic acid, have been determined.

The value $E^{15°}_{MeOH}$ for formic is 1124 ; acetic, 104 ; propionic, 92 ; and from butyric to stearic acid the value remains nearly constant, varying from about 50 to 54.

10. "*The Anomalous Behaviour of the Hydrogen Electrode in Solutions of Lead Salts and the Existence of Univalent Lead Ions in Aqueous Solutions.*" By HENRY GEORGE DENHAM and ARTHUR JOHN ALLMAND.

An attempt has been made to measure the hydrolysis of lead salts by the hydrogen electrode, but results were obtained which were far higher than those recorded by Ley (*Zeit. Physik. Chem.*, 1899, xxx.. 193), and it was also noticed that many hours were required for the electrode to give a constant potential. This has been proved to be due to the reaction $Pb^{\cdot\cdot} + H \rightarrow Pb^{\cdot} + H^{\cdot}$ occurring at the platinum electrode.

The existence of plumbous acetate in aqueous solutions has been conclusively proved by carrying out an experiment of the type described by Richards, Collins, and Heimrod (*Zeit. Physik. Chem.*, 1900, xxxii., 321) for copper, and by Bose (*Zeit. Elektrochem.*, 1907, xiii., 477) for silver. In hot solution, lead reduces lead acetate to plumbous acetate, but the reaction is reversed in the cold, crystalline lead being deposited in the cold parts of the apparatus. The ionic reaction is evidently—

$$Pb^{\cdot\cdot} + Pb \rightarrow 2Pb^{\cdot}.$$

It has also been proved that a rod of lead, immersed in a molar-normal solution of lead acetate, the upper part of which is kept hot by a steam-jacket, forms a thermo-electric cell. A weak thermo-current flows from the hot solution to the colder below, and, after a week, definite traces of spongy lead may be recognised at the junction of the hot and cold solutions.

11. "*Amphoteric Metallic Hydroxides.*" (Part I.). By John Kerfoot Wood.

The author has investigated the amphoteric character of the hydroxides of arsenic and aluminium. Arsenic hydroxide is a very feeble base, the basic constant being of the dimensions of 1×10^{-14}. The acidic constant, as found by the saponification method, has a value of $6{\cdot}3 \times 10^{-10}$, and an N/10 solution of sodium metarsenite is hydrolysed to the extent of 1·4 per cent at 25°. The dissociation constant of arsenious acid, as found by the conductivity method, has a value of $26{\cdot}5 \times 10^{-10}$.

Aluminium hydroxide is a weak base. The chloride is hydrolysed to the extent of about 4 per cent at 25° and is probably transformed into a basic chloride having the formula $Al(OH)Cl_2$. Sodium metaluminate in N/10 solution is hydrolysed to the extent of about 35 per cent at 25°, the acidic constant of aluminium hydroxide being $6{\cdot}3 \times 10^{-13}$.

12. "*The Use of Pyridine Bases as Halogen Carriers.*" By William Ernest Cross and Julius Berend Cohen.

The authors have shown that the process of halogen substitution in the case of aceto-*p*-toluidide and other amides is preceded by the formation of additive compounds (*Proc.*, 1907, xxiii., 326), but attempts to effect substitution in a similar manner by means of the additive compounds of the pyridine bases with bromine failed.

The result, however, suggested the possibility of employing these bases as halogen carriers, an anticipation which has been confirmed by the following experiments:—

Chlorobenzene.—Chlorine was passed into 50 grms. of benzene containing a few drops of pyridine, and the mixture was warmed to 50°. The action proceeded rapidly with evolution of hydrogen chloride. The product was shaken with alkali, dehydrated, and distilled. Some unchanged benzene and a little dichlorobenzene were separated. The yield of pure chlorobenzene was 30 grms.

Chlorotoluenes.—The chlorination proceeds at the ordinary temperature. From 43 grms. of toluene, 25 grms. of mixed chlorotoluenes were obtained, b. p. 150—165°, together with a few grms. of higher boiling products.

Bromobenzene.—A few drops of pyridine were added to a mixture of 50 grms. of benzene and 120 grms. of bromine, which were warmed to 25° in the water-bath. The action proceeds vigorously with the evolution of hydrogen bromide. The temperature was finally raised to 65—70°. The crude product, which boiled at 148—158°, amounted to 60 grms. The same result was produced with quinoline and *iso*quinoline.

Dibromobenzene.—The *p*-dibromo-compound was obtained in a similar manner. From 33 grms. of bromobenzene, 20 grms. of the para-compound, m. p. 87°, were obtained, the remainder being unchanged bromobenzene. No ortho-compound was detected.

Bromotoluene.—Fifty grms. of toluene yielded 87 grms. of bromotoluene, b. p. 178—182°.

4-Chloro-1-bromotoluene.—Fifty-five grms. of *p*-chlorotoluene gave 56 grms. of chlorobromotoluene, b. p. 220—235°, and a small quantity of lower and higher boiling products.

α-Bromonaphthalene.—The *α*-compound was prepared by dissolving 25 grms. of naphthalene in 100 cc. of chloroform, and adding 36 grms. of bromine and a few drops of pyridine. The mixture was left in the cold for twenty-four hours. After purification, 35 grms. of *α*-bromonaphthalene were obtained, b. p. 276—278°.

13. "*Decomposition of Hyponitrous Acid.*" By Edward Divers.

By suddenly drenching dry silver hyponitrite or mercurous hyponitrite at a temperature but little below 30° with a mineral acid, not greatly diluted in the case of hydrochloric acid or sulphuric acid, and only sufficiently so in the case of nitric acid to avoid inducing its oxidising action, Rây and Gañguli (*Trans.*, 1907, xci., 1866) have obtained nitric acid and nitrogen as products of decomposition, in place of much of the nitrous oxide which was to be expected. This interesting observation throws much light on the nature of the decomposition of silver and mercury hyponitrites by heat. These authors, indeed, suggest that the presence of mineral acids has a "specific directive influence" in determining the form of the decomposition, but that is a notion without evident support. That sulphuric acid should be less effective in bringing about the decomposition is sufficiently accounted for by the fact that the comparative insolubility of silver and mercurous sulphates greatly impedes the action of this acid on the hyponitrites and the rise of temperature which attends it.

Through Rây and Gañguli's observations, we are at length in possession of much knowledge of what the products are when hyponitrous acid decomposes, without explosion, by the heat generated in liberating it from its salts. Since hyponitrous acid yields only nitric acid and nitrogen (water and nitrous oxide being here negligible), whilst silver hyponitrite or mercurous hyponitrite yields, besides these, much nitric oxide and some nitrous acid or nitric peroxide, we can now see that production of the latter substances is due to the unstable oxidised silver or mercury. Writing hyponitrous acid as H_2O,N_2O, and its silver salt as Ag_2O,N_2O, we see that $5N_2O$ becomes $4N_2 + N_2O_5$, the water remaining unchanged in the former case, whereas the silver oxide in the latter case is reduced to metal, whilst its oxygen becomes active. Hence we obtain the two equations—

$$5H_2O_2N_2 = 4H_2O + 4N_2 + 2HNO_3$$

and—

$$3Ag_2O_2N_2 = 4Ag + 2N_2 + 2AgNO_3.$$

Similarly, the production of nitric oxide and peroxide is referable to the reducibility of oxidised silver or mercury, and could only come from hyponitrous acid through a highly improbable cumulative resolution of nitrous oxide.

Royal Society of Arts.—His Majesty the King, who is Patron of the Society of Arts has granted permission to the Society to prefix to its title the term "Royal," and the Society will consequently in future be known as the "Royal Society of Arts."

OBITUARY.

PROFESSOR W. A. SHENSTONE, F.R.S.

We regret to have to announce that the death has recently occurred of Prof. W. A. Shenstone, the Senior Science Master at Clifton College, Bristol. The late Professor took an active part in the movement which had in view the reform of methods of teaching science, and his "Text-Book of Inorganic Chemistry" and "Course of Chemistry" are recognised as authoritative books on modern methods of putting before beginners the elements of chemistry in the most scientific and logical way. Other books written by Professor Shenstone include an excellent "Life of Liebig," in the Century Science Series, and "The Methods of Glass Blowing," while he contributed many articles on chemical subjects to scientific magazines. Shenstone conducted some valuable investigations on the preparation of ozone, and succeeded in obtaining far larger yields than had before been held to be possible. His researches on the use of fused silica for making apparatus were attended with a considerable measure of success, and he acted as technical adviser to the firm of Johnson, Matthey, and Co., Ltd., who have put upon the market vessels of all shapes to take the place of those made of glass. Fused silica vessels are transparent and practically unbreakable by sudden changes of temperature. They are not attacked by acids (except hydrofluoric acid), have a high melting-point, and are harder than glass; they have found an extensive application in many important laboratories, especially for fine quantitative work.

NOTICES OF BOOKS.

Immunochemistry. By Svante Arrhenius. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1907.

This book gives a detailed summary of a series of lectures delivered by the author at the University of California, in Berkeley, California, in the summer of 1904. In these lectures Professor Arrhenius described the results obtained by the application of physical chemistry to the toxins and antitoxins, and gave a review of the experimental material which has been collected relating to the chemistry of immunity. Adopting the view of the chemical school of physiologists, who believe that the effects of antitoxins are of a purely chemical nature, he has brought together the numerous quantitative results which have been obtained, especially by Madsen and his fellow-workers, and has shown that, as far as has yet been observed, all the facts which have been accumulated agree with the known laws of physical chemistry for ordinary chemical compounds. The whole tone of the work is stimulative to further research, and the author has produced a convincing exposition of the subject, showing where uncertainties still exist, and in what directions more work is most urgently wanted. In the three years which have elapsed since the lectures were delivered a large amount of research has been done, and the author has taken particular care to take into account the work of recent investigators.

The British Journal Photographic Almanac, 1908. London: Henry Greenwood and Co.

The "British Journal Photographic Almanac" is an indispensable guide for the use of the amateur and the professional photographer who will find in it a mass of useful information. An editorial article on the advances made in colour photography during 1907 is not too technical for the amateur, and at the same time the scientific reader will find that it gives a very fair account of the main features of recent work on the subject. Copious notes on improved apparatus and processes give the worker every opportunity of making himself acquainted with novelties, and help him to decide the question of their special value to him, while the lists of formulæ for the principal photographic processes and for the developing of different makes of plates and papers are very full, and have been carefully compiled. The chemical tables give reliable data relating to the principal substances used in photography, and a bibliography contains a classified list of books on different branches of the subject.

Descriptive Biochemie. ("Descriptive Biochemistry"). By Dr. Sigmund Frankel. Wiesbaden: J. F. Bergmann. 1907.

This book gives a very full account of the chemical and physical properties of substances occurring in animal organisms, and of the methods of isolating, synthesising, and quantitatively determining the substances themselves and their degradation products. Although the arrangement of the text is systematic and orderly it is not perhaps the best that could be devised, for there is no connection between the subjects of successive chapters, the substances treated of being classified according to their chemical constitution without regard to their occurrence in the organism, except in one chapter which is given to a very short survey of the organs, secretions, &c. The discussions of certain groups of compounds are out of proportion to their relative importance; for instance, the albuminous substances which are classified according to Hammarsten's system are given special prominence, and nearly thirty pages are devoted to the consideration of albuminous substances containing prostetic groups. As a dictionary of biochemistry the work has much to recommend it, its thoroughness and the full references to literature being excellent features from this point of view. The very rapid advance of physiological chemistry in recent years has made it difficult even for the specialist to keep pace, and the value of a work such as this, which may be relied upon as being up to date and complete, is correspondingly great. A spectral table with which the book is provided gives reproductions of some important absorption spectra. In connection with these it would appear that one of them, No. 4, is incorrectly named, for it bears a greater resemblance to the spectrum of hæmatin in acid solution than to hæmatoporphyrin in alkaline solution, although there is undoubtedly a similarity between the general features of the two spectra.

Cours de Physiologie Moléculaire. ("Course of Molecular Physiology"). By Leo Errera. Edited by H. Schouteden. Bruxelles: Henri Lamertin. 1907.

The point of view and scope of this book are both decidedly novel, and it deals with a branch of science which has as yet been but little systematically studied. The region in which the botanist and the physician should be able to work side by side to their mutual advantage is too often shunned by both, and it is precisely this region with which the author endeavours to help his readers to become acquainted. Physical chemistry is regarded with suspicion by biologists, and the existing text-books on the subject are as a rule too difficult and too full for a botanist to use profitably. Hence the great value of this book, which may be regarded as a treatise on certain aspects of physical chemistry written specially for botanists. The general purpose is excellent, and the method of carrying it out is equally good. The book opens with a discussion of the general properties of matter in the three states of aggregation, and in this section phenomena which are of special importance with reference to the living cell are treated fully; for instance the pages on surface tension are very lucid and explicit. The

mutual penetration of solids and fluids is next discussed, in each section the general considerations being followed by applications to the special case of vegetable tissues. The next chapter treats of the movement of water in the plant, and transpiration, and the book concludes with an unbiassed discussion of the theories which have been put forward to explain the ascension of water to great heights in trees. Each theory is explained and summarised, and the objections to it are carefully stated; finally the author decides in favour of the theory advanced simultaneously by Dixon and Joly and Askenasy, and based upon the cohesion of the column of liquid.

Annuaire pour l'An 1908. ("Annual for the Year 1908"). Paris: Gauthier-Villars.

This volume contains besides copious astronomical tables, detailed lists of chemical and physical data, last year's volume having given geographical and statistical information generally. The physical tables include barometric and thermometric correction tables, expansion and vapour tension of liquids, indices of refraction, &c., while in the chemical section thermochemical data, the composition of alloys, &c., are tabulated The book contains in addition articles by G. Bigourdain on the distances of the fixed stars, and by E. Guyon on the School of Practical Astronomy attached to the Observatory at Montsouris.

NOTES AND QUERIES.

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

The Mahler Bomb Calorimeter.—A correspondent would like to know the address of the maker of this calorimeter.

MEETINGS FOR THE WEEK.

Monday, 17th.—Society of Arts, 8. (Cantor Lecture). "Theory and Practice of Clock Making," by H. H. Cunynghame, C.B.

Tuesday, 18th.—Royal Institution, 3. "Membranes—Their Structure, Uses, and Products," by Prof. William Stirling, M.A., LL.D., D.Sc., &c.

— Society of Arts, 8. "Banners in Pageantry," by George W. Eve.

Wednesday, 19th.—Society of Arts, 8. "The Law of Treasure Trove," by William Martin, M.A., &c.

— Microscopical, 8. "Eye-pieces for the Microscope," by E. M. Nelson. "The Life History of a New Protophyte," by E. Tozer. "On Dimorphism in the recent Foraminifer, *Alveolina boscii*," by F. Chapman. Exhibitions of Slides illustrating the Life History of some Diptera, by C. L. Curties, and Improved Mercury Vapour Lamp, by J. E. Barnard.

Thursday, 20th.—Royal Institution, 3. "Wood, its Botanical and Technical Aspects," by Prof. William Somerville, M.A., &c.

— Chemical, 8.30. "Action of Thionyl Chloride and of Phosphorus Pentachloride on the Methylene Ethers of Pyrocatechol Derivatives," by G. Barger. "The Preparation of Conductivity Water," by H. Hartley, N. P. Campbell, and R. H. Poole. "Derivatives of Para-diazolminobenzene," and "Study of the Diazo-reaction in the Diphenyl Series," by G. T. Morgan and Miss F. M. G. Micklethwait. "Organic Derivatives of Silicon—Part VI., The Optically Active Sulphobenzylethylpropylsilicyl Oxides," by F. S. Kipping. "Simple Manometer for Vacuum Distillation," by N. L. Gebhard.

Friday, 21st.—Royal Institution, 9. "The Ether of Space," by Sir Oliver Lodge.

Saturday, 22nd.—Royal Institution, 3. "The Art of Florence," by Selwyn Brinton, M.A.

THE CHEMICAL NEWS.

VOL. XCVII., No. 2517.

THE DETECTION OF SODIUM SULPHITE IN THE PRESENCE OF SODIUM SULPHATE AND SODIUM THIOSULPHATE.

By FRANK E. WESTON, B.Sc., F.C.S., and C. W. JEFFREYS.

THE usual method for detecting the presence of these three salts when together is not a completely satisfactory one, since the precipitate obtained on adding $BaCl_2$ solution to the aqueous solution of the mixture contains not only $BaSO_4$ and $BaSO_3$, but also BaS_2O_3, the amount of the latter increasing considerably with the concentration of the $Na_2S_2O_3$ in the original solution; hence, on filtering and washing the precipitate, digesting with dilute *HCl* and filtering, adding Cl water to the filtrate, a white precipitate of $BaSO_4$ may be derived by the oxidation of the sulphurous acid obtained from either the barium sulphite or barium thiosulphate (see Valentin's "Qualitative Analysis").

The authors have arrived at a test by means of which the presence of sodium sulphite can be proved easily in the presence of sodium sulphate and sodium thiosulphate, or in the presence of the sulphates and thiosulphates of the other alkalis.

The principle of the test depends upon:—

a. The insolubility in water of lead sulphate, lead thiosulphate, and lead sulphite.

b. The solubility in a solution of sodium thiosulphate of lead sulphate and lead thiosulphate, and the insolubility in the same of lead sulphite.

The test may be carried out as follows:—To 5 cc. of a solution containing from 0·05 to 0·1 grm. of the mixed salts, add a solution of $Pb(NO_3)_2$ or $Pb(CH_3.COO)_2$ till no further precipitate is produced; a white precipitate* of $PbSO_4$, PbS_2O_3, and $PbSO_3$ is obtained; now add 5 to 6 cc. of a solution of $Na_2S_2O_3$, containing 1 molecular-grm. weight of the crystallised salt per litre of solution, and well shake; filter, and well wash the insoluble $PbSO_3$ on the filter-paper till free from $Na_2S_2O_3$; pour 3 to 4 cc. of dilute H_2SO_4 on the $PbSO_3$, collecting the filtrate in a clean test-tube. SO_2 can be detected in the funnel by smell and sulphurous acid in the filtrate by its decolorising a solution of $KMnO_4$.

In order to test the efficiency of the reaction, the following experiments were performed. Standard solutions of the various salts were made having the following strengths:—

1. Sodium thiosulphate containing Mol./2 $Na_2S_2O_5.5H_2O$, *i.e.*, 124·11 grms. per litre.
2. Sodium thiosulphate containing Mol./20 $Na_2S_2O_5.5H_2O$, *i.e.*, 12·411 grms. per litre.
3. Sodium sulphate containing Mol./20 $Na_2SO_4.10H_2O$, *i.e.*, 16·108 grms. per litre.
4. Sodium sulphite containing Mol./20 $Na_2SO_3.7H_2O$, *i.e.*, 12·608 grms. per litre.
5. Lead nitrate containing Mol./20 $Pb(NO_3)_2$, *i.e.*, 16·549 grms. per litre.

Test Series 1.—Two cc. of Mol./20 solutions were taken and 2 cc. of Mol./20 $Pb(NO_3)_2$ solution added; in each case a thick white precipitate was obtained. Mol./20 $Na_2S_2O_3$ solution was then added till precipitate dissolved, giving a clear solution, and the number of cc. required observed.

(N.B. — It was found by experiment that 2 cc. $Pb(NO_3)_2$ solution was sufficient to precipitate all the sulphate, &c., in each case).

* This precipitate can be washed by allowing to settle, decanting, adding 5 cc. distilled water, shaking, allow to settle, and again decant.

The following average results were obtained:—

i. PbS_2O_3 precipitate required 25 cc. Mol./20 $Na_2S_2O_3$ to dissolve it.
ii. $PbSO_4$ precipitate required 100 cc. Mol./20 $Na_2S_2O_3$ to dissolve it.
iii. $PbSO_3$ precipitate gave with 100 cc. Mol./20 $Na_2S_2O_3$ a thick milky liquid which remained unaltered even with 200 cc. of thio.

Test Series 2.—The insoluble lead salts were formed in precisely the same manner as in Series 1, but were treated with Mol./2 $Na_2S_2O_3$ solution with the following results:—

i. PbS_2O_3 precipitate required 1·2 cc. Mol./2 $Na_2S_2O_3$ to dissolve it.
ii. $PbSO_4$ precipitate required 4·0 cc. Mol./2 $Na_2S_2O_3$ to dissolve it.
iii. $PbSO_3$ precipitate gave with 100 cc. Mol./2 $Na_2S_2O_3$ a thick milky liquid on shaking, and no apparent change even with 200 cc.

Test Series 3.—(A). Two cc. of each of the Solutions 2, 3, and 4 were mixed, and 6 cc. of the $Pb(NO_3)_2$ solution added; a thick white precipitate was obtained, and on filtering the filtrate gave no further precipitate with the $Pb(NO_3)_2$ solution; the precipitate of $PbSO_4$, PbS_2O_3, and $PbSO_3$ was well shaken with 10 cc. of Mol./2 $Na_2S_2O_3$ solution, producing a thick turbid liquid; this was filtered, and the precipitate ($PbSO_3$) well washed with hot water till filtrate gave no reaction for $Na_2S_2O_3$ ($KMnO_4$ and dilute H_2SO_4); 5 cc. of dilute H_2SO_4 were then poured on the filter; SO_2 immediately evolved (smell), and filtrate instantly decolorised a solution of $KMnO_4$.

(B). Two cc. of Na_2SO_4 solution and 2 cc. of the $Na_2S_2O_3$ were mixed, and 4 cc. of $Pb(NO_3)_2$ solution added; a thick white precipitate obtained which dissolved in 4 cc. of Mol./2 $Na_2S_2O_3$ solution; 4 cc. more of the latter solution were added, and to the clear liquid one drop of the Na_2SO_3 solution was added, when a thick precipitate was obtained, insoluble on shaking.

Test Series 4.—In this set of tests Mol. $Na_2S_2O_3$ solution was used for dissolving the $PbSO_4$ and PbS_2O_3, when it was found that 1 to 2 cc. of this solution was sufficient in all cases to completely dissolve these salts formed as in Series 1 to 3.

The authors are further examining the test as to its applicability in the presence of metals forming insoluble sulphites and thiosulphates.

The Polytechnic, Regent Street, W.
February 8, 1908.

EXPERIMENTS ON THE WASTE GASES OF THE CLAUS-CHANCE SULPHUR PROCESS.

By J. C. THOMLINSON, B.Sc.

THE following experiments showing that in this process the chemical reactions take place almost entirely in the kilns in which hydrogen sulphide and air pass over iron oxide, and not at all during the passage of the gases through the condensing plant, &c., to the factory chimney, were made with an apparatus of which the following is a sketch.

The bottle A, which contains 10 cc. *n*/10 iodine solution, made up to 250 cc. water and coloured with starch paste, is connected at D with the supply from which the sample is taken by means of an aspirator B, the water of which running into a measure C, gives us the volume of the sample which under working conditions is very nearly those of normal temperature and pressure.

The bottle is shaken thoroughly as soon as the gas is allowed to enter at D until the iodine solution is colourless, when the volume of the sample is read off by the measure C.

This test gives us the total amount of waste sulphur

which is there as sulphuretted hydrogen and sulphur dioxide.

We now titrate against decinormal caustic soda solution, thus getting the sulphur as sulphur dioxide, which in the reaction with the iodine solution is converted into sulphuric acid; the difference between the two results represents sulphur as hydrogen sulphide.

The equation which represents the reaction of sulphur dioxide and hydrogen sulphide on iodine solution will at once show that the decinormal solution is made up with an equivalent of sodium carbonate, which plays an important part in the reaction

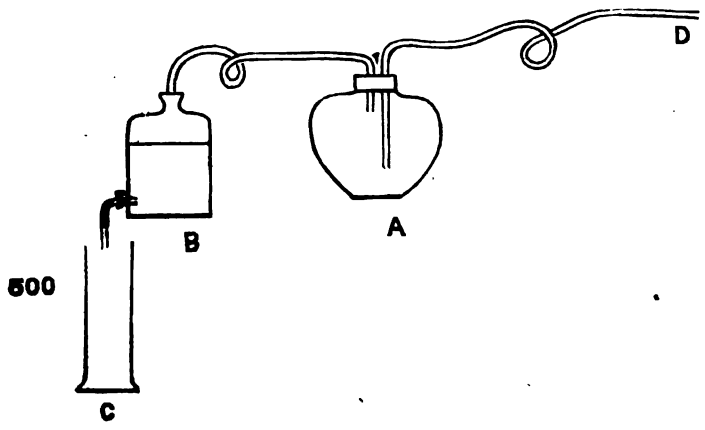
$$2Na_2CO_3 + 4I + SO_2 + H_2S = 4NaI + 2CO_2 + S_1 + H_2SO_4.$$

Example.—The volume of gas drawn off is 500 cc., and the volume of decinormal soda solution used to checking the sulphur dioxide in the sample is 5 cc.

10 cc. *n*/10 iodine solution = 0·016 grm. S = 12·5 grains per cubic foot.

5 cc. *n*/10 NaOH solution = 0·008 grm. = 7·0 per cubic foot.

Hence sulphur as H_2S = 5·5 grains per cubic foot.



THE PREPARATION OF FORMAMIDE FROM ETHYL FORMATE AND AMMONIUM HYDROXIDE.

By I. K. PHELPS and C. D. DEMING.

The action of ammonia on an ester is a typical method for the formation of an acid amide. Hofmann (*Ber.*, xv., 977) states that this reaction is particularly easy when the ester itself is somewhat soluble in water; but that in the case of ethyl formate and aqueous ammonia, when allowed to stand at the ordinary temperature, a considerable part of the acid amide is hydrated to ammonium formate, and the amount of acid amide formed is accordingly diminished. He further states that this hydration goes on to such an extent that a yield much in excess of 70 per cent is impossible.

The work given here records the results of experiments which show that such hydration during reaction may be avoided and the formamide may be obtained in amount equal to that indicated by the theory for the action from ethyl formate and ammonia.

Ethyl formate for use in this work was prepared by treating commercial sodium formate with a mixture of absolute alcohol and concentrated sulphuric acid. The crude product obtained as a distillate was fractioned and portions found to boil between 53° and 56° were treated with fused calcium chloride to remove water and alcohol, and re-distilled after filtering from the calcium chloride. This distillate was then treated with dry ammonia gas obtained by boiling concentrated ammonium hydroxide in a flask connected with a return condenser and leading the ammonia gas obtained in this way through a lime tower. The ammonium formate precipitated was separated by filtration, and then, by fractional distillation, pure ethyl formate distilling within two-tenths of a degree was obtained free from ammonia gas or other impurity.

In all the experiments recorded in the table definite weights of the pure ethyl formate, chilled in an ice and salt mixture, were treated with ammonium hydroxide of known strength similarly chilled, and the temperature of the mass was not allowed to rise above 0° until after the reaction between the formate and the ammonia solution had been largely completed. The formamide produced in each case was obtained by separating from impurities by fractioning *in vacuo* in the usual way and distilling the residue after the low-boiling impurities, largely ammonia, ethyl formate, alcohol, and water, had been removed.

In certain experiments the ethyl formate and ammonium hydroxide were mixed in a 250 cc. distilling flask, and the mixture was fractioned *in vacuo* as soon as it had become homogeneous. In this process the 250 cc. distilling flask containing the mixture was connected to a 100 cc. distilling flask used as a receiver, and the formamide was separated from low-boiling impurities by fractioning *in vacuo* in the usual way, the distilling flask being heated in a water-bath at 60° for fifteen minutes after the pressure on the manometer registered 15 mm. The formamide was then distilled over, by heating the distilling flask in a bath of sulphuric acid and potassium sulphate, and caught in the receiver chilled by a current of cold water (see H. Scudder, *Journ. Am. Chem. Soc.*, xxv., 161).

In other experiments the distillation was not made as soon as the ethyl formate and ammonium hydroxide had become homogeneous. In each of these experiments a definite weight of ethyl formate held in a 250 cc. glass-stoppered reagent bottle was treated with pure, commercial ammonium hydroxide of known strength, after chilling each in a mixture of ice and salt, slowly enough so that at no time during mixing did the temperature of the mixture rise above 0°. The mixture at this time consisting of two layers became homogeneous in about five minutes, but was allowed to stand in the ice mixture for fifteen minutes; for the heat given out showed that the reaction progressed after the mass had become homogeneous. This solution was kept tightly stoppered for a definite time, after which it was transferred to a 250 cc. distilling flask connected to a 100 cc. distilling flask used as a receiver, with the use of the least amount of alcohol to remove the last traces from the side-walls of the bottle. The formamide was separated from low-boiling impurities by fractioning *in vacuo* in the manner described, and the formamide distilled and weighed.

It is obvious from the work recorded in the table that three factors are of influence in the quantitative formation of formamide by the interaction in the cold of ethyl formate and ammonium hydroxide,—the excess of the ammonium hydroxide present, the concentration of the ammonia in the solution, and the time during which the interaction of the two is allowed. From Experiments 1 and 2 of section A of the table it is clear that with fixed amounts of ethyl formate and ammonium hydroxide an increase in the length of the time of the reaction is decidedly advantageous. The comparison of Experiments 1 and 2 with Experiments 5 to 12 shows that increasing the amount of ammonium hydroxide gives a yield in excess of that found with the smaller proportion of ammonium hydroxide. A comparison of Experiments 5 to 12 with one another further

emphasises the point that length of time allowed for the completion of the reaction after the mixture has been kept cool during the first of the reaction long enough to prevent hydration is an important factor. It is clear that it is easily possible to obtain the theoretical amount of amide by allowing the mixture to stand five hours or longer. Two hours standing is not quite sufficient.

No.	Ethyl formate.	Ammonium hydroxide (sp. gr. 0·90).	Time of standing.	Formamide. Theory.	Formamide. Found.
	Grms.	Cc.	Hours.	Grms.	Grms.
			A.		
1.	50	30	4½	30·41	19·06
2.	50	30	240	30·41	23·40
3.	50	50	—	30·41	23·57
4.	50	50	—	30·41	22·60
5.	50	50	1	30·41	28·08
6.	50	50	1	30·41	27·40
7.	50	50	2	30·41	29·33
8.	50	50	2	30·41	29·78
9.	50	50	2	30·41	29·80
10.	50	50	5	30·41	30·48
11.	50	50	5	30·41	30·45
12.	50	50	6½	30·41	30·50
			B. *Treatment with* NH_4OH *and Saturation of Mixture with* NH_3.		
13.	50	10	4	30·41	30·45
14.	50	10	4	30·41	30·00
15.	50	20	4	30·41	30·25

In Section B of the table the results shown were obtained by saturating in the cold, at −10° to 0° for about four hours, the ethyl formate and ammonium hydroxide chilled before mixing in a stoppered reagent bottle fitted with a rubber stopper carrying in one perforation a thermometer dipping into the mixture and in the other the delivery tube for the ammonia gas. This mixture on fractioning *in vacuo* as described above and distilling the formamide left in the distilling flask gave the theoretical amount of formamide.

An experiment showed that a definite weight of formamide and water, when fractioned *in vacuo* as in the process outlined, gave an amount of formamide differing from that taken by less than 0·05 grm.

It is evident that it is possible to obtain from ethyl formate by the action of ammonium hydroxide the theoretical amount of formamide. This may be accomplished by treating the chilled ethyl formate with small amounts of chilled ammonium hydroxide and saturating for some hours in the cold with dry ammonia gas; or, more easily, by treating chilled ethyl formate with larger proportions of chilled ammonium hydroxide and allowing the mixture to stand some hours before distilling *in vacuo*. The essential thing in the operation is to keep the mixture of the ethyl formate and the ammonium hydroxide at a temperature so low that ammonium formate is not a product of the action. —*American Journal of Science*, 1907, xxiv., No. 140.

Influence of Addition of Chloride to the Reaction between Barium Carbonate, Carbon, and Nitrogen. —O. Kühling and O. Berkhold.—The results of this investigation prove that additions of more than 2 per cent of barium chloride lower the temperatures at which a mixture of carbonate and carbon absorbs nitrogen. At temperatures at which the mixture absorbs nitrogen without the addition of any other salt barium chloride does not increase the quantity of cyanide formed. The yield of cyanide is either approximately the same, or else is lower when chloride is present. The lowering of the yield of cyanide is specially noticeable when relatively large additions are made. The yield of cyanamide salt seems to be much diminished by the addition of chloride, and it decreases as the quantity of chloride increases.—*Berichte*, xli., No. 1.

THE INFLUENCE OF LIGHT AND OF COPPER ON FERMENTATION.*

By J. E. PURVIS, M.A., St. John's College,
and
W. A. R. WILKS, B.A., Gonville and Caius College.

(Concluded from p. 81).

IV. THE following is the analysis of the unfermented wort :—

Optical activity for 100 per cent solution = +28·6°.

Copper oxide reducing power in 20 cc. of a 20 per cent solution = 1·052 grms. Cu.

The nitrogen content; 25 cc. of N/10 H_2SO_4 were used and 13·5 cc. N/10 NaHO were required to neutralise the excess after Kjeldahling.

The wort was pitched on May 13 at 5 p.m., and the average temperatures between May 14 at 9 a.m. and May 20 at 9 a.m. were :—

Dark .. .. .. = 23·4° C. Red .. .. = 23·4 C.°
White . .. .. = 23·6 Blue .. .. = 23·3

The following gives the results of the analyses of the various fermentations :—

1. Optical activity for 100 per cent solutions at 15° C.

Dark . .. .. = +5·97° Red .. .. = +4·93
White . .. .. = +4·60 Blue .. .. = +8·08

2. Copper oxide reducing power in 20 cc. of 20 per cent solutions :—

Dark .. = 0·217 grm. Cu Red .. = 0·159 grm. Cu
White .. = 0·148

3. Specific gravity :—

Dark .. .. .. = 987·80 Red .. .. = 987·38
White .. .. = 987·38

4. The nitrogen content; the numbers represent the cc. of N/10 NaHO required to neutralise excess of acid after the distillation of the NH_3 by the Kjeldahl process :—

Dark .. .. = 17·07 cc. Red .. .. = 17·70 cc.
White .. .. = 17·92

5. The acidity. The following numbers represent the amounts of N/10 alkali used to neutralise 50 cc. of each of the fermentations :—

Dark .. .. = 13·6 cc. Red .. .. = 14·5 cc.
White .. .. = 14·4 Blue .. .. = 31·35

In this IV. series, a small leak was noticed in the cell containing the blue solution, so that a little of the copper sulphate was mixed with the wort. The copper sulphate appeared to inhibit the action of the yeast very greatly, as is seen from the optical activity numbers. The bacteria, however, were not affected to the same extent, for the acidity in the blue instead of being less than in the others was more than twice as great. The increased amount of acid would attack the copper vessel, the development of the yeast would be inhibited to a greater extent than the bacteria, and consequently the acidity would be greatly increased.

But the general results and the effects are comparable with those of the wort II. They were both rich worts.

V. The unfermented wort gave the following analysis :—

Optical activity for 100 per cent solution = +11·43°.

The copper oxide reducing power and the nitrogen content were not determined.

The wort was pitched on May 23 at 4 p.m., and the temperature was 21°. And in addition to the four fermentations in the copper vessels, there was also an additional fermentation in a glass beaker under the influence of white light. The average temperatures between May 23 at 5.30 p.m. and May 28 at 9 a.m. were :—

* *Proceedings of the Cambridge Philosophical Society*, xiv., Part 4.

Dark	=24·4° C.	Red	=24·7° C.
White	=24·7	Blue.. ..	=24·9
White (beaker) ..	=24·7		

The following are the results of the analyses of the fermentations :—

1. Optical activity for 100 per cent solutions at 15° C.

Dark	= +5·15°	Red	= +5·00
White	= +5·10	Blue	= +5·13

2. Specific gravity :—

Dark..	=991·43	Red	=991·34
White.	=991·82	Blue	=991·19

3. Acidity. The numbers represent the amounts of N/10 alkali used to neutralise 50 cc. of each fermentation :—

Dark	=20·85 cc.	Red	=13·60 cc.
White	=23·80	Blue	=12·05
White (in glass beaker) ..	=12·90		

The great diminution in the acidity when the fermentation was carried on in the glass vessel compared with the corresponding experiment in the copper vessel, and under the influence of white light, is noticeable.

B.

In the second series of experiments, the fermentations were carried on in sterilised glass vessels, and the fermenting solutions were not of ordinary hopped wort, but contained :—

Glucose	10·00 per cent.
Ammonium sulphate. ..	0·15 „
Ammonium phosphate ..	0·15 „

Of this solution 150 cc. were used in I. series of experiments, and the same volume diluted to about one-half the strength in the II. series of experiments. The experiment marked IA. was conducted in a non-sterilised glass vessel open to the air, and the result showed that the carbon dioxide could easily escape from the other vessels, so that there was nothing to be feared from its action. The other glass vessels were loosely covered with glass-wool, through which thermometers passed into the fermenting wort. The light was filtered through red glass plates for the red rays and through ammoniacal copper solutions for the blue rays, and the effect was compared with the direct effect of white light and with one guarded from contact with any light by the vessel being covered with black cloth. Pure cultures of *S. Cerevisiæ* I. were used to ferment the nutrient solutions.

The optical activity of 100 per cent of the original solutions was = +10·01°. The average temperatures of the series of fermentations between May 28 at 11 a.m. and June 3 at 9 a.m. were :—

I. Dark..	=23·7° C.	II. 23·3° C.	IA. 22·9° C.
White.	=23·3	23·6	
Red ..	=23·7	23·7	
Blue ..	=23·3	22·9	

After the fermentations the following numbers were obtained for the optical activities :—

I. Dark..	= +2·34° C.	II. +1·85°	IA. +2·35°
White.	= +2·35	+1·82	
Red ..	= +2·28	+1·81	
Blue ..	= +2·35	+1·81	

C.

In this series of experiments, four were conducted in unsterilised copper vessels, and two in unsterilised copper vessels, using only red and white light for the latter. The optical activity of a 100 per cent solution was about +16°.

The average temperatures between May 30 at 10.30 a.m. and June 3 at 9 a.m. were :—

I. Glass vessels.		II. Copper vessels.	
Dark ..	- 21·4° C.	White ..	=22·3° C.
White ..	=22·3	Red	=22·0
Red. ..	=22·3		
Blue ..	=21·3		

The values of the optical activities after the fermentations were :—

I. Glass vessels.		II. Copper vessels.	
Dark..	= +3·42°	White ..	= +4·94°
White.	= +3·48	Red. ..	= +7·61
Red ..	= +3·36		
Blue ..	= +3·43		

The numbers obtained from the fermentations in the glass vessels do not show very great differences, whereas those obtained from the copper vessels are very marked. The great difference between the numbers obtained from the copper vessels compared with those of the glass vessels is also very noticeable.

The values of the acidities after fermentation were the following ; the numbers represent the amount of N/10 alkali required to neutralise the acid produced :—

I. Glass vessels.		II. Copper vessels.	
Dark ..	=12·3 cc.	White ..	= 57·4 cc.
White ..	=12·5	Red	= 81·3
Red. ..	=13·3		
Blue ..	=23·8		

The fermentation in the blue light can hardly be compared with the others because the temperature was very low (only about 19°) for a long time, and this probably affected the vitality of the yeast, so that bacterial action became stronger. The numbers obtained from the copper vessels were also very high, and may be explained by the fact that the wort had remained corked up in a bottle for a day ; and although, from the smell, there was no apparent acidification, it is probable there was a development of acid producing bacteria. The acid would dissolve a little of the copper, and thereby retard the action of the yeast.

D.

From a consideration of the results of the fermentations in sections A, B, and C it seemed to be desirable to conduct another series of fermentations in the four copper vessels, in order to discover what amount of copper, if any, was dissolved during the process of the fermentation. And, for this purpose, a litre of hopped wort was placed in each of the vessels, and the fermentations went on for five days under exactly the same conditions as those described in the preceding experiments. At the end of this time, the liquors were filtered, evaporated to dryness, and the residues ignited until all the organic substances were burnt away. What remained was dissolved in acid, and the CuO estimated in the usual way. Owing to an accident, the residue of the fermentation in the red light was lost ; but the following numbers show the amounts of CuO obtained from the three others, in percentages of the original wort.

Dark.. ..	=0·0072 per cent CuO
White ..	=0·0051 „
Blue.. ..	=0·0052 „

There can be little doubt, therefore, that the observed differences in the numbers obtained when the fermentations went on in the copper vessels were due to the solution of a little of the copper influencing the action of the yeast ; and it is of interest to note the smaller quantity of CuO found in the fermentations in the white and blue than in the dark.

General Results.

The more important results of the preceding experiments are :—

1. That fermentation when carried on under sterilised and unsterilised conditions in glass vessels, and under the influence of various spectral colours as well as of white light and also in the dark, was not seriously influenced, as shown by determinations of the optical activities of the fermented solutions. The small differences in the numbers and particularly of the acidities may be owing to experimental errors. Further experiments will be necessary to confirm these differences, and with a stronger light, like that of the arc.

2. That fermentation when conducted in copper vessels, but otherwise under the same conditions, is influenced very considerably, as shown by the marked differences in the numbers obtained from the acidity, optical activity, &c. It is not suggested that this influence was caused by rays of light of varying degrees of refrangibility, except indirectly. It appears that copper dissolved from the fermenting vessels largely determined the course of the fermentations. For example, the results obtained under the influence of blue light prove that the inhibitory effect of this light on the development of acidifying bacteria was to decrease the amount of acid produced in the fermenting wort, and, therefore, to lessen the amount of copper dissolved. On the other hand, the fermentations under the influence of red light and in the dark gave better facilities for a more vigorous growth of these bacteria. The acid produced thereby dissolved a little of the copper; and its inhibitory effect on a normal growth of the yeast, and a regular fermentation, is evident from the varying numbers obtained in the different determinations. The larger amount of CuO obtained in the fermentation in the dark as compared with the others appears to be evidence in favour of this view. But contributory causes may be owing to the differences of temperature; for the temperature of the fermentations in the dark and the red were usually a little higher than in the blue, and the solvent action of the acid on the copper would be thereby increased. At the same time it is probable that, as the fermentations proceeded, the CO_2 produced from the break down of the sugar, would also dissolve a little of the copper, and this also should be added as a further influence.

3. Another fact which is indicated by these experiments is the influence of the original composition of the wort. In a good wort, the yeast appeared to resist the action of the copper better than in a poor wort; for the differences in acidity, &c., are much less marked in the good worts than in the poor ones.

In view of these varying results, it will be of importance to study more systematically the influence of different amounts of copper, and of other metals like silver, upon the growth of yeast and fermentation, a problem which has been kindly suggested by Dr. Horace Brown, who called our attention to some experiments conducted at Rothampstead on the influence of small quantities of copper and silver on the growth of various plants.

The above investigation was conducted in the University Chemical Laboratory.

Lecture Experiments with Ozone.—C. Harries.—To demonstrate the absorption of ozone by turpentine-oil a cylinder about 30 cm. high is filled with ozone from the ozoniser, and well shaken with about 50 cc. of oil of turpentine. If a potassium iodide starch-paper is now introduced into the cylinder it remains absolutely unchanged, showing that all the ozone has been absorbed. To show that ozone ignites with oil of turpentine, a high broad cylinder is filled with ozone, and a piece of blotting-paper saturated with turpentine oil, and dried, is quickly put into the cylinder. After a few seconds the turpentine ignites and burns with a dark red luminous flame, much soot being formed.—*Berichte*, xli., No. 1.

THE ELECTROLYTIC DEPOSITION OF ZINC, USING ROTATING ELECTRODES.*

II.

By T. SLATER PRICE, D.Sc.

In a paper read before this Society on June 12, 1906 (*Transactions of the Faraday Society*, 1906, ii., 85; also Chemical News, vol. xciv., p. 18), a special form of apparatus was described for the electrolytic deposition of zinc (and other metals), using a rotating cathode, and also a modification of the apparatus of Kollock and Smith (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1255) was suggested as being more convenient. Since that time the various methods for the deposition of zinc have been more thoroughly tested by the author, and the present communication gives an account of the results obtained.

The experiments were commenced with the idea of investigating the effect on the quantitative deposition of zinc, using a rotating cathode, of the addition of various electrolytes. A solution of zinc sulphate, of approximately known strength, was made up, and in order to determine the amount of zinc present in an aliquot portion the method of Kollock and Smith was used, since the addition of extraneous electrolytes other than sulphuric acid is then unnecessary, and consequently there is less risk of introducing impurities into the solution. The zinc sulphate used was obtained from Kahlbaum; it was re-crystallised, care being taken that crystallisation took place below 39° C. Having found the strength of the solution, experiments were commenced with the rotating cathode. At the outset, however, a difficulty was met with, since the results with the mercury cathode were always lower than the others. It was at first thought that this might be due to some of the zinc being deposited in the spongy condition when the platinum cathode was used, but further experiments did nor support this view. The method of Kollock and Smith was therefore subjected to a closer examination.

Since electrolytic methods for the quantitative estimation of zinc were in question, it was necessary to analyse the zinc sulphate used by the ordinary methods of quantitative analysis. The most convenient method of doing this, and one which avoids any loss due to manipulation, is to heat the salt in a platinum crucible, and convert it directly into the oxide (*cf.* Fresenius, "Quant. Analysis"). The heating was done very carefully at first, and after all the water of crystallisation had been driven off, the crucible was gradually raised to a high temperature by means of a Mecker burner, and heated till the weight was constant. In same cases the zinc sulphate was weighed directly into the crucible, and in others 10 cc. of a solution containing a known weight of the salt were pipetted into the crucible, and evaporated to dryness on the water-bath. The mean percentage of zinc obtained from seven determinations was 22·74, the greatest deviation from the mean being 0·03. The calculated percentage of zinc in $ZnSO_4.7H_2O$ is 22·74, so that the zinc sulphate used may be taken as pure.

For each electrolytic determination 1 grm. of zinc sulphate, contained in 10 cc. of a solution of the salt, was taken. In some few cases 1 grm. of the sulphate was weighed out directly and used for the determination, this making no difference in the results obtained. All the weights, pipettes, &c., used had been carefully calibrated.

Experiments Using the Rotating Cathode.

In the experiments described in the previous paper the platinum cathode was always silvered before being used, but since Medway (*Amer. Journ. Sci.*, 1904, iv., 18, 56), using a platinum crucible for the rotating cathode, found that it was unnecessary to first coat it with either silver or copper, a number of determinations were made without previous treatment of the cathode. It was found that if the zinc was dissolved off soon after it had been deposited

* A Paper read before the Faraday Society, March 19, 1907.

TABLE I.

Grms. of Na_2SO_4.	Grms. of Na acetate.	Drops of glacial acetic acid (1).	Cc. of 0·880 NH_4OH.	C.	V.	*t*.	Per cent Zn.	Error.
2	1	—	—	2	5·5—6·5	15	22·84	+0·10 (*b*)
2	1	—	—	2	6—7	14	22·82	−0·08 (*c*)
2	1	2	—	2	—	18	22·82	+0·08 (*c*)
2	1	2	—	2	—	14	22·79	+0·05 (*b*)
2	1	3	—	2	6·5	19	22·86	+0·12 (*b*)
3	1	3	—	2	—	14	22·84	+0·10 (*b*)
2	1 [1]	—	—	0·35 (2), 2 (13)	—	15	22·84	+0·10 (*b*)
2	1+1 [8]	2	—	2	—	13	22·85	+0·10 (*b*)
—	2 [19]	—	—	0·25 (7), 0·5 (3), 1 (9), 2 (10)	—	29	22·76	+0·02 (*b*)
2	1	3	0·5 [14]	0·5 (4), 1 (5), 2 (10)	—	19	22·84	+0·10 (*c*)
2	1	6	1 [15]	2	—	20	22·81	+0·07 (*c*)

(*a*) 40 drops = 1 cc. (*b*) Trace. (*c*) All out.

TABLE II.

Grms. of Na_2SO_4.	Grms. of Na acetate.	Drops of glacial acetic acid.	C.	V.	*t*.	Per cent Zn.	Error.
2	1	2	2	6·5	14	22·74	0·00
2	1	2	0·5 (8), 1 (30), 2 (5)	—	43	22·71	−0·03
2	1	2	2	—	14	22·71	−0·03
2	1	—	2	6	15	22·75	+0·01
2	1	—	2	—	15	22·73	−0·01
2	1	—	2	6·5	13	22·72	−0·02
2	1	—	2	—	14	22·79	+0·05
2 (*a*)	1	—	2	—	14	22·71	−0·03

(*a*) In this case the electrode was coated with copper instead of with silver.

the cathode was not affected, but if the deposit was allowed to remain on the platinum for some time it gradually alloyed with it, as is the case when the ordinary method, using a stationary cathode (and anode), is used.

The results obtained are given in Table I., where C is the current used, V is the voltage, and *t* the time of deposition (in minutes). The voltage was not measured in every case. In those cases where the current was gradually increased the numbers in round brackets represent the time (in minutes) during which the current was kept at the value given by the figures before the bracket. The numbers in square brackets denote the number of minutes the electrolysis had been proceeding before the reagent in question was added. The notes denote whether the deposition was complete, or whether a trace of zinc remained in solution. The cathode used had the dimensions given in the previous paper, and the number of revolutions per minute was 600—700. The electrolytes added were sodium sulphate and acetate, since the previous investigation showed that good results were then obtained.

The results are high in every case, so that there is evidently a systematic error. Moreover, in spite of the high results, in most cases a trace of zinc was left in solution. Potassium ferrocyanide was used in testing for zinc, 5 cc. of the solution from which the zinc had been deposited being taken for the test. The test is very delicate, and rough quantitative measurements gave that the amount of zinc left in the solution, as indicated by the term "trace," was from 0·0002 to 0·0006 grm.; if this amount of zinc were allowed for, the percentages of zinc found would be slightly higher than those given.

It is possible that the high result is due to the deposition of a small amount of spongy zinc. The deposition potential of the hydrogen ions on platinum is less than that of the zinc ions, and consequently the former would be deposited in preference to the latter. In spite of the vigorous stirring of the electrolyte it is possible that an excess of hydroxyl (OH) ions would be left in the solution in the neighbourhood of the cathode at the commencement of the electrolysis, with the consequent formation of zinc hydroxide and deposition of spongy zinc (*cf.*, Foerster, "Elektrochemie wässeriger Lösungen," p. 290).

Experiments in which acetic acid was added, or the current gradually increased, gave no better results. In some cases the error was very small, and it was hoped that a good method had been found, but repetition, under what seemed to be the same conditions, gave a bad result; sometimes a series of good results would be obtained, and these would be followed by a series of bad ones (the table does not give the results of all the experiments carried out; those omitted lie between the extreme results given). This is only a particular case of what occasionally occurs in zinc depositions, viz., that certain methods often give good results at first, but further trial shows them to be unsatisfactory.

When ammonia was added all the zinc was deposited, but the results were uniformly high.

The position of the cathode with respect to the anode has an effect on the deposit. If it is placed so that the bottom edge is about level with the lower ring of the anode, the deposit on the lower part is liable to be spongy; the concentration of the stream lines of the current would be greater on this lower part, thus increasing the current density too much. To obviate this the cathode was placed (approximately) in a symmetrical position with respect to the anode ring.

To do away with any error which might be due to impurities in the sodium sulphate and acetate, these salts were re-crystallised; but the results were no better.

The results apparently were independent of the manner in which the cathode was treated, as was shown by a number of experiments.

In all the following experiments, except where specially stated, the electrode was silvered before the zinc was deposited on it. It was found most convenient to dissolve off both the zinc and the silver after each estimation, and not to endeavour to use the same coating of silver throughout all the experiments (*cf.*, Ingham, *Journ. Am. Chem. Soc.*, 1904, xxvi., 1269). The saving in time thus effected, using a rotating cathode for the silvering, compensates for the increased amount of silver used.

The first series of experiments gives some of the results obtained when sodium sulphate and acetate, with or without the addition of acetic acid, are used (see Table II.).

(To be continued).

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, February 6th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

THE PRESIDENT referred to the loss sustained by the Society owing to the death of Mr. W. A. Shenstone, F.R.S. (elected in 1876), and of Mr. R. J. Friswell (elected in 1871).

Certificates were read for the first time in favour of Messrs. Arthur John Allmand, B.Sc., Central Laboratories, Widnes; William Henry Benson Baker, B.A., Frognal Dene, Hampstead, N.W.; Josiah Leonard Bowen, 8, West Field, Lightcliffe, near Halifax; Charles Gilling, 30, Carnarvon Road, Barnet; Alwyne Harcourt Meade, Cedar House, St. Neots; Herbert Richard Neech, 20, Colegrave Street, Lincoln; Thomas Richards Phillips, Stanhope House, Abergavenny; Francis Edward Richards, B.Sc., County Secondary School, Redruth; William Wheatley, B.A., 21, Bairstow Street, Preston.

A ballot for the election of Honorary and Foreign Members was held, and the following were subsequently declared duly elected:—Armand Emile Justin Gautier, Albin Haller, Johann Wilhelm Hittorf, Joseph Achille Le Bel, Henry Louis Le Chatelier, Theodore William Richards, Otto Wallach.

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

*14. "*The Metallic Picrates.*" By OSWALD SILBERRAD and HENRY ABLETT PHILLIPS.

Older investigations on the picrates show so many discrepancies that a systematic revision of the work has been undertaken, with the result that the water of crystallisation and properties of the commoner salts have been definitely established. Several new salts were also described.

*15. "*Some Physico-chemical Properties of Mixtures of Pyridine and Water.*" By HAROLD HARTLEY, NOEL GARROD THOMAS, and MALCOLM PERCIVAL APPLEBEY.

With the view of examining the effect of the gradual replacement of water by pyridine on the electrical conductivity of salt solutions, and of tracing a connection between the properties of the solvent and of the solution, the following physical constants have been determined:—The density, viscosity, and surface tension of pyridine-water mixtures at 0° and 25°, the density and viscosity of one-eighth weight-normal solutions of lithium nitrate in a series of mixtures at 0° and 25°, and the molecular conductivity of these solutions at various dilutions at the same temperatures.

The density and viscosity curves all show a maximum deviation from the line joining the end values in the neighbourhood of 30 mol. per cent pyridine, both at 0° and 25°. No evidence was found for the existence of the discontinuities described by Dunstan, Thole, and Hunt (*Trans.*, 1907, xci., 1718) all the observations lying on smooth curves.

By the application of Stokes's equation respecting the limiting velocity of a small sphere moving in a viscous medium under the influence of a constant force, the variation in the size of the solvent atmospheres attached to the ions at infinite dilution has been calculated.

It was shown to what extent the variations of the molecular conductivity of lithium nitrate solutions with the composition of the solvent can be ascribed to changes—(1) in the coefficient of ionisation, (2) in the fluidity of the solution, and (3) in the aggregation of solvent particles round the ions.

DISCUSSION.

Mr. DUNSTAN pointed out that some misconception had evidently arisen in the minds of the authors as to the curves published by Messrs. Thole, Hunt, and himself (*Trans.*, 1907, xci., 1728). For the purpose of more clearly representing the composition of the hydrates of pyridine, the tangents to the curves at the points of flexure were produced, and this gave rise to the erroneous impression that the curves were built up in sections. He also drew attention to the fact that every such "discontinuity" in the density curve was repeated in the viscosity curve, and instanced the work of Pickering in support of the contention that such hydrates do exist in solution.

Mr. R. J. CALDWELL agreed with the authors that the usefulness of most previous work on strong solutions is impaired by the fact that "volume normal" solutions have been employed instead of solutions made up by weight. He had already measured electrical conductivities of solutions made up by weight, taking account of the density, as the authors appeared to have done.

The specific rotatory power of sucrose varied from 66·5° in pure water to 83·8° in pure pyridine, but until the concentration of the pyridine reached 30 per cent the rotatory power did not vary much from the value obtained in pure water (Wilcox, *Journ. Physical Chem.*, 1901, v., 592). At low concentrations, the pyridine, existing doubtless in a hydrated condition, was prevented from exerting any influence on the dissolved sugar. The values obtained by the authors for the conductivity of lithium nitrate appeared to be entirely analogous, leading to the same conclusion with regard to the pyridine.

Mr. HARTLEY said that he did not believe in the existence of any irregularities in the density or viscosity curves, as the greater the care with which the determinations were made the more nearly did the experimental values lie on smooth curves. The determination of density was so much more accurate an operation than the determination of viscosity, that he did not think the anomalies in the viscosity curves could be explained by those in the density curves. In reply to Dr. Barger, he said that the authors recognised that pyridine possessed residual valencies, although the liquid molecules were probably unassociated, otherwise it would have no dissociating influence on salts dissolved in it.

*16. "*The Constitution of Umbellulone.* (Part III.). By FRANK TUTIN.

Semmler's recent statements (*Ber.*, 1907, xl., 5017) respecting the constitution of umbellulone are based on experiments conducted with "β-dihydroumbellulone" and its derivatives. Since the material employed by Semmler consisted of highly impure umbellulone, there is no evidence in support of the assumption that "β-dihydroumbellulone" is a derivative of umbellulone, but, on the other hand, the experimental facts lead to the contrary conclusion.

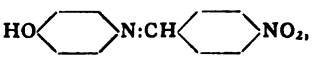
In addition to this uncertainty regarding the source of the preparation which had been called "β-dihydroumbellulone," this has now been shown to be a mixture, consisting chiefly of an unsaturated ketone, but also containing a saturated one, and it can only be from the latter that Semmler has prepared homotanacetonedicarboxylic acid.

Semmler's results, therefore, are devoid of significance in so far as they pertain to the constitution of umbellulone.

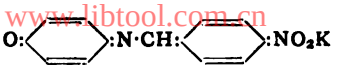
*17. "*Colour and Constitution of Azomethine Compounds.*" (Part I.). By FRANK GEORGE POPE.

The nitrohydroxyazomethine compounds show an entirely different absorption spectrum from that of their alkali salts when the nitro- and hydroxyl-groups are in the para-position to the azomethine group, and, from the similarity of the ·N:CH· grouping to the ·N:N· grouping in many respects, it would seem apparent that the alkali salts of these compounds could be formulated on a di-quinonoid

basis, the free hydroxyl compounds being represented thus:—



and the alkali salts as—



(compare Hewitt and Mitchell, *Trans.*, 1907, xci., 1251).

A similar state of things may also be observed, although to a slightly less extent as regards absorption, when the nitro- and hydroxyl-groups are in the ortho- and para-positions to the azomethine grouping.

The following compounds were described:—p-4-*Nitrobenzylideneaminophenol*, m. p. 168·5°; o-4-*nitrobenzylideneaminophenol*, m. p. 161°; p-3-*nitrobenzylideneaminophenol*, m. p. 154°; o-3-*nitrobenzylideneaminophenol*, m. p. 135°; o-*hydroxybenzylidene*-m-*nitroaniline*, m. p. 132°.

Discussion.

Dr. Hewitt remarked that, whilst the general type of absorption was similar for corresponding azo- and azomethine compounds, replacement of a nitrogen atom by a methenyl group increased the oscillation frequency.

*18. "*The Preparation of l-Benzoin.*" By Alexander McKenzie and Henry Wren.

l-Benzoin, obtained from *l*-mandelamide and magnesium phenyl bromide, melts at 131—132·5°, reduces Fehling's solution, and has $[\alpha]_D$ 105 − 118·6° for $c = 0{\cdot}9232$ in acetone solution.

Discussion.

Dr. McKenzie, in reply to Dr. Lowry and Dr. Lander, stated that no racemisation, either partial or complete, had so far been observed with *l*-benzoin.

19. "*Organic Derivatives of Silicon.* Part V. *Benzylethylsilicone, Dibenzylsilicone, and other Benzyl and Benzylethyl Derivatives of Silicane.*" By Robert Robison and Frederic Stanley Kipping.

Benzylethylsilicone, BzEtSiO, prepared from benzylethylsilicon dichloride (Kipping, *Trans.*, 1907, xci., 720), has little in common with benzyl ethyl ketone; it boils at 305—315° (22 mm.), is not reduced by various reagents, and gives neither an oxime nor a hydrazone; molecular weight determinations in acetic acid solution point to the formula $(BzEtSiO)_3$.

Benzylethylsiliconesulphonic acid is easily obtained by sulphonating the silicone with sulphuric acid; the *barium* salt, $(C_9H_{11}SiSO_4)_2Ba$, is soluble in water, but does not crystallise well.

Dibenzyl ethyl silicol, $Bz_2EtSi{\cdot}OH$, was obtained as an oil; it passes spontaneously into *dibenzylethylsilicyl oxide*, $(BzEtSi)_2O$, a crystalline substance melting at 54°.

Tribenzylsilicyl chloride, Bz_3SiCl, crystallises in prisms melting at 141°, and is decomposed by water, giving tribenzylsilicol.

Dibenzylsilicon dichloride, Bz_2SiCl_2, prepared from silicon tetrachloride and magnesium benzyl chloride, crystallises in massive prisms, and melts at 50—52°; when decomposed with water, it yields a *hydrol* of the molecular formula $Bz_2Si(OH)_2$, which crystallises in long asbestos-like needles melting at about 101° (*α-hydrol*), and also an isomeric *hydrol*, which forms large, transparent prisms melting at about 75° (*β-hydrol*); the latter was recently described by Dilthey (*Ber.*, 1905, xxxviii., 4132). In some cases, only one of these hydrols is formed, and in others both are obtained, the *β*-isomeride predominating, but the conditions which determine their formation are unknown. Both hydrols pass into *dibenzylsilicone* (an oil) when they are heated, and the *β*-compound is readily reproduced by treating this oil with water; the *α*-hydrol is not regenerated in this way. Both hydrols give termolecular *dibenzylsilicone*, $(Bz_2SiO)_3$ (m. p. 98°), when they are heated with acetic anhydride.

The experimental data do not yet afford any explanation of the existence and relationship of these isomeric hydrols.

20. "*The Residual Affinity of the Coumarins and Thiocoumarins as shown by their Additive Compounds.*" By Arthur Clayton.

The coumarins and thiocoumarins combine with mercuric chloride, forming compounds of the type $R,HgCl_2$, where R is a coumarin or a thiocoumarin. This combination takes place with the following coumarins and their sulphur analogues:—Coumarin, 7-methylcoumarin, 4:7-dimethylcoumarin; 3:4:7-trimethylcoumarin, thiocoumarin, 7-*methylcoumarin* m. p. 125—126°, 4:7-*dimethylthiocoumarin* m. p. 118—119°; and 3:4:7-*trimethylthiocoumarin* m. p. 124—125°. The thiocoumarins are prepared by the action of phosphorus pentasulphide on the corresponding coumarins, and unlike the coumarins, yields oximes and phenylhydrazones.

Other oxonium compounds of the coumarins were described.

21. "*The Influence of Foreign Substances on Certain Transition Temperatures and the Determination of Molecular Weights.*" By Harry Medforth Dawson and Colin Gyrth Jackson.

The depression of the temperatures at which changes take place in certain condensed systems on the addition of foreign substances has been examined. The changes investigated were:—(1) The conversion of sodium thiosulphate primary pentahydrate into the corresponding dihydrate at 48·1°; (2) the transformation of sodium bromide dihydrate into the anhydrous salt at 50·67°; and (3) the formation of tachhydrite ($CaCl_2,2MgCl_2,12H_2O$) from calcium and magnesium chloride hexahydrates at 22·40°.

Constants representing the depression of the transition temperature when 1 grm.-molecule of the foreign substance is contained in 100 grms. of the saturated transition solution have been calculated. From a knowledge of these constants, the corresponding invariant points may be utilised for the purpose of obtaining the molecular weights of dissolved substances.

22. "*The Bromination of p-Hydroxydiphenylamine.*" By Alice Emily Smith and Kennedy Joseph Previté Orton.

The bromination of *p*-hydroxydiphenylamine is rendered difficult by the readiness with which oxidation to a quinoneanil, $Ar{\cdot}N{:}C_6H_4{:}O$, is effected. All attempts to prepare mono- or di-bromo-derivatives failed, a tribromo-compound apparently being the primary product of bromination. It is a very remarkable fact that isomeric tri- and tetra-bromo-derivatives are not formed, the successive entrance of the bromine atoms following a single definite course.

The *tri-*, *tetra-*, *penta-*, *hepta-*, and *octa-bromo-p hydroxydiphenylamines*, and the corresponding *benzoxy*-derivatives and *quinoneanils* (*phenyliminoquinones*) were described.

23 "*The Decomposition of Ammonium Dichromate by Heat.*" By William Marrs Hooton.

It is generally stated that ammonium dichromate on ignition decomposes quantitatively into nitrogen, water, and chromium sesquioxide; but Darby, in 1849, pointed out that a little ammonia was always liberated, and the author has found that the gaseous products of decomposition in air or in a vacuum always contain appreciable amounts of oxygen and oxides of nitrogen. Moreover, the solid residue is not homogeneous: it contains dark brown flakes, and evolves water when heated to bright redness.

If, instead of igniting the salt, it is decomposed slowly by heating it in air below its ignition temperature (190°) until the weight is constant, atmospheric oxygen takes part in the change. The final product is a hydrated form of chromium dioxide, having the composition $2CrO_2,H_2O$. It is a glistening black powder, which on being strongly heated yields oxygen, water, and chromium sesquioxide without incandescence. When heated with hydrochloric acid, chlorine is freely evolved. When boiled with potassium hydroxide solution, it yields potassium chromate and chromium hydroxide.

If ammonium dichromate is heated below its ignition temperature in a vacuum or in absence of oxygen, the final product is a dull greenish black powder having the composition $H_2Cr_2O_4$. This is not a hydrated form of chromium sesquioxide, for it incandesces brightly when heated to 400°. Even after boiling with water, filtering, and drying, it still incandesces when heated to 400°. During incandescence, water is formed, but no gas is liberated, and the sesquioxide formed is not bulky. This compound is not acted on by boiling potassium hydroxide solution, and only slowly by hot hydrochloric acid, no chlorine being evolved.

24. "*The Effect of Constitution on the Rotatory Power of Optically Active Nitrogen Compounds.*" (Part II.). By Humphrey Owen Jones and John Robertshaw Hill.

The authors have resolved a set of five optically active nitrogen compounds, and have determined the rotatory powers of the basic ions (compare *Trans.*, 1906, lxxxix., 282).

The compounds contain the *p*-bromophenyl, methyl, and allyl groups with one of the homologous groups, ethyl, *n*- or *iso*propyl, *iso*butyl, or *iso*amyl, and differ from those, forming one of the sets already described only in the replacement of one of the hydrogen atoms of the phenyl group by bromine.

The *n*-propyl, *iso*butyl, and *iso*amyl compounds were resolved by means of *d*-bromocamphorsulphonic acid, the *iso*propyl compound by means of *d*-camphorsulphonic acid, and the ethyl compound by means of *d*-tartaric acid. The following table summarises the results obtained :—

	Melting point of iodide.	Molecular rotatory power— Of ion at 15°.	Of iodide in alcohol.
Ethyl.. ..	142—143°	−31°(?)	−20°
n-Propyl ..	142—143	+141	+144
*iso*Propyl ..	153	+161	+165
*iso*Butyl ..	133—134	+96	+117
*iso*Amyl ..	135—136	+94	+111

The rotatory power of the iodide in chloroform was determined when possible, and was found to be greater than in alcohol; autoracemisation of the iodide occurred in chloroform in all cases.

The maximum rotatory power is found in the propyl compounds just as in the set of unbrominated compounds, also the rotatory power of this set of compounds, with the exception of the ethyl compound, is considerably greater than that of the unbrominated set.

25. "*Malacone, a Silicate of Zirconium.*" By Alexander Charles Cumming.

The author finds that the formula ZrO_2,SiO_2 corresponds more closely with the observed composition of malacone than does the formula $3ZrO_2,2SiO_2$ assigned to it by Kitchin and Winterson (*Trans.*, 1906, lxxxix., 1568).

A detailed examination gave no reason to suspect the identity of the zirconia, or to suspect the presence of an unknown impurity. The presence of argon cannot be explained by the presence of any new radio-active element, as the radio-activity can be sufficiently accounted for by the presence of radium.

26. "*The Reducibility of Magnesium Oxide by Carbon.*" By Roland Edgar Slade.

The isolation of magnesium by direct reduction of the oxide by carbon has been effected at temperatures above 1700°, and the chief hindrance to the preparation of the metal by this reaction has been found to be due to the back reaction which occurs at lower temperatures between magnesium and carbon monoxide.

Various methods were adopted for removing the metal from contact with the carbon monoxide. Rapid evacuation of the vessel in which the reaction occurs, absorption of the magnesium by molten copper, and reduction of magnesia in presence of aluminium, or in a swift stream of hydrogen, have all proved successful.

27. "*The Crystal Form of Halogen Derivatives of Open-chain Hydrocarbons with reference to the Barlow-Pope Theory of Structure.*" By Frans Maurits Jaeger.

The author has determined the crystalline forms of a number of halogen derivatives of open-chain hydrocarbons, such as tetrabromo-$\beta\delta$-dimethylpropane, 1 : 3 : 5-hexatriene, di- and tetra-bromide and tetra-iodoethylene, for the purpose of ascertaining whether predictions concerning their crystalline form, based on the theory of Barlow and Pope, are justified by the experimental results. In accordance with the indications of the theory, it is found that the substances named above exhibit a close morphotropic relationship. The theory also allows of the prediction that tetrabromo-$\beta\beta$-dimethylpropane should be represented by a pseudo-cubic assemblage; actually it is found that, although the compound crystallises in the monosymmetric system, it is pseudo-cubic.

28. "*The Determination of the Rate of Chemical Change by Measurement of the Gases Evolved.*" By Francis Edward Everard Lamplough.

Further work on the above subject has confirmed the results given in a former communication (*Proc.*, 1906, xxii., 280), with the exception of the paragraph referring to the decomposition of ammonium nitrite.

A few experiments have been performed on the action of sodium hypochlorite on carbamide. The rate of evolution of gas does not give results which can be interpreted by a simple law, owing to the complexity of the reaction; the velocity of the reaction, as measured by the rate of evolution of gas, rises to a maximum and then diminishes.

The reaction between nickel carbonyl and iodine has been found to be of a complex nature, even in cases where either reagent is in considerable excess. When the nickel carbonyl is present in great excess, a remarkable phenomenon is met with, the action proceeding in a steady manner until a point is reached at which it abruptly terminates without warning.

29. "*The Temperatures of Spontaneous Crystallisation of Mixed Solutions, and their Determination by Means of the Index of Refraction. Mixtures of Solutions of Sodium Nitrate and Lead Nitrate.*" By Florence Isaac.

Previous experiments on simple solutions established a "super-solubility curve" which marks their temperatures of "spontaneous" crystallisation.

The supersolubility curve for a mixture of three constituents, sodium nitrate, lead nitrate, and water, has now been determined by measurement of the refractive indices.

In the first set of twenty-two experiments, the proportion of lead nitrate to water was kept constant as 3 : 10, whilst the amount of sodium nitrate varied; in the second set of seventeen experiments, the proportion of sodium nitrate to water was kept constant as 3 : 4, whilst the amount of lead nitrate varied.

In both cases it was found that as the temperature of the liquid falls the refractive index rises to a maximum value. A few crystals usually appear in the supersaturated solution before the maximum index is reached, and at, or about, the maximum point spontaneous crystallisation sets in and gives rise to a dense shower of crystals.

In each set, these maximum points determine the "supersolubility" curve.

The two supersolubility curves may be regarded as plane sections of a supersolubility surface for all possible mixtures of the three constituents.

The curves of spontaneous crystallisation were also determined by experiments with the same solutions in sealed glass tubes. These cannot be made to crystallise until they have reached the temperature already determined from the refractive indices.

The solubility curves for these mixtures were also determined, and their relation to the supersolubility curves established.

30. "*Contributions to the Chemistry of the Terpenes.* Part III. *Some Oxidation Products of Pinene.*" By

George Gerald Henderson and Isidore Morris Heilbron.

The acid $C_9H_{15}CO_2H$, obtained from pinene as previously described (Henderson and Gray, *Trans.*, 1903, lxxxiii., 1299), could not be brominated directly, but was converted into its *chloride*, a viscous, colourless oil. When heated with bromine, this yields the *chloride* of a *bromo-acid*, $C_9H_{14}Br{\cdot}COCl$, an oily liquid, from which, with water, the *bromo-acid*, $C_9H_{14}Br{\cdot}CO_2H$, was obtained. This is a crystalline solid, and when boiled with aqueous sodium carbonate yields the *hydroxy-acid*, $C_9H_{14}(OH).CO_2H$, crystallising from water in colourless prisms. Its *sodium* salt is readily, and its *silver* salt very sparingly, soluble in water.

In preparing the bromo-acid, a small quantity of a crystalline, neutral *compound*, apparently of the composition $C_{10}H_{13}OBr$, separated. Along with the hydroxy-acid there was also obtained a small amount of another *acid*, probably of the formula $C_{10}H_{14}O_2$, which is crystalline and insoluble in water. Its *silver* salt crystallises from water in colourless needles.

The ketone previously described (*loc. cit.*) has now been obtained in a pure state, and has the formula $C_9H_{14}O$. On reduction, it yields the *alcohol*, $C_9H_{15}{\cdot}OH$, a colourless, oily liquid, from which a *phenylurethane* and an *acid phthalic ester*, both crystalline solids, have been prepared.

When heated with ammonium formate, the ketone is converted into the formyl derivative of an *amine*, $C_9H_{15}{\cdot}NH_2$, which is a colourless liquid with a disagreeable odour, and is almost insoluble in water. Its *hydrochloride*, which is extremely easily soluble in water, crystallises in silky needles, and its *platinichloride* in pale yellow leaflets.

The chlorinated oxidation product which is separated during the purification of the ketone is a white, crystalline solid of formula $C_{10}H_{15}OCl$. It is slowly decomposed when heated with alcoholic sodium ethoxide, and yields a colourless, crystalline compound, which does not contain chlorine and has a penetrating odour.

31. "*A β-lactonic Acid from Acetone and Malonic Acid.*" By Andrew Norman Meldrum.

When malonic acid and acetone are mixed with acetic anhydride and a little sulphuric acid, the malonic acid dissolves, and after twenty-four hours a new, crystalline acid is obtained, which melts at 97° and decomposes at a higher temperature. The composition and the molecular weight (determined by the boiling-point method) lead to the formula $C_6H_8O_4$.

The substance is saturated; it decomposes easily, under various conditions, into acetone and malonic acid (or, in place of malonic acid, carbon dioxide, and acetic acid), and when heated with aniline it gives, acetone, carbon dioxide, and acetanilide.

Since the acid is monobasic and yields the salts $C_6H_7O_4Ag$, $C_6H_7O_4Na$, $C_6H_7O_4K,H_2O$, it is evidently the *β-lactone* of *β-hydroxyisopropylmalonic acid*,—

$$\begin{array}{l} CMe_2{\cdot}CH{\cdot}CO_2H. \\ \quad\;|\quad\;| \\ \quad O\text{---}C \end{array}$$

PHYSICAL SOCIETY.

A Dinner of the Society was held on Tuesday, February 11th, at the Hotel Cecil, London, when the chair was taken by the President, Prof. J. Perry, F.R.S., and a number of distinguished guests and Fellows of the Society were present, including Sir David Gill, K.C.B., F.R.S.; Sir William Ramsay, K.C.B., F.R.S.; Sir William White, K.C.B., F.R.S.; Sir J. Denison Pender, K.C.M.G.; Rear-Admiral Sir H. B. Jackson, K.C.V.O.; Principal Sir Arthur Rücker, F.R.S.; Sir Joseph Swan, F.R.S.; Col. R. E. Crompton, C.B., R.E.; Prof. W. G. Adams, F.R.S.; Mr. Shelford Bidwell, F.R.S.; Dr. C. Chree, F.R.S.; Mr. W. Duddell, F.R.S.; Prof. Carey Foster, F.R.S.; Dr. R. T. Glazebrook, F.R.S.; Prof. Reinold, F.R.S.; Mr. J. Swinburne, F.R.S.; Prof. S. P. Thompson, F.R.S.; and Dr. W. Watson, F.R.S.

Sir Arthur Rücker, in proposing the toast of "Our Guests," remarked that it was perhaps a little difficult to understand why all the guests that evening were not already Fellows of the Society; if they were not, they certainly ought to be, for the work of such men as Sir David Gill (whom we welcomed back to this country, though the loss to South Africa was great) and of Sir William White was intimately connected with the objects of the Physical Society.

Sir David Gill, in responding, expressed his pleasure at being present as a guest of the Society, and referred to the foremost position hitherto occupied by Great Britain in the world of physics, as shown by the honoured names of Faraday, Maxwell, Kelvin, and others, whose traditions were now being handed down by such men as Lord Rayleigh and Prof. J. J. Thomson.

Sir William Ramsay, in responding to the same toast, dwelt on the relations of physics and chemistry. A great deal of useless physical work was done at times because the physicist determined the physical constants of substances without troubling to ensure the purity of the body under observation. This remark applied, for example, to a great deal of Regnault's work. Chemistry had been defined by Huxley as the dirty part of physics. However true that definition might have been at the time when it was given, chemistry had now outgrown such a statement, and had extended its field not merely into close touch with physics, but with mathematics also. In fact one of the chief difficulties of the chemist at the present time was the solution of the mathematical problems involved in chemistry, and there would be a great opening for "tame mathematicians" who would hold themselves at the disposal of the chemist.

In response to the President, Prof. E. B. Rosa, of the National Bureau of Standards, Washington, expressed his pleasure at being able to be present on this occasion. He had been much interested in visiting the National Physical Laboratory, and observing the great progress that had been made since his last visit five years ago. At the National Bureau of Standards they were making satisfactory headway, and he hoped that the laboratory would shortly be equal to any national laboratory in the world. In the United States they were spending a great deal of money on the science of agriculture, because agriculture was a national asset. He suggested that England similarly might find it a profitable investment to devote the money spent in constructing one battleship per annum to the National Physical Laboratory, instead of preparing for war.

Sir William White, in proposing the toast of "The Physical Society," congratulated the Society on accomplishing so much in a comparatively short life. Unfortunately it became more and more necessary to specialise. Physics was the basis of many of our societies; but, however comprehensive a society might be, new societies sprang up from time to time, and individually we had to be content with a small corner of knowledge.

In responding, The President dwelt on the importance of research. At the present day there were many science teachers and many compilers of books who did no research. They were well up in the letter of science, but not in the spirit thereof, with the result that their writings lacked a most essential quality which could be gained only by actual research. If such men attended the meetings of the Society they would soon develop a taste for research, and would benefit accordingly. He appealed also to the leaders of physical science to attend the meetings, not for their own benefit, but from a sense of duty: for he was sure there was nothing so inspiriting to the younger members as contact with men who had carried out important work. He felt himself that any scientific spirit that he had acquired was due to personal contact in his early days with such men as Kelvin and his brother Thomson.

Dr. CHREE, the President-elect, also responded to this toast, and in a humorous speech described how the membership of the Society might be increased, and how such things as logarithmic spirals might be impressed on the mind of the schoolboy.

In conclusion, THE PRESIDENT proposed the health of the Honorary Secretaries, to which Mr. W. R. COOPER and Prof. W. CASSIE responded.

NOTICES OF BOOKS.

Valentin's Practical Chemistry. By W. R. HODGKINSON. Tenth Edition. London: J. and A. Churchill. 1908.

IN the tenth edition of this book some easy practical work has been introduced in the early chapters on the composition of air and water, diffusion, sulphur, and sulphuric acid, and some compounds of carbon, followed by elementary quantitative work, including both gravimetric and volumetric analysis, and methods of determining molecular weight. The reactions of the metals, arranged in analytical groups, are next treated, and general qualitative analysis schemes and tables are given. The new matter includes in addition discussions of the microscopical structure of some common alloys, illustrated by photographs, and the section on the properties and separation of the rare earths has been enlarged and brought up to date.

The Chemistry of Gas Manufacture. By HAROLD M. ROYLE, F.C.S. London: Crosby Lockwood and Son. 1907.

THE chemistry of the making of gas is treated in outline in this book, which students who intend to take up the manufacture of coal-gas as a special study may find useful as an introductory course. Short accounts are given of the most accurate and rapid methods of testing both the raw materials and the products of gas works, and the experimental directions are sufficiently full for the use of a student who has some knowledge of general chemical analysis. Special attention has been paid to the numerical examples, typical analyses being carefully explained in detail. Photometric methods of testing gas are included, and appendices give the full official instructions for testing coal-gas, besides miscellaneous extracts of matter interesting to gas chemists from English and foreign periodicals.

The Law of Master and Servant. By T. C. JACKSON, B.A., LL.B. London: Macdonald and Martin.

A SUCCINCT account of the law relating to master and servant is given in this book, which contains the full text of the Employers' and Workmen Act, 1875, the Employers' Liability Act, 1880, and the Workmen's Compensation Act, 1906. The interpretation of the Acts is made clear by short discussions of typical cases, and general principles are emphasised, while the tabulated form into which the information is thrown as far as possible makes the book very convenient for employers of labour to consult, in order to decide questions relating to their liabilities. The subject of apprenticeship is considered in one chapter, and another deals shortly with the law of the giving of testimonials and characters.

Syntheses by means of Methyl and Ethyl Adipates.—L. Bouveault and Locquin.—In this paper the authors give a list of the cyclopentanone derivatives of methyl and ethyl adipate, which can be prepared by the action of sodamide, NH_2Na, upon the adipates dissolved in anhydrous ether or in benzene, and enumerates their chief physical constants.—*Comptes Rendus*, cxlvi., No. 3.

CORRESPONDENCE.

HELIUM VACUUM TUBES.

To the Editor of the Chemical News.

SIR,—It is well known that helium vacuum tubes sooner or later become useless in consequence of the gradual absorption of the gas, and there must be hundreds of such tubes which have been thrown aside as no longer serviceable. A method of making such tubes useful again was suggested to me by the paper read at the Royal Society on November 7th by Soddy and Mackenzie. They found that on opening such tubes under mercury the greater part of the occluded gas was liberated by the action of the mercury on the film of volatilised aluminium. To put this to the test, a helium tube which had become useless was opened, a globule of mercury was introduced, and the tube was then exhausted and re-sealed. It showed at first only mercury lines, but on running the tube for a short time the helium suddenly flashed out, and the tube is now serviceable again for furnishing reference lines. For this purpose such a tube containing mercury is even better than a tube showing helium only, as the double yellow and green lines of mercury divide up an otherwise blank gap between yellow and green. The lines shown by the tube now are:—

Helium	6678·4
,, ...	5875·8
Mercury	5790·5
,, ...	5769·6
,, ...	5461·0
Helium	5015·7
,, ...	4922·1
,, ...	4713·3
,, ...	4471·6
,, ...	4388·8

and some others in the violet besides hydrogen, 6563·0 faintly.

On gently warming the tube its brilliancy increases considerably. Both helium and mercury lines became brighter, but on further heating the mercury lines became intensely brilliant at the expense of the helium lines, and at one stage the curious effect was produced of the upper half of the capillary illuminated by mercury, and the lower half by helium, so that in the spectroscope the lines belonging to mercury were picked out from those belonging to helium.—I am, &c.,

W. MARSHALL WATTS.

Davy-Faraday Laboratory,
February 7th, 1908.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Berichte der Deutschen Chemischen Gesellschaft. Vol. xli., No. 1, 1908.

Constitution of the Fatty Acid Salts of Beryllium.—B. Glassmann.—The fact that the action of acetic acid anhydride on beryllium acetate, Be_4Ac_6O, gives the normal beryllium salt, $(CH_3CO_2)_2Be$, is confirmation of the constitution which the author deduced for the fatty acid salts of beryllium. He has found that beryllium not only forms salts of the type Be_4Ac_6O, but also of the type Be_2Ac_2O with oxyacids and some haloid fatty acids, *e.g.*, beryllium lactate,—

$$CH_3.CH(OH).C<\begin{matrix}O\\O\end{matrix}>Be$$
$$O \qquad .H_2O.$$
$$CH_3.CH(OH).C<\begin{matrix}O\\O\end{matrix}>Be$$

Among other salts which, from their methods of formation, physical and chemical properties, and especially in their power of crystallising from acid solution, are to be regarded as ortho-salts, may be mentioned bismuthyl acetate, $BiO(CH_3{\cdot}CO_2)$; zirconyl tartrate, $ZrO(C_4H_4O_6)$; zirconyl acetate, $Zr(CH_3CO_2)_2O$, &c.

Carbon Suboxide.—Otto Diels and Paul Blumberg.—Diels and Wolf have explained the formation of carbon suboxide from malonic ester by supposing that a symmetrical reaction occurs. Thus :—

$$CH_2\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix} = 2C_2H_4 + 2H_2O + C\begin{matrix}\equiv CO\\\equiv CO\end{matrix} \quad . \quad . \quad I.$$

While Michael thinks that the compound is a β-oxypropiolic acid lactone,—

$$CH_2\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix} = 2C_2H_4 + 2H_2O + C\begin{matrix}\equiv C\\\equiv CO\end{matrix}>O \quad . \quad II.$$

If the formula is $C\begin{matrix}\equiv CO\\\equiv CO\end{matrix}$ the calculated values for the molecular refraction and molecular dispersion are $M_D = 15{\cdot}49$, $\gamma - \alpha = 0{\cdot}749$; $\gamma - \alpha$ is the molecular dispersion for the red (α) and blue (γ) hydrogen line, while for $C\begin{matrix}\equiv C\\\equiv CO\end{matrix}>O$ the corresponding values would be $M_D = 13{\cdot}57$, $\gamma - \alpha = 0{\cdot}435$. Thus the molecular dispersion of the substance of Formula I. is nearly double that of the substance of Formula II. Moreover, since, according to Brühl, in unsaturated heterocyclic ring systems there is a decided depression of the values of the refraction and dispersion, according to Michael's formula M_D and $\gamma - \alpha$ would be less than 13·57 and 0·435 respectively. The author's experiments, however, show that this is not the case. For M_D they have obtained the value 16·6, and for the dispersion in two series of experiments 0·736, 0·739, 0·862. This indicates that Michael's formula must be incorrect. It is interesting to notice that both the molecular refraction and dispersion of carbon suboxide found by experiment are high. Generally substances with the system $>C=C-C=<$ of double binding, show a decided "exaltation" of their molecular refraction and dispersion, while those with cumulated unsaturated atomic groups, *e.g.*, $\begin{matrix}CH_3\\CH_3\end{matrix}>C=C=CH_2$, are normal. Carbon suboxide belongs to a new type in which only double bonds are present, $O=C=C=C=O$, and in this also "exaltation" occurs.

Action of the Silent Electric Discharge on Damp Methane.—Walther Löb.—When methane saturated with water is exposed at the ordinary temperature to the action of a silent discharge, a white substance insoluble in all solvents is obtained. Simultaneously methyl esters of fatty acids are formed. The insoluble substance gives on analysis values which agree well with the formula $C_9H_{15}O$, or a polymer. All preparations of this insoluble substance contain traces of ash which consist of silicate. The appearance of higher aliphatic acids is easily explained if it is remembered that damp methane always undergoes the changes $CH_4 + H_2O = CO + 3H_2$ and $CO + H_2O = H.COOH = CO_2 + H_2$. The ethylene residues may then unite, and the following reactions occur :— $H.COOH + (CH_2{:}CH_2)_x = CH_3(CH_2)_{2x-1}.COOH$.

MISCELLANEOUS.

The British Association, Dublin Meeting, Sept. 2nd.—The following have been elected by the Council of the British Association to be presidents of sections at the meeting of the Association to be held in Dublin in September next under the general presidency of Mr. Francis Darwin, F.R.S. :—Section A (Mathematical and Physical Science), Dr. W. N. Shaw, F.R.S., Director of the Meteorological Office; Section B (Chemistry), Prof. F. S. Kipping, Professor of Chemistry in University College, Nottingham; Section C (Geology), Prof. J. Joly, F.R.S., Professor of Geology and Mineralogy in the University of Dublin; Section D (Zoology), Dr. S. F. Harmer, Superintendent of the University Museum of Zoology, Cambridge; Section E (Geography), Major E. H. Hills, C.M.G.; Section F (Economic Science and Statistics), Lord Brassey; Section G (Engineering), Mr. Dugald Clerk, M.Inst.C.E.; Section H (Anthropology), Prof. W. Ridgeway, Professor of Archæology in Cambridge University; Section I (Physiology), Dr. John Scott Haldane, F.R.S., University Reader in Physiology at Oxford; Section K (Botany), Dr. F. F. Blackman, F.R.S., Professor of Botany in the University of Leeds; Section L (Educational Science), Prof. L. C. Miall, formerly Professor of Biology in the University of Leeds. Invitations to deliver evening discourses during the meeting of the Association at Dublin have been accepted by Prof. H. H. Turner, F.R.S., Savilian Professor of Astronomy at Oxford, who will take as his subject "Halley's Comet"; and Prof. W. M. Davis, of Harvard University, whose lecture will be entitled "The Lessons of the Colorado Cañon."

NOTES AND QUERIES.

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

Biological Chemistry Examination.—I should be obliged if any reader would advise me as to best books from which to obtain the information necessary for the Examination in Biological Chemistry of the Institute of Chemistry.—P.

MEETINGS FOR THE WEEK.

MONDAY, 24th.—Royal Society of Arts, 8. (Cantor Lecture). "Theory and Practice of Clock Making," by H. H. Cunyngham, C.B.

TUESDAY, 25th.—Royal Institution, 3. "Membranes—Their Structure, Uses, and Products," by Prof. William Stirling, M.A., LL.D., D.Sc., &c.

—— Royal Society of Arts, 4.30. "Irrigation in Egypt under British Direction," by Sir Hanbury Brown, K.C.M.G.

—— Faraday Society, 8. "Hydrolysis as Illustrated by Heats of Neutralisation," by V. H. Veley. "Study of the Sulphur Anion and of Complex Sulphur Anions," by J. Knox.

WEDNESDAY, 26th.—Royal Society of Arts, 8. "Problem of Road Construction with a view to Present and Future Requirements," by H. S. Hele-Shaw, LL.D., F.R.S., and Douglas Mackenzie.

THURSDAY, 27th.—Royal Institution, 3. "Wood, its Botanical and Technical Aspects," by Prof. William Somerville, M.A., &c.

FRIDAY, 28th.—Royal Institution, 9. "Explosive Combustion, with Special Reference to that of Hydrocarbons," by Prof. W. A. Bone, F.R.S.

—— Royal Society of Arts, 8. (Shaw Lectures on Industrial Hygiene). "The Removal of Dust and Fumes in Factories," by Dr. John Scott Haldane, F.R.S.

—— Physical, 5. "Contact Potential Differences Determined by means of Null Solutions," by S. W. J. Smith and H. Moss. "Experimental Examination of Gibbs' Theory of Surface Tension as the Basis of Adsorption, with an Application to the Theory of Dyeing," by Mr. Lewis.

SATURDAY, 29th.—Royal Institution, 3. "The Art of Florence," by Selwyn Brinton, M.A.

THE CHEMICAL NEWS.

Vol. XCVII., No. 2518.

THE ABSORPTION SPECTRA OF THE VAPOURS OF BENZENE AND ITS HOMOLOGUES AT DIFFERENT TEMPERATURES AND PRESSURES, AND LIKEWISE OF SOLUTIONS OF BENZENE.*

By WALTER NOEL HARTLEY, F.R.S., D.Sc.,
Royal College of Science, Dublin.

The author having been engaged since the year 1877 in investigating and correlating the physical and chemical properties of aromatic substances in relation to their chemical structure or constitution, he has latterly found it desirable that several very definite compounds should be examined in a state of vapour, as well as in solution.

The work of E. Pauer (*Annalen*, 1897, lxi., 363), W. Friederichs (*Zeit. f. Wissenschaftliche Photographie*, 1905, p. 633), and of L. Grebe (*loc. cit.*, 1905, p. 363) is referred to in detail. The vapours of benzene and several of its derivatives have been examined (1) at different temperatures and constant pressure; and (2) at different pressures, the temperature being constant. The previous measurements of Pauer, Friederichs, and Grebe have been confirmed, and reconciled where they do not show complete agreement with each other. The records of temperature and pressure, and the shortening of the exposure of the photographic plates, constitute important differences between the work of the former investigators and that of the author.

Details of the following photographs are given :—

Absorption Bands in the Spectrum of Benzene Vapour at different Temperatures and a Barometric Pressure of 755·5 mm.

Temperatures.	Number of bands photographed and measured.
12·5°	55
25	84
43	82
53	56

Absorption Bands in the Spectrum of Benzene Vapour at 11·5° and different Pressures.

Pressures in mm.	Number of bands measured.
778	36
483	38
253	46
21	44

The same at 100° and different Pressures.

683	9
589	13
478	14
381	16
279	17
172	18

The same at 100°.

767	5
591	9
484	9
332	12
206	13
142	11
99	14
88	15

The same at 100°.

Pessures in mm.	Number of bands measured.
92	25
69	36
43	50

The same at 100°.

67·5	31
52·5	54
37·5	60
28·5	72
22·5	75
15·5	88
9	52
5	38
4	30

Absorption Bands in the Spectrum of Toluene Vapour at different Temperatures and constant Pressure.

Temperatures.	Number of bands measured
10°	16
30	20
40	16
50	20
60	23
70	21
80	24
90	23
100	18

The Absorption Spectrum of Toluene Vapour at different Pressures and constant Temperature.

Pressures in mm.	Number of bands measured.
763	18
563	16
371	18
174	15
43	15

The Absorption Bands of Ethylbenzene Vapour at different Temperatures.

Temperatures.	Number of bands measured.
16·5°	19
40	18
70	8
100	2

General absorption occurs here.

The same.

20	17
36	15
52	5
71	3
100	Complete absorption.

The Absorption Bands of o-Xylene Vapour at different Temperatures.

Temperatures.	Number of bands measured.
20°	23
45	21
72	
100	No bands, general absorption.
121	

Absorption Bands of m*-Xylene Vapour at different Temperatures.*

Temperatures.	Number of bands measured.
11°	26
40	41
70	6
100	5

General absorption occurs between 2652 and 2429.

* Abstract of a Paper read before the Royal Society, Dec. 12, 1907.

The same, *p*-Xylene Vapour.

Temperatures.	Number of bands measured.
10°	30
40	25
70 } General absorption from	5
100 } 2790 to 2416.	7

The same, Cymene Vapour.

17·5°	0
40	7
70	9
100	9

The same, Mesitylene Vapour.

18·5°	2
45	2
72	2
100	2
120 } General absorption.	
140 }	

The measurements are given of similar groups of bands which occur in the vapour-spectra of benzene, toluene, ethyl benzene, and the three isomeric xylenes; benzene and toluene being compared at ordinary temperatures and also at 30° below their respective boiling-points. A tabulated statement is also made of the heads of strong bands which appear to be common to benzene and its homologues. The intensities of the bands in the benzene vapour-spectrum at 100°, and different pressures, was compared with those at temperatures below its boiling-point, and it was seen that the bands at 100° are almost identical with those at lower temperatures, but with this difference, that, at lower temperatures, some of the bands at the less refrangible end of the spectrum are feeble and less well defined. The vapour-spectrum of benzene is divided into groups of bands which are caused by the overlapping of two or more similarly constituted spectra differing in intensity. The strong bands number fifty-four, there being twenty-seven in each of two spectra. In addition, there are thirty feeble bands, which also fall into two series of similar groupings, but with less regularity. The entire number of bands observed between 12·7° and 25°, under a pressure of 759·5 mm., are thus resolved into four spectra, of which two are composed of strong and two of weak bands.

Summary and Conclusions.

As regards the vapour-spectra, it is proved that benzene at 100° C. has the same molecular mass as at 25° or 12·7°.

The absorption bands at 100° are almost identical with those at lower temperatures, with variations as to definition in the less refrangible rays. The important influence of the position of the substituted hydrogens in benzene, upon the number and position of the bands in the spectra of its homologues, is clearly demonstrated.

Variations in the spectra of benzene at different temperatures and pressures are explained by the fact that there are two different kinds of absorption which are sharply defined and may be differentiated. First, there is the general absorption, which is broadened and extended towards the less refrangible rays by rise of temperature; secondly, there is the selective absorption, which includes all the narrow individual bands and groups of bands; they are not widened and displaced by rise of temperature, and such changes of this nature that they undergo are the effect of the overlying general absorption. The selective absorption is best studied by raising the general absorption to a maximum (at 100°), and studying the spectra produced by reduction of pressure. In this manner, any changes due to general absorption are eliminated. From the fact that increased sharpness and definition of the narrow bands is easily produced by rise of temperature, and also by reduction of pressure, the general absorption is clearly shown to be caused by encounters between the molecules, and the numerous narrow bands are to be ascribed to the vibrations of the atoms or atom-complexes within the molecules. This confirms the conclusion drawn from the study of solution-spectra published in 1881 (*Journ. Chem. Soc.*, xxxix., p. 153), in 1882 (*loc. cit.*, xlvii., p. 685), and 1885 (*Phil. Mag.*, 1885, [5], xix., p. 35).

The similar groups of bands occurring in benzene and toluene, and the close similarity between the spectra of toluene and ethylbenzene, with the further resemblance between *m*-xylene and toluene and ethylbenzene, is evidence that the mode of vibration within the benzene nucleus or ring-structure is in a great measure unaffected by the side-chain substitution.

A distinction is drawn between the absorption spectra of vapours, called *vapour-spectra*, and of solutions, called *solution-spectra*, and the relationship of one to the other is explained. Previous investigations carried on by the author for many years are briefly referred to, and it is shown how the views entertained have been confirmed by the investigation of the *vapour-spectra*. Attention is drawn to the insufficiency of ordinary chemical formulæ to represent the constitution of organic compounds, particularly of those like benzene which are of an endothermic character, since they do not take into account the distribution of energy in the molecule, and this obscures the view of the physical character of chemical structure or constitution. In short, whereas bonds and linkings in the formulæ usually written belong to a conception of chemical structure which is statical, the molecular constitution of such substances as are under discussion, when based upon the evidence derived from their optical properties, is essentially dynamical. ("Single, double, or treble linkings are simply an incomplete method of representing the relation of the carbon-atoms to each other at some particular phase of their vibrations," *Phil. Mag.*, 1885, xix., p. 55). The relation of *solution-spectra* to *vapour-spectra* is shown, by reference to the results obtained by Pauer, Hartley, and Dobbie, and by Grebe. The view entertained by Baly and Collie (*Chem. Soc. Trans.*, 1905, lxxxvii., p. 1332) that benzene has seven and no more than seven *solution-bands*, indicative of a definite making and breaking of a double linkage of the carbon atoms in the ring, has been carefully examined, and the author finds this to be incompatible with well-ascertained facts. From the measurements and numerical relations of the wave-lengths of bands in *solution-* and *vapour-spectra*, it is explained how four, six, seven, eight, or nine bands may be recognised in *solution-spectra*, six of which are similarly constituted, and four of these are not only similarly constituted but very nearly of equal width, intensity, and persistency; that is to say, they have the same coefficient of extinction, and in all other respects an almost exact similarity. They correspond with four groups of *vapour-bands* which are formed by the four different series of bands which overlap, and they occur where they overlap to the greatest extent.

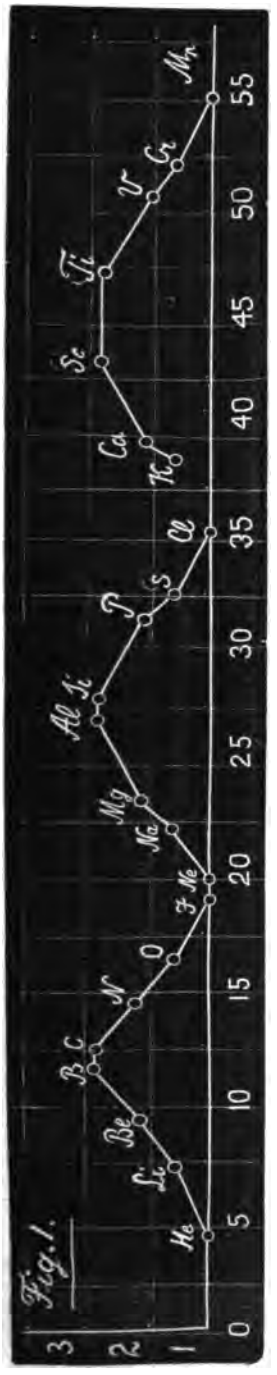
Density of Graphite. — H. Le Chatelier and S. Wologdine. — The authors have performed a series of determinations of the density of graphite, using mixtures of acetylene bromide and ether. The specimens were subjected to a careful purification, and the results showed that both natural and artificial graphites when perfectly pure have a density of 2·255 (water at 4°), the mean temperature of the graphite being 15°.—*Comptes Rendus*, cxlvi., No. 2.

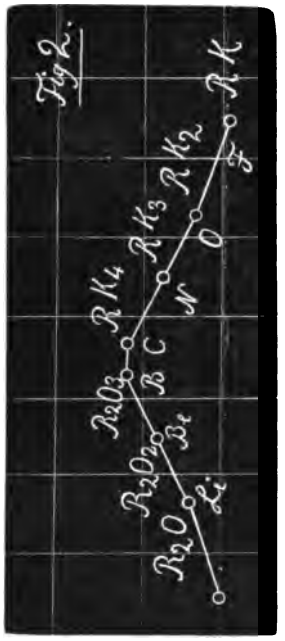
Royal Institution.—On Thursday next, March 5, at 3 o'clock, Prof. Sir John Rhys begins a course of two lectures at the Royal Institution on "Early British History and Epigraphy," and on Saturday, March 7, Prof. J. J. Thomson commences a course of six lectures on "Electric Discharges through Gases." The Friday Evening Discourse on March 6 will be delivered by Prof. John Milne on "Recent Earthquakes," and on March 13 by Chevalier G. Marconi on "Transatlantic Wireless Telegraphy."

ON THE SYMMETRY IN THE LAW OF ATOMIC WEIGHTS.

By Prof. Dr. N. DELAUNAY.

IN the diagram (Fig. 1) the abscissæ represent the atomic weights of the chemical elements, and the ordinates of the elements are 0, 1, 2, 3; 3, 2, 1, 0; and so on. The diagram, if prolonged to uranium, represents the law of Mendeleeff, because the elements having the same ordinates in ascending branches form a group; for example, Li, Na, K . . . The elements, having the same ordinate in descending branches, also form a group; for example, O, S, Cr . . . Each wave of the curve represents the valency as in Fig. 2. Each wave has an individual character, and the details of the numerical properties of the system are apparent in the diagram, Fig. 1.





But the chief point of interest presented by our diagram consists in the new and unexpected fact, *the complete symmetry of the first and the second waves, and the symmetry of the upper part of the third wave.*

This symmetry causes the sum of the numbers equidistant from the ends of each period to be constant, as follows:—

He + F = 4+19 = 23	Ne + Cl = 20	+35·45 = 55·45
Li + O = 7+16 = 23	Na + S = 23	+32·07 = 55·12
Be + N = 9+14 = 23	Mg + P = 24·48	+31·02 = 55·30
B + C = 11+12 = 23	Al + Si = 27·11	+28·40 = 55·51

Ka + Cr = 39·11 + 52·14 = 91·25
Ca + V = 40·07 + 51·38 = 91·45
Sc + Ti = 44·12 + 48·15 = 92·27

Kief, December 28, 1907.

THE ELECTROLYTIC DEPOSITION OF ZINC, USING ROTATING ELECTRODES.*

II.

By T. SLATER PRICE, D.Sc.

(Concluded from p. 90).

Experiments Using the Rotating Cathode (continued).

THE results shown above are very satisfactory, and confirm the statement in the previous paper that good results are obtained in the presence of 2 grms. of sodium sulphate plus 1 grm. of sodium acetate, the addition of free acetic acid being unnecessary. If no acid is added the electrolyte is slightly cloudy, because of the precipitation out of a trace of zinc hydroxide, but this cloudiness disappears immediately the current is started; it does not seem to bring about the deposition of spongy zinc, which would affect the result. In all cases the deposits were firm and adherent and of a light grey colour, and no zinc was left in solution, as indicated by the ferrocyanide test. It will be noticed that coppering the electrode has the same effect as silvering it. The deposition potential of zinc is altered when it is deposited on a metal with which it alloys readily (*cf.*, Spitzer, *Zeit. Elektrochem.*, 1905, xi., 345), and it may possibly become lower than that of hydrogen, or at all events close to it. The formation of spongy zinc would thus be avoided. This, however, is a point for further investigation. Coehn (*Zeit. Phys. Chem.*, 1901, xxxviii., 612), using a solution of sodium zincate, finds that the deposition potential of zinc on platinum cathodes is lower, by about 0·02 volt, than on cathodes of gold, silver, and copper. He states that this is due to the ease with which zinc alloys with platinum. This is contrary to what one would expect, since zinc alloys more readily with silver and copper than with platinum.

In all the above determinations the number of revolutions per minute of the cathode was 600—700. Table III. shows that from a speed of about 300 revolutions per minute onwards the results are satisfactory. In each case the electrolyte contained 2 grms. of sodium sulphate and 1 grm. of sodium acetate; the current was 2 amps. and the time of electrolysis fourteen minutes.

* A Paper read before the Faraday Society, March 19, 1907.

TABLE III.

Revolutions per minute	240	460	690	860
Per cent Zn..	22·70	22·73	22·75	22·74
Error	−0·04	−0·01	+0·01	0·00

In the first case the deposit was not a good one, so that 240 revolutions per minute is not a safe speed to work at.

That fourteen minutes afford ample time for the deposition of the zinc from 1 grm. of zinc sulphate is shown by Table IV. The number of revolutions was 600—700, and the other conditions, with the exception of the time, as given above.

TABLE IV.

Time (in minutes) ..	10	12	14	22
Per cent Zn..	22·44	22·74	22·73	22·75
Error	−0·30	0·00	−0·01	+0·01

There is one point to notice in connection with the drying of the deposit of zinc after washing it with alcohol. In all cases this was done in the steam oven. Foerster, in a recent paper in the *Zeit. Angew. Chemie*, 1906, xix., 1842, states that the deposit (of zinc) was dried carefully over the bare flame. This latter method, which is commonly used in drying a number of electrolytic deposits, is likely, in the case of zinc, to lead to high results, owing to the products of combustion of the gas acting on the zinc. In a series of experiments which I made the deposit was dried in an air oven at 100°—110° C. The results were always high, and varied greatly among themselves. It was afterwards found that the bottom of the oven was faulty, and that the waste gases from the burner got into the oven and acted on the deposit, discolouring it slightly.

Tables V. to VIII. give the results obtained, using different electrolytes. The number of revolutions per minute of the cathode was in all cases 600—700.

Ammonium Sulphate and Ammonia.—In each case 3 grms. of ammonium sulphate were used (Table V.). In every case, with the exception of the first, the zinc was completely deposited. The deposit was dark in colour, and decidedly crystalline. The results are uniformly high, but the error is very small. Satisfactory results for zinc in the presence of ammonia do not seem to have been obtained previously.

TABLE V.

Cc. of 0·880 ammonia.	C.	V.	*t.*	Per cent Zn.	Error.
0·75 (*a*)	2	4—5	14	21·28	−1·46
1·5	2	4—5	20	22·79	+0·05
1·5 [10]	2	—	20	22·82	+0·08
2	2	4—5	20	22·77	+0·03
2	2	—	14	22·78	+0·04
5	2	—	20	22·80	+0·06

(*a*) This volume of ammonia was slightly more than that necessary to dissolve the precipitate first formed.

Caustic Soda.—Four grms. of caustic soda were used in each case (Table VI.). In each case the zinc was completely deposited, but the deposit was very dark in colour, although firm and adherent. It does not appear to affect the result whether the solution be electrolysed in the cold or previously heated to boiling. Exner (*Journ. Am. Chem. Soc.*, 1903, xxv., 896) and Ingham (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1269), using a rotating anode, recommend the adoption of the latter course. When a solution containing 4 grms. of caustic soda, without any zinc sulphate, was electrolysed for twenty minutes, the alteration in weight of the cathode was −0·0001 grm., *i.e.*, within the error of experiment. The high results are therefore not due to impurities in the caustic soda.

TABLE VI.

C.	V.	*t.*	Per cent Zn	Error.
2	3·5	20	22·83	+0·09
2	3·75	20	22·88	+0·14
0·5 (5), 1 (10), 2 (10)	2·5—4	25	22·79	+0·05
2 (*a*)	2·5—3	20	22·87	+0·13
2 (*a*)	2·5—3	19	22·88	+0·14

(*a*) In these cases the solution was heated to boiling, by means of a ring burner arranged under the funnel, before the electrolysis was commenced.

Sodium Acetate and Acetic Acid.—Exner and Ingham both recommend that the solution be heated to boiling before the electrolysis is commenced. Using a rotating cathode, the results, when such a course is adopted, are not satisfactory (see Table VII.). Even in the last case, where the error appears to be very small, some zinc was left in solution. Using cold solutions, the deposition is complete, giving an adherent deposit somewhat darker in colour than when some of the acetate is replaced by sulphate. The results, although they are uniformly high, are more satisfactory than those given in the previous paper; the error is small.

TABLE VII.

Grms. of Na acetate.	Drops of glacial acetic acid.	C.	V.	*t.*	Per cent Zn.	Error.
3	2	2	6—6·5	14	22·79	+0·05
3	2	2	6·5—7	14	22·79	+0·05
3	2	0·5 (5), 1 (10), 2 (10)	3·5—7	25	22·79	+0·05
2	—	2	6·5—7	14	22·81	+0·07
3 (*a*)	2	2	3·4—4·5	14	22·64	−0·10
5 (*a*)	2	2	3—3·5	14	22·73	−0·01

(*a*) Solution boiled before the electrolysis was commenced.

Ammonium acetate as electrolyte gave very dark deposits and high results, as, for instance, 23·85 per cent.

Sodium Sulphate (Table VIII.).—In the previous communication it was stated that good results could be obtained using sodium sulphate alone as an electrolyte. Further investigation has shown, however, that the method is not satisfactory and that the results are uncertain. Occasionally one obtains good results, but they seem to depend too much on fortuitous circumstances, such as the position of the cathode with respect to the anode. If the former is fixed too low down, the zinc which is first deposited on the lower portion is dissolved off towards the end of the experiment.

TABLE VIII.

Grms. of Na_2SO_4.	C.	V.	*t.*	Per cent Zn.	Error.
5	2	5—5·5	14	22·30	−0·44
3	0·5 (2), 1 (2), 2 (15)	6	19	22·63	−0·11
3	0·5 (3), 1 (3), 2 (15)	—	21	22·51	−0·23
3	0·5 (2), 1 (2), 2 (15)	—	19	22·45	−0·29

In one experiment 2 cc. of ammonia were added ten minutes after the commencement of the electrolysis; after ten minutes more all the zinc had been deposited, giving as the result 22·78 per cent.

A few experiments were done, using no extraneous electrolyte and cooling with ice, as described in the previous paper. When the electrode was not previously silvered the results were very unsatisfactory—*e.g.*, 22·67, 22·43, and 21·21 per cent. When the electrode was silvered the results were 22·67 and 22·73 per cent. Here again, however, an extended experience has shown that the results depend to a great extent on the position of the cathode, so that the method could not be used for the ordinary quantitative determination of zinc, for which, as a matter of fact, it was never intended. Traces of zinc are very liable to be left in solution.

Experiments using a Mercury Cathode and Rotating Anode.

It has been stated that the method of Kollock and Smith, using a mercury cathode and rotating anode, was always found to give low results (in the case of zinc). A number of experiments were therefore made to find out the cause of this. In order to obtain results comparable with those of Kollock and Smith their method of working was adopted, *i.e.*, the electrolysis tube containing the mercury (or amalgam) was weighed complete, and not simply the mercury or the amalgam resulting from the electrolysis.

Some of the results obtained are given below. In every case the mercury (or amalgam) was washed three times with each of the following liquids: water, absolute alcohol, and dry, freshly distilled ether. The mercury used had been previously purified by distillation. Six drops (40 drops = 1 cc.) of concentrated sulphuric acid were added; the current was 5 ampères, the voltage 7, and the time allowed for electrolysis fifteen minutes—much longer than was really necessary. Before being weighed, the apparatus was allowed to stand in the balance case at least twenty minutes.

Per cent Zn.	Error.
22·63	−0·11 (*a*)
22·67	−0·07
22·77	+0·03
22·59	−0·15
22·65	−0·09
22·61	−0·13
22·54	−0·20

(*a*) Six washings each with alcohol and ether, three with water.

With one exception, and that the only one out of fifty or more determinations, the results are low. A glance at Kollock and Smith's figures shows that their results were sometimes high and sometimes low. The reason of this discrepancy may possibly be as follows:—In order to dry the amalgam (or the mercury) after it had received the final washing with ether, it was put into a desiccator, which, in my experiments, was then evacuated. Kollock and Smith do not say whether the desiccator was evacuated or not, so presumably it was not; the results would then be liable to error, as shown by the following figures: The weight of the tube plus amalgam after being in the desiccator for two hours (no vacuum) was 73·4114 grms. The tube with its contents was again put into the desiccator, which was then evacuated. During the process of evacuation bubbles, presumably of ether vapour, could be seen escaping from the surface of the amalgam. The weight after this treatment was 73·4088 grms., a loss in weight of 2·6 mgrms. In another experiment, even after drying in a desiccator (no vacuum) for five hours, the weights were 74·4473 and 74·4468 grms. respectively, so that under the conditions used by Kollock and Smith it would take a very long time before the weight became constant. It may be objected that mercury would lose in weight in the vacuum desiccator; that this is not so is shown by the following figures:—

Time in vacuum desiccator (hours)	0	3	24	41
Weight of tube and mercury (grms.)	70·2163	70·2163	70·2161	70·2158

The low results are not due to the deposition of the zinc being incomplete. In all cases the liquid syphoned off before the current was stopped showed no trace of zinc.

On testing the washings obtained during the treatment of the amalgam after the current had been stopped it was found that both those with water and those with alcohol showed the presence of a trace of zinc. The amount was too small to be estimated, but rough tests indicated that it was not enough to account for the low results. Further investigation showed that the action of water on zinc amalgam is fairly rapid; if the latter is allowed to stand in contact with water for a few hours it becomes coated with a layer of zinc hydroxide, and the water readily responds to the ferrocyanide test for zinc.

It is possible that during the washing of the amalgam some of it is mechanically carried away. To test this a weighed quantity of amalgam was repeatedly subjected to the same treatment as in the actual determination, *i.e.*, three washings each with water, alcohol, and ether respectively, and drying in a vacuum desiccator. The successive weighings obtained were 67·1313, 67·1286, 67·1234 grms., *i.e.*, a decrease in weight after each set of operations. It was especially noticeable during the washing with ether that the surface film of the amalgam broke up, and portions of it were mechanically carried away. Even if pure mercury is washed with ether a black scum, presumably of mercury, is formed, which gives the mercury a very dirty appearance, and is mechanically carried away as the washing is proceeded with. A series of tests with mercury alone, washing with water, alcohol, and ether, gave the following weighings: 66·8966, 66·8948, 66,8946, 66·8928, 66·8915, 66·8892, and 66·8872 grms. respectively—again a decrease after each operation. The amalgam and mercury used in these tests were cold. In the actual determination of zinc, if it was observed that any amalgam was mechanically carried away—and that very seldom happens—the results of the experiment were rejected. The amalgam gets very hot during the electrolysis, and the surface film does not form so readily then as when cold. The chemical action of the amalgam on water would be accelerated by rise in temperature.

In order to diminish the time necessary for washing the amalgam, as well as the number of operations, a series of experiments were carried out to see if the washings with ether, or even with ether and alcohol, could be avoided. It was then necessary to dry the amalgam in the air oven at 100—110° C. Under these conditions the amalgam does not lose in weight by volatilisation of mercury, as shown by the following figures:—

Duration of heating (mins.).	Weight (grms.).
0	76·0570
35	76·0569
0	73·2869
35	73·2869
0	61·4821
60	61·4818

Mercury alone, under these conditions, loses considerably in weight. In the acual determinations the amalgam was heated just long enough to dry it. Some of the results are given in Table IX.

TABLE IX.

Number of washings given with —		Per cent Zn.	Error.
Water.	Alcohol.		
3	3	22·59	−0·15
3	3	22·61	−0·13
6	6	22·62	−0·12
12	12	22·52	−0·22
1	3	22·55	−0·19
1	3	22·61	−0·13
—	6	22·52	−0·22
—	6	22·65	−0·09
3	—	22·70	−0·04
3	—	22·62	−0·12
6	—	22·60	−0·14

The results are no better than when ether, in addition to water and alcohol, is used. It is somewhat difficult to draw considerations from them, since they are so very irregular. One might perhaps be inclined to say that an increase in the number of washings increases the error, but it must be admitted that there is considerable irregularity, which is perhaps to be expected, since it is impossible

to keep the conditions under which the washings are carried out the same.

If any mercury is carried away, either mechanically or chemically, it should be possible to prove its presence in the washings. This was done as follows (*cf.*, Fresenius, "Qual. Analysis," 10th edit., p. 145):—Six determinations of zinc were carried out in the manner already described, three washings with water and three with alcohol being given in each case. The washings were collected (no globules of mercury could be seen in them) and evaporated down on the water-bath to a small bulk, small quantities of nitric and sulphuric acids having previously been added. The solution so obtained was electrolysed over night, using a platinum anode and a small cathode of pure copper. The cathode was afterwards washed and dried and put into a piece of combustion tubing, which was then drawn out to a capillary on either side of the copper. The part of the tubing containing the copper was heated to a low red heat for some time. After cooling a film could be seen in each of the capillaries, and examination with the microscope showed it to consist of opaque globules. A small amount of iodine was brought into contact with one of the films, and the whole gently warmed A yellow deposit resulted, which, under the microscope, was seen to consist of a number of yellow crystals, with a few scarlet ones interspersed. On standing for some time the yellow crystals gradually became scarlet in colour. There is thus no doubt that the film was mercury, which must have come from the washings. Whether it is mechanically carried away or chemically dissolved during the washing remains undecided.

The above results seems to show that the uniformly low results obtained by Kollock and Smith's method for the estimation of zinc are due to loss of zinc and mercury during the washing of the amalgam.

(These results, of course, only hold for zinc, which is never so satisfactory to deposit electrolytically as most of the other metals).

Since the publication of the first paper on the electrolytic determination of zinc the suggested alteration of Kollock and Smith's method, in which the amalgam is run off through a tap funnel, has been tried by various workers in this laboratory. It has not been found to be as satisfactory as, at first trial, it seemed to be. An error is likely to arise from the splashing of the mercury when poured into the funnel; this is easily obviated by putting some water into the latter before the mercury is poured in. The water can then be pipetted off before the solution of zinc sulphate is run in. If the electrolyte is syphoned off and replaced by distilled water before running off the amalgam, portions of the latter are liable to stick to the sides of the funnel, and thus vitiate the result. The better method is to run off the amalgam directly, without syphoning off the electrolyte; but even then it requires some practice before this can be done successfully, *i.e.*, so that the amalgam runs off dry. In most cases a drop of the electrolyte follows the amalgam, which has then to be washed, although not so thoroughly as with the usual method, since the drop of electrolyte lies on the surface of the amalgam. This drop contains sulphuric acid, and consequently some of the amalgam is decomposed. Any appreciable decomposition of the amalgam while actually in the leg of the funnel and not in contact with the electrode (the negative leading wire is bent down into the part of the leg above the tap) is obviated by the fact that a bubble of gas collects between the amalgam and the electrolyte and prevents further decomposition. That, in practised hands, the method gives quite as good results as the ordinary one is shown by the following results: 22·69, 22·66, 22·66, 22·69 per cent Zn.

The results communicated in the present paper seem to indicate that the most satisfactory method for the electrolytic deposition of zinc is that in which a rotating cathode is used, the electrolyte consisting of a solution of 2 grms. of sodium sulphate and 1 grm. of sodium acetate to each grm. of zinc sulphate.

A NEW METHOD OF DETERMINING VAPOUR DENSITIES.*

PART I.

By PHILIP BLACKMAN.

THE apparatus used for this method consists of a long glass bulb, with a glass stopper at one end, and at the other end a capillary tube also carrying a tap. Two threads of mercury are introduced, one to close the tap, the other near the bulb to form an air manometer. A weighed quantity of the substance to be experimented on is introduced in a small tube, the stopper fixed and wired on, and the apparatus heated in the vapour of a liquid boiling at a temperature above that at which the substance vaporises. A small quantity of mercury must also be introduced into the bulb to aid in sealing it. Let p = atmospheric pressure and $t_1°$ = temperature of the apparatus when the substance of weight, w, was introduced; V = volume of the bulb; $t_2°$ = temperature of the vapour; L, l = volumes of the air-gauge at $t_1°$ and $t_2°$ respectively; H, h = respective volumes of the space in the capillary between the bulb and the mercury at $t_1°$ and $t_2°$; the vapour density compared with hydrogen at 0° and 760 mm. is given by Formula I., or (as H and h are very small compared with V) Formula II. The apparatus gives excellent results quickly and with ease:—

$$\frac{31068\ wl\ (273 + t_1)}{p(V + h)\left(L - l\,\frac{V + H}{V + h}\right)} \quad \text{I.}$$

$$\frac{31068\ wl\ (273 + t_1)}{pV\ (L - l)} \quad \text{II.}$$

I must tender my thanks to R. Blair, Esq., Executive Officer of the L.C.C., and to the authorities of the Hackney Technical Institute, Dalston Lane, N.E., for the facilities granted me in carrying out the research.

THE REACTION BETWEEN POTASSIUM-ALUMINIUM SULPHATE AND A BROMIDE-BROMATE MIXTURE.

By F. A. GOOCH and R. W. OSBORNE.

WHEN the water solution of a neutral aluminium salt is boiled, hydrolysis may take place until an equilibrium is brought about between the free acid formed and other active products. If a product is inert toward the acid set free in the liquid, or if the acid is continuously removed or destroyed, the process goes on until no further hydrolytic action is possible under the conditions.

In the basic acetate process for the separation of alumina, the insoluble aluminium compound is a basic salt inert toward the free acetic acid formed under the conditions.

In Chancel's method of precipitating alumina, by the action of sodium thiosulphate upon the boiling solution of the soluble aluminium salt, the insoluble product is likewise a basic salt, in this case the sulphate, and the sulphuric acid set free is fixed as sodium sulphate, while the thiosulphuric acid formed in metathesis is destroyed at the temperature of the reaction with formation of the comparatively inactive sulphur dioxide and sulphur; though, as Norton has shown, the basic salt is not quantitatively insoluble until the mixture is superheated under pressure (*Ber.*, 1900, xxxiii., 548).

In Stock's process (Norton, *Am. Journ. Sci.*, 1901, xii., 118) for the determination of alumina, aluminium sulphate in solution is heated at the boiling temperature with a

* Abstract of a Paper read before the Chemical Society, January 16, 1908. Compare CHEMICAL NEWS, 1907, xcvi., 223; *Journ. Chem. Soc.*, 1907, xcii., Abs. II., 931.

TABLE I.

	$KAl(SO_4)_2.12H_2O$ taken. Grms.	Time of heating. Hours.	KBr taken. Grms.	$KBrO_3$ taken. Grm.	Al_2O_3 taken. Grm.	Al_2O_3 found. Grm.	Error. Grm.
1.	1·0012	1·0	3·6	1·0	0·1078	0·1070	−0·0008
2.	0·5017	2+2·5	2·0	0·5	0·0539	0·0529	−0·0010
3.	0·5029	3+2·5	2·0	0·5	0·0541	0·0559	+0·0018

TABLE II.

No.	Time. Hours.	$KAl(SO_4)_2.12H_2O$ taken. Grm.	KBr used. Grms.	$KBrO_3$ used. Grm.	Bromine liberated. Grm.	Theory for bromine. Grm.	Error in terms of bromine. Grm.	Error in terms of Al_2O_3. Grm.
		A.—Theory: 6Br to $2KAl(SO_4)_2.12H_2O$.						
1.	0·5	0·5000	1·8	0·5	0·2052	0·2527	−0·0475	−0·0101
2.	1·5	0·5000	2·16	0·6	0·2064	0·2527	−0·0463	−0·0097
3.	2·0	0·5000	2·16	0·6	0·2084	0·2527	−0·0443	−0·0094
4.	2·5	0·5000	2·16	0·6	0·2099	0·2527	−0·0408	−0·0091
5.	3·5	0·5000	2·16	0·6	0·2119	0·2527	−0·0408	−0·0087
6.	4·0	0·5000	2·16	0·6	0·2120	0·2527	−0·0407	−0·0086
		B.—Theory: 5Br to $2KAl(SO_4)_2.12H_2O$.						
1.	0·5	0·5000	1·8	0·5	0·2052	0·2106	−0·0054	−0·0011
2.	1·5	0·5000	2·16	0·6	0·2064	0·2106	−0·0042	−0·0009
3.	2·0	0·5000	2·16	0·6	0·2084	0·2106	−0·0022	−0·0005
4.	2·5	0·5000	2·16	0·6	0·2099	0·2106	−0·0007	−0·0001
5.	3·5	0·5000	2·16	0·6	0·2119	0·2106	+0·0011	+0·0002
6.	4·0	0·5000	2·16	0·6	0·2120	0·2106	+0·0014	+0·0003

TABLE III.

	Time. Hours.	$KAl(SO_4)_2.12H_2O$. taken. Grm.	KBr taken. Grms.	$KBrO_3$ taken. Grms.	Theory for bromine. Grm.	Bromine found. Grm.	Error in terms bromine. Grm.	Error in terms Al_2O_3. Grm.
		A.—Theory: 6Br to $2KAl(SO_4)_2.12H_2O$.						
1.	3	0·5000	0·32 (*a*)	0·09 (*a*)	0·2527	0·1437	−0·1090	−0·0232
2.	3	0·5000	3·2	0·09	0·2527	0·1814	−0·0713	−0·0152
3.	3	0·5000	0·32	0·90	0·2527	0·1853	−0·0674	−0·0144
4.	3	0·5000	3·2	0·90	0·2527	0·2182	−0·0345	−0·0073
5.	3	0·5000	6	2	0·2527	0·2199	−0·0328	−0·0069
6.	4	0·5000	6	2	0·2527	0·2229	−0·0298	−0·0063
7.	5	0·5000	6	2	0·2527	0·2320	−0·0207	−0·0044
		B.—Theory: 5Br to $2KAl(SO_4)_2.12H_2O$.						
1.	3	0·5000	0·32 (*a*)	0·09 (*a*)	0·2106	0·1437	−0·0669	−0·0143
2.	3	0·5000	3·20	0·09	0·2106	0·1814	−0·0292	−0·0062
3.	3	0·5000	0·32	0·90	0·2106	0·1853	+0·0252	−0·0054
4.	3	0·5000	3·2	0·90	0·2106	0·2182	+0·0076	+0·0016
5.	3	0·5000	6	2	0·2106	0·2199	+0·0090	+0·0019
6.	4	0·5000	6	2	0·2106	0·2229	+0·0123	+0·0026
7.	5	0·5000	6	2	0·2106	0·2330	+0·0214	+0·0045

(*a*) These amounts are nearly equivalent to the acidic ion of the aluminium salt.

mixture of potassium iodide and potassium iodate. The sulphuric acid produced hydrolytically is fixed by the iodide-iodate mixture, and comparatively inert iodine is set free and taken up by sodium thiosulphate to form sodium iodide and sodium tetrathionate. In this process, as Moody has shown (*Am. Journ. Sci.*, 1905, xx., 181), the first insoluble product is a basic salt; but prolonged boiling of the mixture of aluminium sulphate, potassium iodide, and potassium iodate finally brings about the complete hydrolysis of the insoluble basic salt, so that the entire amount of iodine set free in the process, when properly collected and titrated, may serve as an accurate measure of the acid produced and therefore of the acidic ion of the aluminium salt.

In an extension of this process to other elements Moody found that a sufficiently prolonged treatment with the iodide-iodate mixture completely liberated the acidic ion from the sulphates of iron, chromium, cobalt, nickel, ammonium, and from stannic chloride. The hydrolysis of zinc sulphate under similar conditions comes to an end before the acidic ion is entirely liberated and when the product is one-fifth sulphate and four-fifths hydroxide.

In the work of which the present paper is an account, the reaction of a mixture of potassium bromide and potassium bromate upon aluminium sulphate has been studied. Assuming that the acidic ion is entirely liberated from the aluminium salt, the reaction should follow the equation—

$$2KAl(SO_4)_2+5KBr+KBrO_3+3H_2O=$$
$$=2Al(OH)_3+4K_2SO_4+3Br_2.$$

For this work a bromide-bromate solution was made up by dissolving 36 grms. of potassium bromide and 10 grms. of potassium bromate (the proportions indicated in the equation) in water and making up to 500 cc. Pure crystallised potassium alum was the aluminium salt used, and this was weighed out exactly in every experiment.

The first set of experiments (Table I.) was made to find out whether precipitation is complete when the bromide-bromate mixture acts upon the aluminium salt. In every experiment a portion of the alum was weighed out, dissolved in a small amount of water in a beaker, and a portion of the bromide-bromate solution was added. In Experiment 1 the mixture was boiled over a flame until at the end of an hour no more bromine seemed to be liberated

and the cooled liquid was colourless. The precipitate was, so far as possible, transferred to an ashless filter-paper, washed, ignited, and weighed as Al_2O_3; but to get the entire amount of precipitate it was necessary to dissolve from the beaker, by means of hydrochloric acid, a closely adherent film of precipitate; and from the solution the dissolved alumina was recovered by precipitation with ammonia and determined separately. In Experiments 2 and 3 the precipitation was brought about by passing a current of steam into the solution, interrupting the process to concentrate the liquid by evaporation without boiling, and again passing in steam.

In these experiments the precipitation proved to be complete, or nearly so; though in No. 3 there is obvious contamination of the precipitate, due perhaps to the prolonged treatment in glass. As will appear, however, the process of hydrolysis did not go to the point of forming aluminium hydroxide.

The degree to which the acidic ion is removed hydrolytically from the salt under the conditions is shown in the following series of experiments (Table II.), in which portions of the alum were treated with the bromide-bromate mixture under conditions which permitted the collection and titration of the bromine set free in the reaction.

The apparatus used consisted of a Voit flask, used as a distilling flask, sealed to the inlet tube of a Drechsel wash-bottle, used as a receiver, to the exit tube of which was sealed a Will and Varrentrapp absorption tube. The Voit flask was charged with 0·5 grm. of alum dissolved in a little water and 25 cc. or 30 cc. of the bromide-bromate mixture. The solution was boiled for the time indicated and the bromine liberated passed in a current of hydrogen, sent through the whole apparatus, to the receiver containing in the cylinder and trap a solution of 4 grms. of potassium iodide in 200 cc. of water. The iodine set free by the action of the bromine liberated in the reaction was titrated by *n*/10 sodium thiosulphate with the aid of a starch indicator.

From these experiments, in which approximately three times the amounts of potassium bromide and potassium bromate, corresponding to the complete hydrolysis of the alum, were used, it is obvious that the hydrolysis is not complete. At the end of an hour nearly five-sixths of the acidic ion have been liberated, and this proportion is not much exceeded after four hours boiling, the liberation of bromine proceeding very slowly during the greater part of this time.

In the series of determinations given in Table III. the proportions of potassium bromide and potassium bromate with reference to one another and to the aluminium salt were varied in order to test the effect of such variation on the course of the action.

In the result of Experiment 1, in which the amounts of bromide and bromate were equivalent to one another and to the acidic ion of the aluminium salt, it will be noted that the liberation of the bromine falls considerably short of five-sixths of the equivalent of the acidic ion. In Experiment 2 the bromide was increased tenfold, and in Experiment 3 the bromate tenfold with similar though incomplete effects. In Experiment 4, in which both the bromide and the bromate amount to ten times the theoretical equivalent of the acidic ion, the results show a liberation of bromine somewhat in excess of the five-sixths proportion. In Experiments 5, 6, 7, further increase in the amounts of bromide and bromate and in the time of boiling advanced the reaction so that amounts of bromine were liberated considerably in excess of the five-sixths proportion. These results seem to indicate that the deficient hydrolytic effect is advanced by large increase in the proportions of either the bromide or the bromate or both, and would seem to confirm the natural inference that the products of the action of the bromide and the bromate upon aluminium sulphate take part essentially in the hydrolytic action as well as the sulphate itself. These products naturally increase with the concentration of the reacting substances. With a very large increase in the amounts of the bromide and bromate and prolonged boiling, it would be natural to expect the completion of the hydrolysis to the point of liberating bromine equivalent to the entire amount of the acidic ion.

Experimental difficulties, such as the necessity and difficulty of supplying water frequently during the boiling, the periodical titration of the iodine liberated in the receiver, made of doubtful value experiments extended over many hours. When, however, the residue left in the Voit flask in Experiment 7 was treated with a mixture of 1 grm. of potassium iodine and 0·5 grm. of potassium iodate, the iodine set free on boiling for an hour longer indicated that the acidic ion had been very nearly liberated.

The iodine-iodate mixture is extremely sensitive to the action of small amounts of free acid. Experiment showed that the bromide-bromate mixture is also a very delicate indicator of free acid; 0·00018 grm. of sulphuric acid proving to be sufficient to liberate bromine from the bromide-bromate mixture when boiled in the Voit flask under the experimental conditions.

That the progress of the hydrolytic reaction is so much more rapid in the case of the iodide and iodate is apparently due to the specific action of these substances upon the basic aluminium sulphate rather than to a more exact removal of the free acid.

It will be recalled in this connection that, as Moody has shown (*Am. Journ. Sci.*, 1906, xxii., 184), the iodide-iodate mixture, taken in moderate amount, does not further hydrolyse the basic salt produced in the action upon zinc sulphate. A reasonable excess of the bromide-bromate mixture is able in a moderate time to carry the hydrolysis of aluminium sulphate to a fairly definite point corresponding nearly to the removal of five-sixths of the acidic ion, while the iodide-iodate mixture under similar conditions of prolonged action removes practically all the acidic ion.

Some experiments to test the effect of a mixture of potassium chloride and potassium chlorate indicated that the hydrolysis of aluminium sulphate under otherwise similar conditions is very slight compared with that produced by the bromide-bromate mixture or by the iodide-iodate mixture.—*American Journal of Science*, 1907, xxiv., p. 167.

THE PREPARATION OF ACETAMIDE BY THE ACTION OF AMMONIUM HYDROXIDE AND ETHYL ACETATE.

By I. K. and M. A. PHELPS.

IT has been stated by Hofmann (*Ber.*, xv., 977) that the action of aqueous ammonia upon ethyl acetate at ordinary temperatures yields after several days' standing considerable amounts of acetamide, but that the amount of acetamide by no means corresponds to the amount of ethyl acetate taken. Hofmann further states that, according to a communication from Dr. Bannow, the yield of acetamide, even when formed in large quantities, is usually not much above 70 per cent of that theoretically demanded. In this same communication Hofmann makes a similar statement in regard to the action of ethyl formate.

In a former paper from the Kent Chemical Laboratory of Yale University (*Am. Journ. Sci.*, xxiv., 173; CHEM. NEWS, xcvii., 86) conditions have been shown under which very nearly the theoretical yield of formamide by the action of ammonium hydroxide and ethyl formate is obtained. Now it has been found that conditions closely similar will give theoretical yield as well in the case of ethyl acetate and aqueous ammonia.

For the work given here ethyl acetate of commerce was treated in a separating funnel with sodium carbonate solution, and, after separating from this, was washed with distilled water. The ethyl acetate thus purified from acid

impurities was separated as completely as possible from the water, dried over fused calcium chloride, and then treated again with a fresh portion of fused calcium chloride before fractioning. Portions boiling between 77° and 77·2° were taken as pure ethyl acetate.

Definite portions of the pure ethyl acetate were weighed, and, after chilling below zero in an ice and salt mixture, were mixed in a stoppered reagent bottle with definite volumes of ammonium hydroxide. In some of these experiments the ammonium hydroxide was the pure concentrated ammonium hydroxide of commerce; in others the ammonium hydroxide was made more concentrated by saturating at −10° the pure concentrated ammonium hydroxide of commerce with dry ammonia gas obtained by heating concentrated ammonium hydroxide in a flask connected with a return condenser and drying further the ammonia by passing it through a lime tower; while in a third series of experiments the product obtained by mixing in the cold in a stoppered reagent bottle the ethyl acetate and ammonium hydroxide was saturated in the cold with dry ammonia gas obtained in the manner given above. In every case, after the solution had stood a sufficient time in the reagent bottle stoppered tightly so that the ammonia gas should not escape, it was transferred to a 250 cc. distilling flask, connected with a 100 cc. distilling flask in the usual way for a vacuum distillation, with the use of the least amount of absolute alcohol to rinse the sides of the bottle. The low boiling impurities, ammonia, alcohol, and water, were removed by fractioning *in vacuo* in the usual way, the 250 cc. flask being heated in a bath of hot water finally at 60° for fifteen minutes after the pressure on the manometer registered 15 mm. The acetamide left in the flask was distilled by heating the flask in an acid potassium sulphate bath at 140° to 150°, and was collected in the receiver, cooled by a stream of cold water, and weighed.

No.	Ethyl acetate.	Ammonium hydroxide.		Reaction time.		Acetamide.	
						Theory.	Found.
	Grms.	Cc.	Sp. gr.	Days.	Hrs.	Grms.	Grm.
	A.—*Treatment with* NH_4OH.						
1.	50	50	0·90	3	22	33·57	21·70
2.	50	50	0·90	6	19	33·57	25·60
3.	50	50	0·90	13	—	33·57	29·00
4.	45·4	50	0·90	126	—	30·80	30·36
5.	50	75	0·90	3	23	33·57	26·89
6.	50	75	0·90	6	—	33·57	30·15
7.	50	75	0·90	8	—	33·57	31·18
8.	50	75	0·90	13	—	33·57	34·10
	B.—*Treatment with* NH_4OH *Saturated with* NH_3.						
9.	50	50	—	3	19	33·57	21·03
10.	50	50	—	12	—	33·57	32·80
11.	50	50	—	49	—	33·57	33·12
12.	50	78	—	3	22	33·57	28·81
13.	50	78	—	6	22	33·57	32·53
	C.—*Treatment with* NH_4OH *and Saturation of the Mixture with* NH_3.						
14.	50	50	0·90	3	16	33·57	25·78
15.	50	50	0·90	6	—	33·57	33·71
16.	50	50	0·90	12	6	33·57	33·82
17.	50	50	0·90	20	—	33·57	33·47
18.	50	75	0·90	—	23	33·57	17·72
19.	50	75	0·90	2	—	33·57	30·08
20.	50	75	0·90	3	—	33·57	31·63
21.	50	75	0·90	4	—	33·57	33·62
22.	50	75	0·90	4	6	33·57	34·00

The experiments of Section A are those in which the pure ammonium hydroxide of commerce was used with the ethyl acetate, and after standing suitably the mixtures were distilled *in vacuo* as given above.

The experiments of Section B were conducted in the same way as those in Section A, except that the ammonium hydroxide used was saturated at −10° with dry ammonia before mixing in the cold with the ethyl acetate.

The experiments of Section C were conducted in the same way as those of A, excepting that the entire mass of ethyl acetate and ammonium hydroxide after mixing in the cold was saturated with dry ammonia gas at −8° to −10°.

From an inspection of the results recorded in Section A it is seen that the volume of ammonium hydroxide taken for a given weight of ethyl acetate, as well as the time allowed for the interaction of the ethyl acetate and ammonia, influences the yield of acetamide. The theoretical yield can be obtained with the proportion and concentration of the reagents used here only on long standing. Two weeks' standing at ordinary temperatures with so large an amount as 75 cc. of the ammonium hydroxide for 50 grms. of ethyl acetate will give the yield required by theory, although for smaller proportions of the ammonium hydroxide that time is not sufficient.

It is evident from the results given in Section B that a solution of saturated aqueous ammonia tends to give a larger yield of acetamide in a given time than can be obtained by weaker aqueous ammonia.

In Section C the results show that in shorter time than by the procedure in experiments given in A and B of the table the theoretical yield of acetamide may be obtained by saturating in the cold the mixture of ethyl acetate and ammonium hydroxide, and allowing it to stand either four or six days according to the proportion of the aqueous ammonia present.

It is evident that the time of completion of the reaction is dependent upon the concentration of the ammonia.

It was found that the mixture of ammonium hydroxide and ethyl acetate became homogeneous in the experiments of Section A in about three days, in B in somewhat less time, and twenty-four hours in C. In Experiment 18 the mass became homogeneous at the end of twenty-three hours, and in this single instance distillation was made as soon as this phenomenon appeared. It is evident that the formation of acetamide progresses slowly, and is not at an end as soon as the mass becomes homogeneous.

It was found by experiment that a known weight of pure acetamide treated with 10 cc. of water and fractioned *in vacuo* could be recovered with a loss of less than 0·05 grm. The acetamide tends to hold traces of water; and it was not found possible to remove it by fractional distillation *in vacuo* without danger of loss of very small amounts of acetamide.

The presence and amount of ammonium salt in the acetamide obtained in the procedure outlined above were tested for by the use of a solution of sodium cobalti-nitrite. An experiment showed that 0·0002 grm. of ammonium chloride could be readily detected in the presence of 0·50 grm. of acetamide. The acetamide obtained directly by fractioning *in vacuo* as given above was found to contain traces of ammonia and ammonium salt. In Experiment 8 the crude material was transferred after weighing the product obtained from the vacuum distillation to a watch-glass, and allowed to stand in a desiccator over sulphuric acid for twenty-four hours, and the loss sustained was 0·62 grm., presumably largely water with some ammonia. Some of this loss must have been acetamide also, for by a separate experiment with pure acetamide re-crystallised from benzene it was found that acetamide continually lost in weight in a sulphuric acid desiccator. The acetamide from Experiment 8 after being dried showed the presence of not more than 0·30 grm. of ammonium salt, estimated by the amount of precipitate produced with sodium cobalti-nitrite as compared with the amount of precipitate obtained under similar conditions with ammonium chloride, pure acetamide, and sodium cobalti-nitrite. The material obtained in Experiment 22 was re-distilled with an air condenser under ordinary atmospheric pressure, and yielded 27·5 grms. of product boiling between 221° and 222°. This product showed on testing with sodium cobalti-nitrite no ammonium salt. Theoretically, more ammonium salt might be present in those cases where the standing is

longest. But it was found on re-distillation, under ordinary atmospheric conditions, of the acetamide obtained directly by the processes given above, that ammonium salt was not present in sufficiently large amounts in the different experiments to be noticeable.

It is clear from the work given that acetamide with only traces of impurity may be obtained in quantities barely less than quantitative for the amount of ethyl acetate taken, if ethyl acetate and ammonium hydroxide are mixed in the cold and allowed to stand a suitable length of time. Increasing the amount of ammonium hydroxide employed shortens the time of standing necessary for a theoretical yield, and increasing the concentration of ammonia by saturating the mixture of ethyl acetate and ammonium hydroxide in these proportions with ammonia gas further diminishes, by one-half or more, the time of standing.—*American Journal of Science*, 1907, xxiv., p. 429.

THE DANGER OF OVER SPECIALISATION.*

By L. H. BAEKELAND.

In the ever-recurring discussion of our methods of education and of our pursuits in life, it has been asserted over and over again that "this is the age of specialists."

Is this really so? Does this age create more specialists than former epochs in history? If this be the case, does this tendency keep on increasing, and if so, may it not ultimately impede the higher development of mankind, and reduce us to mere automatic machines?

The political economist tells us that division of labour increases and improves production. We also know that in any pursuit of life specialisation enables us to more thoroughly master the details of a subject.

On the other hand, we ought to admit that even to-day, truly great men, who have achieved distinction by exercising a beneficial influence on the development of our race, were not merely specialists. They were persons of broad general tendencies, although sometimes their superiority was more accidentally manifested in some special line of work. If, to stave this assertion, I started to mention a list of names, I might possibly omit many men of merit known or preferred more particularly by any of you. But I shall take the liberty of turning my argument, by challenging you to name any truly great man who was merely a specialist in one single small branch of human activity.

That one-sided pursuits are apt to make us very narrow-minded will be conceded by many whose misfortune it has been to have to work or live with people who led such a specialised existence. Even the professional fields of specialised activity may lead to short-sighted pettiness. Andrew Carnegie ("The Empire of Business") reinforces my own belief, based on personal experience, when comparing the better class of business men to artists, he wrote:—"I have learned that the artistic career is most narrowing, and produces such petty jealousies, unbounded vanities, and spitefulness, as to furnish me with a great contrast to that which I have found in men of affairs. Music, painting, sculpture, one would think, should prove most powerful in their beneficent effects upon those who labour with them as their daily vocation. Experience, however, is against this."

This apparent shortcoming of artists may be explained by the fact that as a class they are generally very ignorant outside of their own art, which requires more skill than knowledge, and what is worse, to many of them exact knowledge, which might help to broaden their views, is almost repulsive.

But—to come back to first principles—we ought to consider all pursuits of life from a broad general standpoint. I dare say that human life includes, as its noblest attributes, three fundamental tendencies to which all others converge, directly or indirectly. Indeed, nature prompts us—

First, to develop ourselves physically and intellectually—the latter word including all moral development.

Second, to reproduce ourselves, and lend our short existence as individuals for the physical and mental betterment of our race, towards a higher goal of absolute good.

Third, to enjoy life in its material and intellectual comforts as far as the latter contribute directly or indirectly to the two first-named functions. This idea includes naturally the production of wealth and the better use of the same.

Whether we be scientists, philosophers, labourers, artists, merchants, money-lenders, beggars, or thieves, we all obey those laws which predetermine the ultimate destiny of mankind. Whoever, in some way or another, works in harmony with these dictates cannot help being a benefactor to his own race and to himself in particular.

No individual whatever can try to divest himself of any of the above-mentioned attributes or functions of life, without jeopardising in some degree or another the progress of his race.

Let us imagine, for an instant, a society only composed of four distinct classes:—One, wealth-producing but vicious; a second, very moral but inactive; a third, very intelligent but bodily weak; while a fourth class would be composed of physical athletes, very stupid. Fortunately for the welfare of our race, in such a heterogeneous society, free intermarriage would tend to offset the one-sided grouping of these abnormal individuals or specialists—to call them by another name—and would bring about more homogeneity for their descendants. Furthermore, education—the great leveller of one-sided tendencies—would prove another active factor for accomplishing this result. When I speak here of education in its broadest sense, I do not merely limit myself to so-called school education; but I include in this term all influence towards mental development, proceeding from any source whatsoever, as, for instance, self-culture and environment. But, whenever education tends to develop one of our faculties beyond reasonable necessity and to the detriment of other functions, we drift towards mental deformity—a freak; and this in about the same manner as a particular muscle exercised beyond normal requirements will leave the remainder of the body insufficiently developed and out of harmony with the other anatomical parts.

Many fundamental errors have been committed by such men as spoke or wrote of the culture or the civilisation of a given nation, without according full importance to above considerations. Moreover, history teaches us that a one-sided or specialised education has been the defect of nations of the past, even to a greater extent than it occurs in our present civilisation. Many examples can we give to show that such a one-sided culture was largely to blame for the downfall of at one time powerful races. The Greeks, in their over specialisation of art, neglected beyond measure the study of nature. Had her philosophers steadied their thoughts by giving more attention to the careful observation of natural phenomena, instead of dreamingly searching a solution for all problems by analytical reasoning, they would not have been led astray into casuistry and sophistry and scepticism. The great laws of nature might have opened their minds to a better understanding of equity and rights of man; while now history has to record that even the most progressive and radical Greek philosophers proclaimed chattel slavery as an indispensable institution of society. In the same way, a large part of their literature was devoted to beautifully sounding, well-polished sentences, dealing mostly with imagination. The Greek writers, in their search for effect, gave their fancy full play whenever they described the war exploits of their heroes, with the result that they put themselves on record in history as the biggest braggarts in prose and in rhyme.

* Read before the New York Section of the American Chemical Society. From *Science*, 1907, xxv., No. 648.

As another example of one-sided culture let me remind you of the inhabitants of India, who became overawed by the conception of the immensity of the universe, and the relative insignificant smallness of man. Exaggerating this feeling, they too failed to grasp the full meaning of harmony in nature, and so neglected to give sufficient attention to the material development of their race. This doomed to stagnation an otherwise very intellectual people; it rendered possible their subjugation under the strong and forceful arm of warlike tribes, morally less developed, but physically better adapted for the perpetuation and multiplication of their sturdier race.

In the same way, the Roman Empire fell as a result of the wilful ignorance of the true principles of equity; her poorer classes, or vanquished foes, were denied their natural rights by their aristocratic masters. This heterogeneity of the people led to all the excesses which brought about the fall of what once had been a mighty empire.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Annual General Meeting, February 14th, 1908.

Prof. J. PERRY, F.R.S., President, in the Chair.

THE SECRETARY read the report of the Council for the past year:—

Since the last Annual General Meeting, thirteen ordinary science meetings and one informal meeting of the Society have been held. Of these twelve were held at the Royal College of Science; one, that on June 14th, was held at University College, by invitation of Prof. J. A. Fleming, F.R.S.; and one, that on June 28th, at the Central Technical College, by invitation of Prof. W. E. Ayrton, F.R.S. The average attendance at the meetings has been 58 as compared with 50 during the preceding year.

The third Annual Exhibition of Apparatus by manufacturers was held on December 13th, when the attendance of Fellows and visitors amounted to about 200.

Light refreshments are now provided before the afternoon meetings and after the evening meetings. This innovation appears to be appreciated, and it is hoped that the opportunity thus afforded will enable Fellows to become personally acquainted with each other, and to interchange opinions more readily than has been possible hitherto.

The number of ordinary Fellows now on the roll, as distinct from Honorary Fellows, is 437, an increase of 11 on the number last year; 27 new Fellows have been elected, two Fellows have been reinstated, and two Honorary Fellows, namely, Prof. Gabriel Lippmann and Prof. Simon Newcomb, have been elected. There have been 11 resignations, the names of two Fellows have been struck off the list for non-payment of subscriptions; and the Society has to mourn the loss by death of 6 Fellows, namely, one Honorary Fellow, P. J. C. Jules Janssen, and 5 Ordinary Fellows, namely, Lord Kelvin, Sir W. Perkin, J. R. Brittle, J. MacFarlane Gray, and J. W. Kearton.

The report was adopted.

THE TREASURER read his report for the year 1907:—

The position of the Society this year shows a decided improvement. There are more new members than usual, and subscriptions have been paid more punctually. The balance in bank has increased by nearly £240, more than £100 of which, however, is due to composition-fees and recovered income tax. The value of the securities has declined somewhat owing to the general depression, but this is probably of a temporary nature. There are no outstanding liabilities, and the income shows a healthy tendency to exceed the expenditure.

The report was adopted.

The following Officers and Council were elected for the ensuing year:—

President—C. Chree, Sc.D., F.R.S.

Vice-Presidents—Those who have filled the Office of President, together with W. Duddell, F.R.S.; H. M. Elder, M.A.; Prof. J. A. Ewing, F.R.S.; and W. Watson, D.Sc., F.R.S.

Secretaries—W. R. Cooper, M.A., and Prof. W. Cassie, M.A.

Foreign Secretary—Prof. S. P. Thompson, D.Sc., F.R.S.

Treasurer—Prof. H. L. Callendar, M.A., F.R.S.

Librarian—W. Watson, D.Sc., F.R.S.

Other Members of Council—A. Campbell, B.A.; W. H. Eccles, D.Sc.; A. Griffiths, D.Sc.; J. A. Harker, D.Sc.; Prof. C. H. Lees, D.Sc., F.R.S.; T. Mather, F.R.S.; A. Russell, M.A.; S. Skinner, M.A.; S. W. J. Smith, M.A., Prof. L. R. Wilberforce, M.A.

Dr. CHREE then took the Chair and delivered an Address.

The Address mentioned that whilst the losses of the Society during the past year had been few, they included two most distinguished Fellows—Lord Kelvin and Sir W. H. Perkin, who both joined the Society in 1875. It was hardly the place to refer to Perkin's work, as it was his discoveries in chemistry that had brought him distinction. Lord Kelvin had been one of the earliest Presidents of the Society. During his lifetime British physicists had the satisfaction of feeling assured that their number included the man who was universally recognised as the foremost in their branch of knowledge. There had already appeared obituary notices of Lord Kelvin by old pupils and others who knew him intimately. The account by Prof. Ayrton in *The Times* gave a particularly life-like portrait. Lord Kelvin was active in a great variety of fields, his work appealing to very different types of mind. The fact that he an eminent pure scientist, was the inventor of many instruments of high practical utility, had done a great deal to impress the average Englishman with a sense of the value of science. Another side of Lord Kelvin's activity, his speculations as to matters such as the age or internal state of the earth, appealed strongly to the popular imagination. But apart from what appealed directly to the public Lord Kelvin's writings contained a vast amount of what was at once solid and highly original. He had made contributions of high value to hydrodynamics, heat, elasticity, magnetism, electricity, and optical theory.

Whilst an able analyst, Lord Kelvin seemed to take comparatively little interest in analysis for its own sake. His interest seemed always to centre in the physical result which the analysis enabled him to reach. He had such a constant flow of new ideas that it was repugnant to him to spend time in perfecting or extending analysis more than was immediately necessary at the time. One very pleasing feature in Lord Kelvin's character was his generosity in recognising the work of younger and unknown men.

Passing to the question of the progress of the Society, the speaker said that during the last five years the membership had increased by about 7 per cent. With the increased number of persons concerned with science, an increase of membership seemed a natural consequence, but it should be remembered that with the continual increase of specialisation new societies tended to arise. Considering modern tendencies, it was perhaps a little strange that so few ladies had availed themselves of the fact that they were eligible to the Fellowship of the Society.

The speaker referred to the fact that tea and light refreshments were now provided at the meetings, and hoped the departure would be generally appreciated. Referring to a resolution of the Council inviting readers of papers and others to be considerate in their demands on time when addressing the Society, the speaker expressed a hope that Fellows would not be found lacking in reasonableness. When several papers were down for reading, it was clearly

impossible for all the authors to go into minute details without exhausting the patience of the meeting. In general, what was most appropriate was a summary intelligible to those who were not specialists in the particular subject of the paper.

The speaker then proceeded to refer to the magnetic results obtained by the National Antarctic Expedition of 1901-4. The expedition had been furnished with magnetographs, and the reduction and discussion of the curves had been entrusted to the National Physical Laboratory. Thanks to the acquiescence of the Officials of the Royal Society and the Director of the National Physical Laboratory, he was able to give a general preliminary account of some of the results, a full discussion of which would appear in the official publications of the Expedition. Before entering on a description of the results, he spoke of the nature of the preparations that should in his opinion be made in the case of any future National Scientific Expedition. It was most important that the observers should have a special preliminary training lasting over a good many months, and should be practised in the use of the instruments they would have to employ in the course of the expedition. These instruments ought thus to be ready for use and fully tested months before the date when the expedition was to set out.

A programme, based at once on special scientific knowledge and on common sense, should be got out in good time, so as to admit of sufficient rehearsals by the observers prior to their departure. A form of judicial inquiry after the return of the expedition into the value of the results obtained might be useful in securing that meritorious scientific work would not be overlooked, as compared to what appealed more directly to the popular imagination.

After paying a tribute to the assistance he had received from Mr. Bernacchi, the Physicist of the National Antarctic Expedition, and from members of the staff of the National Physical Laboratory, the speaker exhibited and described a number of lantern-slides relating mainly to the diurnal inequalities of the magnetic elements in the Antarctic. A few slides of corresponding Kew results were shown for intercomparison. Comparing slides of actual records taken at Kew and in the Antarctic, the speaker dwelt on the relatively highly disturbed nature of the latter. In the Antarctic, the declination and horizontal force magnets were practically never at rest. So large and incessant were the disturbances, that no idea of the nature of the regular diurnal inequality was obtainable from mere inspection of individual curves. Diurnal inequalities, however, derived from the curves of single months, and still more those derived from the curves of a whole season of the year, proved to be of a comparatively smooth character. Slides were exhibited showing the nature of these inequalities for the several elements.

CORRESPONDENCE.

COPPER AND BRASS INSTITUTE.

To the Editor of the Chemical News.

Sir,—A meeting of copper and brass manufacturers, engineers, and others, was held in Manchester on February 13th, 1908. Mr. W. H. Johnson (Messrs. Richard Johnson, Clapham, and Morris, Ltd., Manchester) was elected to the Chair.

It was unanimously resolved to form a Copper and Brass Institute.

The impetus to this movement was given by a letter from Mr. W. H. A. Robertson, of Bedford, which appeared in several papers on January 24th.

The objects of the Institute are similar to those of the well-known Iron and Steel Institute, viz.:—

1. To afford a means of communication between members of the trades in question, bearing upon their respective manufactures, excluding all questions connected with wages and trade regulation.
2. To arrange periodical meetings for the purpose of discussing practical and scientific subjects relating to the manufacture, working up, and use of the non-ferrous metals.

It is not the intention of the founders to limit the Institute to the copper and brass trades, but to include all those connected with the commercially important non-ferrous metals and their alloys, such as lead, zinc, tin, aluminium, nickel, silver, gold, platinum, &c., and their alloys.

In order to obtain a much wider and fuller discussion than was possible at the preliminary meeting, and to define the constitution and method of procedure of the Institute, it is proposed to hold a meeting in the Midland Hotel, Manchester, on Tuesday, March 10th, at 4 p.m., to which all those interested are most cordially invited. This letter is the only public summons to the meeting that will be issued.

All who hope to attend the meeting or take an interest in the formation of the proposed Institute, are requested to send their names to any of the following:—

William H. Johnson, care of Rd. Johnson, Clapham, and Morris, Ltd., Manchester.
H. C. H. Carpenter, Professor of Metallurgy, The University, Manchester.
G. G. Poppleton, care of The Wholesale Traders' Association for the Hardware and Metal Industries, Birmingham.

Manchester, February 17th, 1908.

NOTES AND QUERIES.

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

Biological Chemistry Examination.—(Reply to P.).—If P. will call at the Institute, I shall be pleased to show him the books in the Library which would assist him in preparing for the Examination.—R. B. Pilcher, Registrar.

MEETINGS FOR THE WEEK.

Monday, March 2nd.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Considerations affecting the 'Strength' of Wheat Flours," by J. L. Baker and H. F. E. Hulton.
Tuesday, 3rd.—Royal Institution, 3. "Membranes—Their Structure, Uses, and Products," by Prof. William Stirling, M.A., LL.D., D.Sc., &c.
Wednesday, 4th.—Royal Society of Arts, 8. "Modern Dairy Practice," by L. M. Douglas.
Thursday, 5th.—Royal Institution, 3. "Early British History and Epigraphy," by Prof. Sir John Rhys, M.A., &c.
—— Chemical, 8.30. "Solubility of Iodine in Water," by H. Hartley and N. P. Campbell. "Traces of a New Tin Group Element in Thorianite," by Miss C. de B. Evans.
Friday, 6th.—Royal Institution, 9. "Recent Earthquakes," by Prof. John Milne, F.R.S., &c.
Saturday, 7th.—Royal Institution, 3. "Electric Discharges through Gases," by Prof. J. J. Thomson, F.R.S.

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ON THE

PHYSICAL ASPECT OF THE ATOMIC THEORY.*

By Prof. J. LARMOR, Sec.R.S.

THE lecture began by setting out a physical reason *à priori* why matter should be constituted of discrete particles instead of being continuous. The requirements of physics demand an ether to serve as the means of communication between portions of matter out of contact with each other; and space can hardly be conceived as *fully* occupied simultaneously by two media, matter and ether; hence the matter must be constituted of discrete centres or nuclei, determining permanent collocations of energy in the ether, which are, in fact, primordial atoms and their fields of force. The feasible problem of atomic physics is to build up an adequate idea of the dynamic constitution of these ethereal fields of force; there is the problem beyond, to determine the intrinsic constitution of the central nuclei to which they are attached, which may remain permanently beyond our ken. The expansion of our ideas about the atoms and their structural connection with the ether was traced from their origin in Descartes, through Huygens and Newton down to the more definite modern types of representation, as regards various essential features that are afforded by the vortex atom and the electron.

In the hands of the physicists, especially Newton and Young, the atom had already become a complex structure capable of definite inherent periods of free vibration, but so far as physics was concerned the same substance might include various kinds of atoms. The fundamental advance of Dalton, which assured an adequate domain to chemistry as an exact science, was the proof that each compound substance is definite as regards its molecule, and that all atoms of the same elementary body are identical. Whether this absolute identity points to the atom of each chemical element being a dynamically balanced structure of primordial atoms, one of a limited number of possible definite types of structure—which would be a perfectly reasonable way of accounting for this remarkable identity—remains an open question. The periodic relations of the elements, connected most closely with the name of Mendeleeff, certainly indicate that, whatever may be the case as regards the kernel, the outer structure of the atom, so to speak, which is the link through the ether between the nucleus and the outside world, is constituted on the basis of a common ultimate element which may be the electron.

The remark of Maxwell seems still to retain its force, that the mechanism of biological evolution could hardly reside in atoms, primordial or other, which had not much vaster underlying complication than is needed for their purely physical relations. The facts of biology may possibly demand a hypothesis such as the above, that atoms not in intimate contact interact through the ether according to general physical laws in the manner required to constitute the physical cosmos; but that there may also be a closer inter-penetration of atomic nuclei in which far more complex agencies are involved.

The mechanical atom of the earlier physicists, considered in this physical aspect as an unknown core determining the field of activity in the surrounding ether, has had, since Faraday's discoveries in electrolysis, to take on a more definite form as the electrical atom. The result had been fully reached by Faraday himself, though it needed to be enforced later by Helmholtz, that the energies which have play in chemical combination are of electrical origin, implying thereby, according to Maxwell's interpretation, energies of intrinsic stress and motion brought to bear from atomic stores located in the adjacent ether. This doctrine has led on to the modern theory of purely electric atoms which was already demonstrable on theoretical grounds, of course in a way less definite than we now know it, before the very remarkable discovery of electrons actually free had been reached, through the phenomena of radio-activity either electrically induced or spontaneous. Here, again, there is the same choice of points of view open to tentative development. We may proceed on a limited hypothesis as if the electrons are the sole primordial atoms; or we may assume that there are various ultimate atoms which have existence and structure of their own, of type largely unknown and independent of the ether, and that the electrons which are associated with them, whether temporarily or intrinsically, form merely one feature of their constitution, viz., their means of communication with the ether, and through it with other atoms at a distance to form an ordered universe.

In any case we are right in following out the hypothesis, there being, in fact, none other open to us, that the purely physical manifestations of atoms—those, namely, that, owing to the simple inter-connection involved in their common seat in the ether, aggregate into the definite physical qualities of matter in bulk—are in the main or in most circumstances practically a group by themselves, and that they are thus capable of being investigated on these broad simple principles of dynamics, which Newton definitely formulated as a suitable foundation for the analysis of general physical activity as it presents itself in the universe. This so-called mechanical hypothesis has been eminently the fruitful one; it pointed the way to the principle of the conservation of energy, and is now elucidating the wider principle of its definitely limited availability; it gave a rational explanation of the spectrum and of radiation in general, which has proved a reliable and precise guide to investigation of phenomena far below the surface, such as the selective dispersion of light and the magnetic action on radiation; it reduced electrical phenomena to order and control, and connected them with light. It must therefore be presumed to be available as the clue for the further elucidation of pressing problems, such as the nature of the transmission of gravitation and of the intimate operation of chemical affinities.

The tendency to reject dynamical analysis as artificial in such subjects as electro-dynamics, which received some stimulus from the theoretical writings of Hertz, seems to overlook the fact that it was precisely as a compact working basis suitable for the formulation of experience in its more general aspects, that the Newtonian scheme of dynamics was put forward by its author. In the course of time that scheme has become wider and more elastic, through the generalisations of Lagrange and Hamilton, expounded forcibly on the physical side by Kelvin, Helmholtz, and various others. But to take over the final results, and dress them in new language devoid of the dynamical implication, seems to involve a misreading of scientific evolution.

This position may be enforced by a quotation from the final exposition of Newton's views on the scope of Natural Philosophy in general, inserted by himself at the end of the famous "Queries" ("Opticks," Ed. 3, p. 377):—"To tell us that every Species of Things is endow'd with an occult specifick Quality by which it acts and produces manifest Effects is to tell us nothing. But to derive two or three general Principles of Motion from Phænomena, and afterwards to tell us how the Properties and Actions of all corporeal Things follow from those manifest Principles, would be a very great step in Philosophy, though the Causes of those Principles were not yet discovered. And therefore I scruple not to propose the Principles of Motion above mention'd, they being of very general Extent, and leave their Causes to be found out." Then he proceeds to associate his Laws of Motion with an atomic theory.

* Abstract of the Wilde Lecture delivered before the Manchester Literary and Philosophical Society, March 3, 1908.

A review of the electrical side of the atomic theory requires a consideration of the phenomena of ionisation in solutions. The theoretical difficulties which have presented themselves in this subject were discussed, in particular the nature of the energy changes which must occur when a salt is dissolved, and thus split into separate ions. Reasoning from the processes of the voltaic cell, as expounded after Faraday by Helmholtz, the view is advanced that an equivalent of purely local potential energy of affinity with the solvent must be exhausted in order to provide for the separation of the ions, but without much violent motional disturbance such as would diffuse partially away into the form of heat. This absence of such motional dissipation of the energies of affinity, as indicated, for example, by their almost complete mechanical availability in a Daniells cell, is perhaps connected with the intimate contacts in confined spaces which are characteristic of the processes at the electrodes by which the chemical change is effected. It is suggested that a similar mode of explanation applies to the very high, sometimes nearly complete, mechanical availability (Berthelot) of the energy of chemical transformations in dense media such as liquids and solids, as contrasted with dilute systems such as gases, which the recent work of Nernst and his pupils has brought again to the front.

The lecture passes on to touch on those extensive branches of chemical physics to which the constitution of the atom is not essential, where only a statistical grasp of the molecular associations and dissociations that are taking place is required. The quantitative theory of chemical equilibrium and of progress of chemical change, as regards dilute systems, comes under this head, of which the prototype and the most highly developed example is the kinetic theory of gases. The modern theory of electrodynamics as based on the displacements and motions of electrons is in the main analogous; and the theory of gravitation, when it comes to light, will be of the same kind.

In particular the molecular aspect of reaction in gases is passed under review. Reasons are brought forward for holding that in gases all ultimate reactions are of necessity mono- or bimolecular. If this be so, the important work now proceeding with regard to the effect of impurities in promoting or inhibiting gaseous reactions, must lead to fuller knowledge of the transient molecules or radicles which are formed in the destructive encounter of a pair of the reacting molecules, and are the carriers or intermediaries leading finally to poly-molecular change; while the same transient combinations may be approachable independently from another side as affording the interpretation of the complex banded spectra of emission or absorption in gaseous media.

The very remarkable and most fruitful and prophetic symbolic theories of molecular structure, especially for the complex molecules of organic chemistry, have not yet proved capable of dynamical interpretation; it seems necessary, however, to admit on account of the wide range of physical properties that are nearly atomically additive that stereochemical collocations do represent in some real way the actual aggregation of the atoms instead of mere symbolical representation of it. Recent investigation appears to bring out in certain cases a somewhat definite relation between the configuration of the molecule and the crystalline form of its physical aggregations, which, though reasonable, could not have been foreseen *à priori*; exact crystallographic measurements may thus in time afford another intimate clue to the molecular structures in related series of compounds.

Royal Institution.—Professor Milne will be unable to deliver his Discourse at the Royal Institution on "Recent Earthquakes" on Friday, the 6th instant. The Discourse on that date will be delivered by Professor Love on "The Figure and Constitution of the Earth." Professor Milne's Discourse is postponed until March 20.

ESTIMATION OF COCOANUT OIL IN BUTTER.

By RAYMOND ROSS, F.I.C., and JOSEPH RACE, A.I.C.

In reference to the papers by Mr. T. R. Hodgson which recently appeared in the CHEMICAL NEWS (vol. xcvi., pp. 273, 288, 297), on the estimation of cocoanut oil in butter by means of $KMnO_4$, we should like to point out that the process as devised by him is in our opinion unworkable.

The process essentially consists of the oxidation of 20 cc. of a 0·1 per cent solution of the saponified fat by means of 50 cc. of decinormal $KMnO_4$ and 50 cc. of H_2SO_4 (50 per cent). The mixture is heated on the water-bath for at least half-an-hour, and subsequently titrated with standard oxalic acid or ferrous ammonium sulphate. The author recommends the use of the latter.

Firstly, we should like to point out that H_2SO_4 of the strength prescribed exerts under the conditions laid down a considerable action on $KMnO_4$. Thus, on treating 20 cc. of water and 50 cc. of decinormal $KMnO_4$ on the water-bath for thirty-five minutes with varying amounts of 50 per cent H_2SO_4, the following results were obtained:—

20 cc. of water + 50 cc. of decinormal $KMnO_4$—	Cc. of decinormal oxalic acid required.
+ 5 cc. H_2SO_4 (50 per cent)	48·0
+ 10 " "	42·5
+ 15 " "	31·0
+ 25 " "	22·4
+ 40 " "	18·5
+ 50 " "	13·7

From these results it is evident that the quantity of $KMnO_4$ remaining depends largely upon the amount of acid present. If, however, only small quantities of H_2SO_4 are used, concordant results can be obtained, and we therefore tried Mr. Hodgson's process using only 5 cc. of 50 per cent acid. Two samples of butter and two of cocoanut oil treated in this manner gave the following oxygen equivalents:—

	Oxygen equivalent.
Butter No. 1	60·0
Butter No. 2	62·3
Cocoanut oil No. 1	54·7
Cocoanut oil No. 2	57·6

Butter No. 2 was farmer's butter of known origin and purity. These results being unsatisfactory from the point of view of differentiation we varied the process by effecting the oxidation in alkaline solution, as by this means we thought that the two fats might vary in their oxygen equivalents owing to the formation of varying amounts of hydroxy acids. That this was not the case is shown by the following figures:—

	Oxygen equivalent.
Butter No. 2	57·3
Cocoanut oil	49·1

We thought, however, that it might be of interest to know to what extent oxidation took place with various fats and fatty acids when treated with $KMnO_4$ in slightly acid solution without previous saponification. The following table gives the results obtained by oxidation of small quantities of the substance with a large excess of permanganate and 5 cc. of 50 per cent acid.

Substance.	Oxygen equivalent.
Butter	2·9
Butter fatty acids	3·6
Cocoanut oil	1·8
Cocoanut oil fatty acids	0·8
Palm oil fatty acids	19·8
Lactic acid	20·7
Acetic acid	4·3
Oleic acid	15·4
Stearic acid	3·3
Glycerol	116·0

Further, working as before but in alkaline solution, after saponification we obtained the following figures:—

Substance.	Oxygen equivalent.
Butter fatty acids	48·0
Cocoanut oil fatty acids	43·0
Cotton-seed oil fatty acids	46·7
Lactic acid	37·6
Oleic acid	55·3
Stearic acid	14·7
Cotton-seed oil	75·3

From the above results it is clear that as a means of detecting adulteration the process is quite useless.

It will be observed that there is a great difference in the oxygen equivalents of saponified and unsaponified fats, and that this difference also extends to the fatty acids is shown by the following:—

Oxidation in Acid Solution with previous Saponification.

Substance.	Oxygen equivalent.
Butter fatty acids	45·6
Cocoanut oil fatty acids	40·1
Cotton-seed oil fatty acids	43·8

It is therefore evident that after saponification considerably higher results are obtained than with untreated fats and fatty acids. The reason for this is probably that when the soap solution is decomposed by acid, the fatty acids are suspended in the liquid in a very fine state of division. If this were the case it might be expected that the more concentrated the soap solution the lower would be the oxygen equivalents obtained. This deduction is supported by the figures given below, which were obtained by oxidation of varying quantities of butter-fat in alkaline solution, the titration being made immediately after slight acidification.

Weight of butter-fat used.	Oxygen equivalent.
0·015	88·0
0·045	56·9
0·090	48·9

The difference in the oxygen equivalents of the fats and their fatty acids must be due to the glycerol and the soluble fatty acids. As both butter and cocoanut oil contain approximately equal quantities (10 per cent) of glycerol, which has an oxygen equivalent of about 122·0 in acid solution, it is evident that the glycerol present can only account for a difference of 12 in the oxygen equivalent, assuming that none of it is lost during the evaporation of the alcoholic soap solution. It therefore follows that the soluble fatty acids, which are only present in very small quantities, must have a considerable oxygen equivalent.

Lastly, we should like to call attention to the difficulty experienced in obtaining a good end reaction owing to the retention of the hydrated oxides of Mn by the insoluble fatty acids liberated on the addition of acid. This is the case with both oxalic acid and ferrous ammonium sulphate, but in the latter case there is the additional difficulty of the yellow colour due to the oxidised iron salt. It is possible that the addition of phosphoric acid might overcome this difficulty.

ON THE VOLUMETRIC ESTIMATION OF LANTHANUM AS THE OXALATE.

By W. A. DRUSHEL.

NEARLY thirty years ago Stolba stated that cerium, lanthanum, and didymium may be estimated by treating their oxalates with potassium permanganate in the presence of sulphuric acid, but gave no experimental evidence in the form of analytical results (*Sitzber. d. Böhm. Gesell. d. Wissenschaften*, iv., July, 1879; *Zeit. Anal. Chem.*, xix., 194). Later this statement of Stolba was confirmed by a paper from the Kent Chemical Laboratory of Yale University (Browning, *Am. Journ. Sci.*, 1899, viii., 451), in which it was shown that cerium may be estimated by precipitating cerium oxalate with a definite amount of a standard solution of ammonium oxalate used in excess. The precipitated cerium oxalate was decomposed by dilute sulphuric acid, and the oxalate estimated by permanganate, and the ammonium oxalate in excess of the amount required for the precipitation was also estimated by permanganate. By this process the results were checked.

The work to be described was undertaken to determine the best conditions for the estimation of lanthanum as the oxalate, and also to furnish the desirable experimental data in support of Stolba's original statement.

For this work about 10 grms. of pure ammonium lanthanum nitrate were prepared by separating the lanthanum and didymium from the cerium in a kilogrm. of the mixed sulphates by Mosander's chlorine method. The mixture of lanthanum and didymium chlorides thus obtained, having been shown to be free from cerium by the hydrogen peroxide test, was converted into a mixture of ammonium lanthanum nitrate and ammonium didymium nitrate. By fifty re-crystallisations about 40 grms. of pure ammonium lanthanum nitrate were obtained. This salt was dissolved in 80 cc. of water, and the solution through a depth of 19 cc. showed no trace of absorption bands. A few cc. of the solution evaporated to dryness and ignited gave a pure white oxide. Out of this solution of the double nitrate about 10 grms. were re-crystallised for the experimental work of this paper. The procedure is as follows:—

From a neutral lanthanum solution (a 1 per cent ammonium lanthanum nitrate solution being used in this work) the oxalate is precipitated by a measured amount of standard *n*/10 oxalic acid, or ammonium oxalate after the addition of a few drops of acetic acid. The precipitate is thoroughly stirred and allowed to settle. It is then filtered through a perforated crucible fitted with an asbestos felt. After thoroughly washing with water the crucible and precipitate are placed in a beaker with 100 to 300 cc. of water and 10 to 30 cc. of (1:4) sulphuric acid. The contents of the beaker are heated nearly to boiling, and at once titrated to colour with standard potassium permanganate. The filtrate is similarly titrated as a check on the titration of the precipitate. The lanthanum is calculated as La_2O_3 from the two titrations. The mean of the two closely agreeing values thus obtained is taken.

The solution of ammonium lanthanum nitrate used in this work was standardised by evaporating measured portions to dryness, and carefully igniting the residue to constant weight.

TABLE OF RESULTS.

(Lanthanum .. .. 138·9)

	La_2O_3 taken as the double nitrate.	La_2O_3 found.		Average.	Error.
		Precipitate.	Filtrate.		
	Grm.	Grm.	Grm.	Grm.	Grm.
1.	0·0148	0·0152	0·0144	0·0148	0·0000
2.	0·0148	0·0149	0·0139	0·0144	−0·0004
3.	0·0296	0·0302	0·0291	0·0296	0·0000
4.	0·0296	0·0302	0·0293	0·0297	+0·0001
5.	0·0592	0·0599	0·0586	0·0593	+0·0001
6.	0·0592	0·0598	0·0585	0·0592	0·0000
7.	0·1184	0·1191	0·1179	0·1185	+0·0001
8.	0·1184	0·1191	0·1182	0·1187	+0·0003
9.	0·2368	0·2376	0·2362	0·2369	+0·0001
10.	0·0148	0·0149	0·0145	0·0147	−0·0001
11.	0·0148	0·0150	0·0147	0·0148	0·0000
12.	0·0296	0·0298	0·0293	0·0295	−0·0001
13.	0·0592	0·0596	0·0589	0·0593	+0·0001
14.	0·1184	0·1190	0·1182	0·1186	+0·0002
15.	0·1036	0·1040	0·1029	0·1035	−0·0001

In Experiments 1 to 9 ammonium oxalate was used in making the precipitation, in 10 to 15 oxalic acid was used.

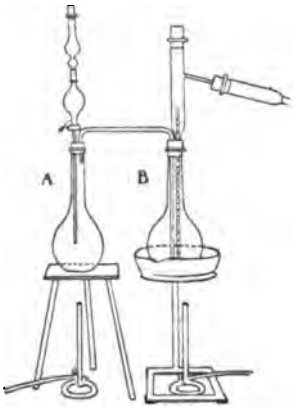
In conclusion, the author acknowledges his indebtedness to Prof. Philip E. Browning for helpful suggestions during the progress of the work.—*American Journal of Science*, xxiv., p. 197.

THE USE OF ZINC CHLORIDE IN THE ESTERIFICATION OF SUCCINIC ACID.

By I. K. and M. A. PHELPS.

In a former paper from the Kent Chemical Laboratory of Yale University (*Am. Journ. Sci.*, xxxiii., 368) it has been shown that in the action of succinic acid with ethyl alcohol containing hydrochloric acid to form diethyl succinic ester, the largest yield from a known weight of succinic acid is obtained where maximum dehydration is accomplished. In the work given here the action of zinc chloride in forming diethyl succinic ester in the mixture of succinic acid and ethyl alcohol both with and without the addition of hydrochloric acid is shown.

The apparatus figured was used in all of the experiments recorded here. Two round bottom flasks of 500 cc. capacity, each provided with inlet and outlet tubes held in rubber stoppers, were connected as shown. Of these, B, connected to a condenser through a Hempel column carried a thermometer, and from flask A an inlet tube adjusted to dip beneath the liquid to the same depth as the thermometer. The flask A carried a separating funnel provided with a drying tube, as well as the exit tube to the flask B. In the flask B succinic acid was heated, by means of a bath of acid potassium sulphate, in some experiments with a definite amount of absolute alcohol alone, in others with the same amount of absolute alcohol containing hydrochloric acid gas, while from the flask A gaseous alcohol in most cases, and in a few cases gaseous alcohol with hydrochloric acid, was driven over into the mixture in B where esterification took place. The crude succinic ester



left in flask B was freed from impurities by treating with sodium carbonate solution after first removing the zinc chloride by washing with water. The ester was freed from carbonate by rinsing with distilled water containing sodium chloride. The mass of ester carried mechanically with the several wash-waters was extracted by shaking out separately three times with ether. The ether extracts and the succinic ester were gathered in a 250 cc. distilling flask fitted in the usual way for a vacuum distillation with a 100 cc. distilling flask used as a receiver, and, after fractioning off low boiling impurities, largely ether, alcohol, and water, was distilled and collected in the receiver, cooled by a stream of water striking it constantly, and then weighed.

The pure zinc chloride of commerce was freshly fused for use in the experiments. The alcohol employed was made as anhydrous as can be obtained by successive treatments with fresh quicklime. The alcohol containing hydrochloric acid was charged with the dry gas in the proportion of 10 grms. to the litre. The succinic acid used was in most cases the pure acid of commerce, in the others pure succinic acid made by re-crystallising the product formed by the hydrolysis of the pure ester in the presence of nitric acid.

The result obtained in Experiment 1 of the table was found by heating with an acid potassium sulphate bath in the flask B a known weight of succinic acid with 40 cc. of the total amount of absolute alcohol used in presence of 10 grms. of zinc chloride at a temperature of 100—110°, while driving into it the remainder of the alcohol in the form of vapour from flask A. All vapours from the flask passed through the Hempel column to the condenser. The Hempel column had an active surface of beads of 10 cm. in height and a diameter of 2 cm. At its lower end it was in connection with a tube 5 cm. in length and of 0·5 cm. bore, and had an opening blown in its side 1·5 cm. from the end. By the use of a column of this construction the hot vapour is enabled to go upward while the condensed liquid flows downward readily. It was found that by the use of this column neither succinic ester nor succinic acid distilled in such amount, if at all, that it could be detected in the liquid distillate. The impure ester in flask B, when all alcohol as vapour from flask A had been passed into it, was cooled, and then poured into a separating funnel containing water with ice, using a small amount of ether to rinse the ester from the flask, and the zinc chloride was removed as far as possible. After separating the ester from this solution any acid impurities were neutralised with an excess of sodium carbonate in solution, and the ethereal solution was then washed with distilled water. The aqueous solutions in which the ester had been washed were shaken out three times separately with ether. The ethereal extracts were gathered in a 250 cc. distilling flask connected in the usual way for a vacuum distillation with a 100 cc. distilling flask used as a receiver. The low boiling impurities, ether, alcohol and water largely, were separated by a vacuum fractionation, the 250 cc. flask being heated in a bath of hot water at 60° finally for fifteen minutes after the manometer registered 15 mm., and the succinic ester was then distilled and weighed.

The procedure in case of Experiments 2 and 3 was the same excepting that the alcohol used was charged with hydrochloric acid in the proportion of 10 grms. to the litre; and in case of No. 3, and, also, in case of all other experiments in the table where only 1 grm. of zinc chloride was used, the rinsing with cold water before neutralising with sodium carbonate was omitted. In Experiments 4 to 10 the 40 cc. of alcohol heated with the succinic acid contained 1·25 per cent of hydrochloric acid gas, while absolute alcohol in amounts recorded in the table distilled into this mixture heated at 100—110°.

No.	Succinic acid.	$ZnCl_2$.	Alcohol with HCl.		Reaction time.		Succinic ester.		
							Theory.	Found.	Per cent.
	Grms.	Grms.	Cc.	Per cent.	Hrs.	Mins.	Grms.	Grms.	
1.	50	10	200	0	2	30	73·7	66·90	90·8
2.	50	10	200	1·25	0	50	73·7	71·25	96·7
3.	50	1	200	1·25	0	45	73·7	69·40	94·2
			160	0					
4.	50	10	40	1·25	4	0	73·7	69·70	94·6
			160	0					
5.	50	10	40	1·25	0	45	73·7	72·00	97·7
			60	0					
6.	50	1	40	1·25	0	20	73·7	53·15	72·1
			60	0					
7.	50	1	40	1·25	0	55	73·7	52·05	70·6
			160	0					
8.	50	1	40	1·25	1	0	73·7	70·30	95·4
			160	0					
9.	50	1	40	1·25	0	45	73·7	71·78	97·4
			160	0					
10.	50	1	40	1·25	0	50	73·7	71·88	97·5

From an inspection of the results in the table, it is evident that in presence of zinc chloride to the amount of 10 grms. with the proportions of succinic acid and alcohol given in the table, a fair yield of succinic ester is possible. Introducing hydrochloric acid and shortening the time of the

reaction tends to increase the yield as shown by Experiment 2. Reducing the amount of zinc chloride present gives satisfactory results, as is clear by comparing Experiment 5 with 9 and 10. Although the amount of alcohol present in 6 and 7 during the reaction is double that theoretically required to esterify the acid present, it is not sufficient for the esterification under the conditions of the experiments. The simplest conditions of all those given in the experiments where a yield is satisfactory are those under which 8, 9, and 10 were made.

Hence, it is clear that in presence of zinc chloride diethyl succinic ester is easily obtained in large amount closely approximating that theoretically possible from a known amount of succinic acid. This is most easily done by heating at a temperature about 100° succinic acid with alcohol containing a small amount of hydrochloric acid in presence of zinc chloride in small quantity, while gaseous alcohol is driven into the mixture.—*American Journal of Science*, xxiv., p. 194.

THE BEHAVIOUR OF MOLYBDIC ACID IN THE ZINC REDUCTOR.

By D. L. RANDALL.

THERE has been a difference of opinion in regard to the degree of reduction obtained when molybdic trioxide, in sulphuric acid solution, is passed through the column of amalgamated zinc as applied in the Jones reductor. Jones (*American Institute Mining Engineers*, xviii., 705), who first determined molybdenum by this method, considered that the reduction goes to the condition represented by the formula $Mo_{12}O_{19}$, the same degree of reduction that Wernke (*Zeit. Anal. Chem.*, xiv., 1) obtained with zinc and sulphuric acid in a closed flask. Doolittle (*Journ. Am. Chem. Soc.*, xvi., 234) and Eavenson found that, by varying the strength of the acid and the speed at which the molybdenum was passed through, different degrees of reduction might be obtained. They calculated no formula corresponding to the degree of reduction obtained by them which was lower than that represented by $Mo_{12}O_{19}$. W. A. Noyes and Frohman (*Journ. Am. Chem. Soc.*, xvi., 553), by taking pains to replace the air in the reductor flask by carbon dioxide, were able to obtain a reduction to the form of Mo_2O_3. Blair (*Journ. Am. Chem. Soc.*, xxvii., 747) and Whitfield, however, were unable to press the reduction below the condition represented by the symbol $Mo_{24}O_{37}$. Miller (*Journ. Am. Chem. Soc.*, xxv., 919) and Frank in repeating the experiments of Blair and Whitfield obtained in general the same results, though by taking extraordinary precautions they were able to get a reduction to a point a little below midway between the conditions represented by the symbols $Mo_{24}O_{37}$ and Mo_2O_3.

The ease with which the reduced molybdenum solution is oxidised by the air has been noted, and suggests the possibility of charging the reductor flask with some oxidiser unaffected by air, which shall anticipate the oxidising effects of the air as the reduced molybdenum compound comes through the reductor and register the oxidation.

In the first experiments an excess of a standard solution of potassium permanganate was used in the receiver. But it was found, by running blanks, that somewhat more than the theoretical amount of permanganate was used up. Table I. shows the results of experiments made by charging the reductor flask with 20 cc. of approximately tenth-normal standard potassium permanganate, passing 300 cc. of warm dilute (2·5 per cent) sulphuric acid through the reductor, adding 20 cc. of standard ferrous sulphate solution and titrating with permanganate to colour.

This excessive reducing action on the permanganate must be due either to impurities in the zinc, to small particles of zinc worked through the asbestos layer at the bottom of the reductor, or possibly to the hydrogen formed in the reductor. That the last mentioned possibility is a

TABLE I.

$FeSO_4$.	$KMnO_4$ used.	$KMnO_4$, theory.	Difference.
Cc.	Cc.	Cc.	Cc.
20	24·45	23·25	1·20
20	23·88	23·25	0·63
20	25·40	23·25	2·15
20	24·90	23·25	1·65

sufficient cause of the effects obtained was shown by passing hydrogen, formed by the action of hydrochloric acid on zinc in a Kipp generator and washed with water and caustic potash, through 23 cc. standard permanganate diluted with 300 cc. of hot dilute (2·5 per cent) sulphuric acid, adding 20 cc. of a solution of standard ferrous sulphate, and titrating back with permanganate. The results obtained by such action of hydrogen during fifteen minutes is shown in Table II.

TABLE II.

$FeSO_4$.	$KMnO_4$ required.	$KMnO_4$ theory.	Reduced by hydrogen.
Cc.	Cc.	Cc.	Cc.
20	24·6	23·1	1·5
20	24·7	23·1	1·6
20	23·6	23·1	0·5

Having seen that potassium permanganate could not be used in the reductor flask, ferric alum was next tried as an oxidiser. The only objection to the use of this salt, that at the usual dilution of 500—600 cc. an excess of ferric alum colours the solution strongly and makes the end-point in the titration somewhat difficult to recognise, is overcome by the addition of a few centimetres of phosphoric acid which renders the solution colourless.

For the work with the ferric oxidiser the C. P. ammonium molybdate of commerce was re-crystallised and found to contain 81·55 per cent of molybdenum trioxide by treating weighed portions in a platinum crucible with nitric acid and evaporating to dryness on the steam-bath and igniting gently and weighing the molybdic anhydride formed. The ferric iron solution for use in the reductor flask was prepared by dissolving 100 grms. of the crystallised salt in one litre of water. The column of zinc in the reductor was 36 cm. in length. The procedure was to charge the reductor flask with 20 or 30 cc. of the iron solution and 4 cc. of phosphoric acid, and to pass through the reductor in succession 100 cc. of hot dilute sulphuric acid (2·5 per cent.), the ammonium molybdate dissolved in 10 cc. of water and acidified with 100 cc. of the hot dilute acid (2·5 per cent), 200 cc. of the hot dilute acid, and finally 100 cc. of hot water. The solution was titrated while still hot with approximately tenth normal permanganate standardised against ammonium oxalate.

The molybdenum as it passed through the lower part of the reductor was green, but on coming in contact with the ferric salt was changed to a bright red colour. The results in the following table are calculated on the assumption that the molybdenum was reduced to the form of Mo_2O_3. The close agreement with theory indicates that the reductor is able to reduce molybdenum to that form and that the reduction does not stop at a point represented by the formula $Mo_{24}O_{37}$ or $Mo_{12}O_{19}$.

TABLE III.

Ammonium molybdate taken.	Iron sol.	H_3PO_4.	$KMnO_4$ used.	MoO_3. Found.	MoO_3. Theory.	Error.
Grm.	Cc.	Cc.	Cc.	Grm.	Grm.	Grm.
0·2000	20	4	30·38	0·1628	0·1631	−0·0003
0·2000	20	4	30·45	0·1632	0·1631	+0·0001
0·2000	20	4	30·33	0·1626	0·1631	−0·0005
0·3000	30	4	45·65	0·2447	0·2447	—
0·3000	30	4	45·80	0·2455	0·2447	+0·0008
0·3000	30	4	45·73	0·2451	0·2447	+0·0004
0·3000	30	4	45·76	0·2453	0·2447	+0·0006
0·3000	30	4	45·68	0·2448	0·2447	+0·0001
0·3000	30	4	45·64	0·2446	0·2447	−0·0001
0·3000	30	4	45·71	0·2449	0·2447	+0·0002

It having been shown that molybdenum may be successfully and uniformly reduced to the condition of Mo_2O_3 by anticipating any previous action of air and registering the oxidation by the action of a ferric salt, the method was then applied to the determination of phosphorus in ammonium phospho-molybdate precipitated in the usual manner.

For this work a solution of microcosmic salt was made up 1·2 grms. to the litre and the phosphorus content determined by evaporating 50 cc. in a platinum crucible and igniting to form the sodium metaphosphate.

With the exception of using an equivalent amount of ammonium molybdate instead of molybdic anhydride, the method given by Blair was used for making up the molybdate reagent ("Chem. Analysis of Iron, Sixth Ed., p. 97). According to this method, 100 grms. of pure molybdic anhydride and 400 cc. cold distilled water are thoroughly mixed and the mixture is treated with 80 cc. of strong ammonia (0·90 sp. gr.). When the solution is complete, the liquid is filtered slowly and with constant stirring into a mixture of 400 cc. of strong nitric acid (1·42 sp. gr.) and 600 cc. distilled water. Then 50 mgrms. of microcosmic salt dissolved in a little water are added, the mixture is agitated thoroughly, the precipitate is allowed to settle for twenty-four hours, and the solution is filtered before using.

In order to have iron present during the precipitation of the phospho-molybdate, a solution of ferric nitrate was prepared and used in each experiment. A solution of the C. P. ferric nitrate of commerce, $Fe(NO_3)_3,9H_2O$, was made up to contain 150 grms. to the litre, with enough nitric acid added to give the solution an amber colour. To free the iron solution from traces of phosphorus, 400 cc. of the molybdenum solution were added to the ferric nitrate and the whole well shaken and allowed to stand for twenty-four hours.

To measured portions of the phosphorus solution, in a 300 cc. Erlenmeyer flask, were added 150 cc. of the iron solution filtered and warmed to 35° C. The flask was stoppered with a rubber stopper and shaken for five minutes. The precipitated phospho-molybdate was allowed to settle, and was then filtered on asbestos in a perforated crucible and washed with a solution of ammonium acid sulphate (15 cc. ammonia, 25 cc. sulphuric acid, 1 litre water). The Erlenmeyer was washed out with a solution of 20 cc. of water and 5 cc. of ammonia, and this was poured on the asbestos in the crucible. The molybdenum solution was acidified with 10 cc. of strong sulphuric acid and was passed through the reductor into the ferric alum solution. The molybdenum solution was preceded by 100 cc. of hot water and followed by 200 cc. of the hot dilute acid and 100 cc. of water. The reduced solution was titrated immediately with approximately tenth normal permanganate. In the following table are shown results thus obtained in precipitating phosphorus as the phospho-molybdate, passing the acidic solution through the reductor into a solution of ferric alum, and titrating the ferrous salt which is formed.

TABLE IV.

P taken. Grm.	P found. Grm.	Error. Grm.
0·003645	0·003673	+0·000028
0·003645	0·003697	+0·000052
0·003645	0·003638	−0·000007
0·003645	0·003726	+0·000081
0·003645	0·003630	−0·000015
0·003645	0·003661	+0·000016

These results are calculated on the assumption that the ammonium phospho-molybdate contains phosphorus and molybdenum in the proportion given by the symbol $(NH_4)_3,12MoO_3PO_4$, and that the reduction proceeds to the condition represented by the symbol Mo_2O_3.—*American Journal of Science*, xxiv., p. 313.

THE DANGER OF OVER SPECIALISATION.*

By L. H. BAEKELAND.

(Concluded from p. 107).

After the advent of Christianity, the despotic Church of Rome retarded the progress of all Christendom as soon as she tried to specialise all human knowledge, so as to make it agree with her own bible. The result was that long and sad period of the dark Middle Ages. In the meantime, Saracen and Jew, on the north coast of Africa, or on the Iberian Peninsula, were able to cultivate science less trammelled by a restrictive religion. To their broader activity do we owe it that scientific investigation was kept alive until the day when the dawn of Reformation enabled backward Christendom to resume again the search for truth.

But, even now, our educational system is still much under the chilling effect of that cloud during which the Middle Ages hid the light of true knowledge. Respectable pedagogues have taken care to hand us down from generation to generation a curriculum which includes most of what formerly was erroneously called *a complete education*. In the latter, ancient literature, holy or profane, has always played a paramount importance. In its programme scant consideration is given to more real modern knowledge which refers broadly to the world we live in, or to the burning questions of the day. I know of many instances where, under the name of liberal education, such an antiquated tuition is still dealt out to the younger generation of both sexes. In fact, many well-meaning persons think that this is the kind of respectable training most desirable for a rich young man of good family and good manners. In reality, such an education is merely an over specialisation of the kind of culture which was meted out to studious sons of patricians some two thousand years ago. For our modern requirements, it is an anachronism, if not a positive danger: a danger—because it is liable to select as standards the undeveloped or erroneous thoughts of antiquity. In many instances, the tendencies of the ancients clash with our more advanced ideas of truth and justice—even if the latter are not always consistently practised by modern society.

The French Revolution encouraged some reforms in this antiquated system of education. But even to-day modern science and modern thought are grudgingly allowed a very small place in the classic curriculum so faithfully defended by some pedagogues. Small wonder, then, if we hear so many respectable people use flowery rhetoric on such inconsistent themes as "science versus religion," or "science versus art"; as if there were any *versus* possible whenever we speak of science as true science, religion as true religion, and art as true art—as if truth were different, whether expressed scientifically, religiously, or artistically!

Luckily for the progress of humanity, now and then some young men, less blessed with worldly goods or wealthy parents, and more eager to make a living by their own work and education, have been compelled to give a vigorous kick to the classic curriculum fetish. Some of them decided to take their education "à la carte"—as President Eliot expressed it so picturesquely. They were compelled to select substantial and up-to-date meals, more suitable to their eager modern appetites; they had to shun the stale and indigestible dishes of education made up in antiquity, to please the palates of bygone times.

Unfortunately, the very cause of this new tendency has carried us so far as to seriously threaten us with the pitfalls of the other extreme.

Furthermore, the fact that scientific learning has found unceasing applications in the production of wealth has fostered the constantly increasing tendency for finding in scientific education or scientific pursuits a mere means of earning a living or making money. This has led into

* Read before the New York Section of the American Chemical Society. From *Science*, 1907, xxv., No. 648.

scientific vocations a large number of persons who in their profession expected to find a quick and easier means for making a living, but outside of this stimulant possessed few, if any, of the qualifications of the true scientist. Impractical in their selection, they deceived themselves by choosing an occupation which less than any other leads to wealth or power. But once having decided to enter a scientific profession, they soon became aware that the call is for specialists, and they were forced to specialise one thing or another by their employers, whether the latter were manufacturers, merchants, or even some educational institutions whom they served as teachers.

In accordance with this same tendency we find manufacturers who, themselves without other training excepting what long experience has taught them, blame our colleges, universities, or technical schools because they do not turn out graduate chemists who can jump right away into their manufacturing works fully acquainted with all the intricacies of the processes; of course, all this with the prospect of a small salary so as to act in competition with a few able and better paid men who had to sacrifice a lifetime in order to acquire experience.

That greed or ignorance should make such claims is quite natural; but that we should find teachers or students who are willing to admit such abnormal educational methods, and change them into a kind of apprenticeship, is a matter of regret for anybody who believes in education as a means for the healthy mental development of his country.

What is worse, our own way of living shows beyond doubt that we all have undergone, more or less, the effects of over specialisation against which I have come to protest. Too much have we learned to look upon our usefulness in life as depending almost exclusively on the concentration of most of our energies, most of our thoughts, upon a narrow line of specialised action. Without knowing it we drift into a mere routine occupation that makes automatic machines out of us. For all generalities of life which do not fall immediately into our own specialities, we are willing to assume respectable conventionality: We are willing to join the herd of docile and unthinking sheep who are following a leader. In science as well as in politics, we are ready to follow this leader, for better or for worse, as long as we can shift upon him our own responsibilities of thought or action.

Busily burrowing along like moles, in the pursuit of our own little specialities, we are dizzily preoccupied with our specialised routine work. We lose the desire of coming once in a while upon the surface of the earth to take a stimulating look at the grand view of nature and its inspiring entity. Once upon a while, we are rather disturbed in our narrow scientific beliefs when some Curie announces radium or radio-activity, or when some Ramsay upsets our orthodoxy by pronouncing the words: evolution of elements. We get fairly shocked when a Crookes speaks of death of matter.

Just in the same way, after admitting as holy faith that weight and matter are constant or indestructible, some day, somebody may have to rouse the most timid of us and force us into the belief that gravitation, like all other energies, can be modified into any of them, or better perhaps, that gravitation, being the more stable of all energies, is the final energy toward which light, heat, and electricity tend to change. Who knows but that ultimately a less neglected study of gravitation may allow us a glimpse into the secret of the destiny of our universe?

I admit many of you will smile at these unorthodox hypotheses or conjectures. Yet, let me ask you: With what methods have we thus far measured any possible changes in weight? We have pinned all our faith, all our beliefs, on a mechanical instrument called a balance. A very delicate method indeed, if judged from our conceited one-sided standpoint of specialists. We are proud if we possess a balance which can weigh 1/100 of a mgrm.; we work ourselves into awe and admiration before an instrument such as the one I saw two years ago which can detect a difference of one-thousandth of a mgrm. A one-thousandth of a mgrm.! How infinitesimally small such a weight appears to our limited conceptions; and yet, what a ponderous quantity this same weight becomes if we try to compare it with the mass of an electron. Our whole science of chemistry is based on the fundamental law of the conservation of matter as formulated by Lavoisier and accepted by us as an axiom. However, by what means has this law been verified, if not by balances more crude, more imperfect, than that clumsy instrument which cannot weigh anything beyond 1/1000 of a mgrm.? It is high time that science should discover a more delicate means for determining small weights than a mere mechanical balance; then, but only then, may we be able to demonstrate beyond doubt whether all the assumptions on which we base our chemistry are correct, or whether we simply have been building a whole science on false premises.

While we are at this subject let us continue this act of self-examination. When we speak of the descriptive part of the science of chemistry, when we describe any reactions, any compounds, any laws, we all refer these to phenomena which take place within an abnormally small range of temperature. Lately, Dewar opened our eyes to some unexpected phenomena which occur at very low temperatures; on the other hand, the electric furnace so ably manipulated by our regretted Moissan enabled him to establish many unsuspected facts at temperatures which our imperfect thermometric methods do not allow us to measure accurately. Yet, if we will drop for a moment our one-sided considerations and look upon everything in true proportions, we must admit that the range of temperatures within which we have studied natural phenomena is disappointingly small, as compared with the possible range of temperature of the universe.

Not so long ago, chemists had no better definition for organic compounds than to designate them as those that were produced under the intervention of vital forces; inorganic bodies, on the contrary, were supposed to be made under the influence of ordinary physical forces. We all know since how Liebig and Wöhler disposed of this mistake by the memorable discovery of the synthesis of urea from inorganic bodies. Nevertheless, many of us to-day are prone to think that the more delicate organic bodies, as, for instance, the constituents of the protoplasm, will never be obtained synthetically. These doubters point to the fact that as soon as we try to imitate these subtle, synthetic reactions which take place in the living cell we remain powerless to accomplish anything beyond splitting or simplifying the molecule. And yet, let me ask you, what are the laboratory methods with which we try to imitate the subtle biological processes? Heating, boiling, distilling, desiccation, precipitation, electric currents, every one of them barbarously destructive methods, with which we blast away at exceedingly delicate compounds. We might just as well try to imitate the melodious music of a Gounod by firing some dynamite cartridges between the delicate strings of a piano?

One-sided as we are, we witness every day of our lives the fact that all vegetation accomplishes its processes of synthesis or assimilation under the indispensable action of light; nevertheless, thus far we have tried very little to avail ourselves of this powerful yet delicate source of synthetic energy. Up till now photochemistry has scarcely been used for any other purposes but the art of photography.

What have we done to utilise the effect of pressure in the study of natural phenomena? Very little, even if we take in consideration some half-hearted attempts in this direction. What are the pressures we dispose of as compared with those which exist in the centre of the earth? We hear of mines about one mile deep of which the tunnels are submitted already to such a tremendous natural pressure that their walls snap together shortly after an excavation is made, leaving the miner barely time to get out, so as to save his life. If we calculate the pressures existing at these depths we come to very awe-inspiring figures. But

if again, we invoke the sense of proportions, we must recognise that a mine one mile deep is a mere insignificant and imperceptible pin prick as compared to the size of the earth. After such considerations, can we expect to duplicate certain chemical or physical processes which have been going on under tremendous pressures in the bosom of the earth? Or shall we try to find means to enormously increase the pressures of which we have thus far disposed in our laboratories, and have considered sufficient, although they are absurdly small.

And how about the element of time in chemical reactions? We all now are aware of the fact that even an explosion of dynamite takes an appreciable and measurable time. On the other hand, Berthelot, in his memorable studies on esterification, has demonstrated that in some cases it requires sixteen years of continuous action before the limit of esterification is reached and a final equilibrium is maintained. We are not inclined to patiently study reactions which take months or years, and yet, in the great laboratory of nature, phenomena are accomplished just the same whether their fulfilment requires seconds or æons. But in our lives, which are of such an infinitesimal shortness if compared with eternity, we look at everything according to the very short lapse of time which is allotted to our little individual existence. We refer and compare everything to it, in about the same way as I suppose the may-fly does to her own little life, after she has become accustomed to the fact that her existence is counted only by a few hours.

I am perfectly aware that these and many other philosophical conceptions are receiving consideration from such broad-minded scientists as have not grown up to consider science as divided in water-tight compartments. For them the borderland between the different fields of specialised science becomes the favourite hunting-ground for the philosopher. To the latter, scientific pursuits mean something broader, something higher than a mere concentration on a special field, to the exclusion of all others.

On the other hand, over-specialised science is apt to degenerate into a mere hobby, where all conceptions of true proportions and harmony are lost. The corner grocer who knows all about the prices and qualities of sugar, coffee, and tea, and little else, is nothing less than an exaggerated example of over-specialised knowledge. In the same way, I am sorry to say it, I have met many an example of so-called scientists whose science does not rank higher than what is involved in the pursuits of my boy when he is eagerly engaged in the collection of cancelled postage stamps. Knowledge does not contribute necessarily to the wisdom of the individual, unless that knowledge be sufficiently diversified to stimulate his thinking powers. The scientist who spends all his time in purely theoretical work and looks down upon the man who tries to find industrial applications for our knowledge, shows just as much unwarranted one-sidedness as the so called "practical" man or empiricist who expresses contempt for purely scientific pursuits.

For fear that I may be misinterpreted, let me repeat that I shall be the last to deny that every one of us is compelled to specialise more or less, in order that we may become thorough in some one branch of human activity and in order to develop our individual usefulness. I am aware that even the dullest specialist, who does conscientious work, will be of some use to the community: If he be engaged in scientific research work, and carefully records well-observed facts, he renders a service to mankind; he presents us with his own home-made little bricks, which in time will be used by the architects of science to build up the ever-increasing edifice of knowledge.

I hope, I need scarcely add, that I further believe that well-recorded scientific facts of small immediate importance may in time become immensely valuable as compared with elegant but wrongly conceived theories based on hasty generalisations.

I believe, also, that in these times of unbalanced industrialism and greed, the law of self-preservation commands us to select a speciality as a bread-winning pursuit. I am fully aware that insufficient pecuniary resources compel many of us to curtail our preliminary studies to the very minimum consistent with what we absolutely need so as to enter into a remunerative trade or profession.

But however light-weighted our educational baggage may be, when we enter practical life, nothing but our own indifference, our bad judgment, our lack of aspiration towards nobler aims, prevents us from remedying this. Every day of our life, as long as we live, is given to us for increasing by self-culture the slender outfit with which we left school. And self-culture, in order to be effective, ought to be directed so as to counteract any one-sided tendencies resulting from our specialistic daily occupations.

The majority of individuals give by far the largest amount of their work, their endeavours, their thoughts, to the production of wealth, or to put it simpler: the art of making money. Yet, engrossed as we are in this one-sided occupation, very few of us think it worth while to undertake the study of that science which investigates the laws of production and distribution of wealth. Ignoring the true, if elementary, principles of political economy or believing in a perverted political economy which has been invented to serve the ends of a few as against the rights and interests of the many, we help to perpetuate the main cause of numerous social ailments. The scant attempt of serious attention which is given to this branch of knowledge by any but a few specialists, has rendered possible the exaggerations and irregularities of our system of industrialism. It has helped to keep in bondage many deserving men of exalted character, but unable to develop their possibilities, as they might do, under a wiser system. Who does not know of some otherwise highly developed individual who now is treated with contempt because he committed the crime unpardoned by our modern society, of failing to master that greedy art of accumulating money for himself, or for others.

Over-specialists as we are in our daily pursuits, we are ever prone to scorn the politicians; we think we have done all our duties as citizens if on election day we take time to cast our vote instead of standing all day on the golf links, but only to find out afterwards that we have supported men who, through ignorance and selfishness, hoodwink us and prevent us making our country the true democratic republic so simply and forcibly defined by Lincoln as: a government of the people, by the people, and for the people.

If we have any fault to find with our politicians and lawmakers we should blame none but ourselves and that tendency of over-specialisation which keeps us in our own narrow routine and lets the politician-specialist rule us and the country as well.

If political economics is a science of momentous interest to everybody alive, it is specially of interest to the chemist, who, thorough believer in the laws of nature, can not fail to admit the same universal yet simple laws in sociology; and who, therefore, is less apt to be misled by those juggleries of reasoning which are so cleverly used to favour private interests against the weal of the community at large. Political economy, different from most sciences, can be mastered without any preparation whatsoever, excepting the relinquishment of all bias and all petty ideas of greed, conceit, or inequity.

But what shall I say about our criminal neglect of eugenics, a science which goes to the very roots of our lives; a knowledge which deals with the future of our children, the happiness and betterment of our race, and yet so neglected that its very name is scarcely known in our usual vocabulary. In the meantime, we go on in our happy-go-lucky-slipshod way; we assume the tremendous responsibility of parentage, and we jeopardise the health and happiness of our children and grandchildren by our carelessness. Instead of trying to bring together in marriage, by orderly, careful, and methodic selection, such persons as are physically and mentally best fit for ennobling our race, we leave this important matter entirely to the whim of chance, blinded

by emotion or prejudice. Our actions in this as in many other instances, are but the logical outcome of a thoughtless one-sided education which does not deal with these subjects, while under the name of *belles-lettres* our thoughts are still further perverted in prose and in rhyme by romantic novelists, who in their own way write on the subject of love and marriage. Neither should we be astonished, if frequently those who feel proudest or brag loudest about their ancestry make very light work of their own lives, as far as their actions involve any responsibility towards their offspring.

Our one-sidedness of conceptions has fraught our whole social system with inconsistencies: we grant the unwarranted privilege to vote to illiterate blacks and whites, tramps, or idlers; but from the intelligent, virtuous, and active woman who is the mother of our children we absolutely withdraw the *right* to participate in the affairs of the nation.

Our lack of broad-mindedness is shown in many other ways. We admit the principle of evolution, but when it comes to concede rights and friendliness towards animals —fellow-beings—we fall short of our theories: we eagerly forget that other living creatures enjoy life and suffer, feel, and think as we ourselves, if not exactly in the same way. Some of us claim to be civilised, and yet find high pleasure and recreation in hunting, killing, maiming, and torturing defenceless animals, although we go on criticising the Spaniards who enjoy the gore of a bull-fight. And even those of us who admit the savage cruelty of hunting and kindred sports do not hesitate to elevate, propagate, and degenerate certain species of domestic animals with the express purpose of killing them for food. We do not see anything inconsistent in the fact that, scientific though we are, and while we talk snobbishly of our refined taste, we are much less particular than plant-eating animals, and we keep feeding on corpses of fellow creatures.

We call ourselves scientists because we believe in the laws of nature. In our studies and our research work we have never-ending opportunities for admiring the marvellous harmony of nature, the invariable laws of God. Yet when we hold our annual banquet of scientists we fail to see that we blaspheme the God of law and order and deny the immutability of his laws by asking him in prayer (and in this similar to savages) to disturb these eternal laws of nature so as to grant us some petty favours, forgetting that we are merely insignificant little dots in the immensity of the universe.

Let me conclude this essay by repeating the main points mentioned therein:

If specialisation may be advantageous for increasing our productiveness in a given field of activity, over-specialisation, on the other hand, may develop one-sidedness; it may stunt our growth as men and citizens; even for persons engaged in scientific pursuits it may render impossible the attainment of true and general philosophic conceptions.

If I have succeeded in convincing some of us that over-specialisation does not bring forth the very best there is in us, if I have contributed ever so little to keep us aloof from the life of dizzy automatic machines, if I have succeeded even in the smallest degree in stimulating you to nobler endeavours, then I shall indeed feel very amply rewarded by your kind attention.

Synthesis of Racemic Dihydrocamphoric Acid.—L. Bouveault and R. Locquin.—Alkyl cyclopentanone carbonic ester can be transformed by the action of alcoholic potash in excess into the potassium salt of adipic α-alkyl-substituted acid. With absolute alcohol the ethyl ester of the same acid is obtained. Disubstituted cyclic ethers behave similarly, giving α and α' substituted adipic ethers. The authors have used this method to synthesise α-methyl α'-isopropyladipic acid. The active form of this acid (dihydrocamphoric) has already been obtained by fusing camphoric acid with caustic potash.—*Comptes Rendus*, cxlvi., No. 2.

PROCEEDINGS OF SOCIETIES.

THE INSTITUTE OF CHEMISTRY.

Annual General Meeting, March 2nd, 1908.

Prof. Percy F. Frankland, LL.D., F.R.S., President, in the Chair.

The Thirtieth Annual Meeting of the Institute of Chemistry was held at 30, Bloomsbury Square, on Monday, March 2, 1908.

The Annual Accounts were received on the motion of Mr. A. Gordon Salamon, the Hon. Treasurer, who said that, owing to the increase in the number of candidates for the Examinations and the exercise of proper economy in expenditure, the year 1907 was financially one of the most satisfactory for the Institute within recent years. He remarked, however, that the work of the Institute was growing, and that therefore greater funds would be required, especially in view of the approaching expiry of the lease of the Institute's house. The Annual Subscription, a guinea, was lower than that of almost every other professional body, and he thought that the time had come for considering the desirability of raising the subscription so as to enable the Institute to extend its work on behalf of the profession.

Mr. E. W. Voelcker, in seconding the reception of the accounts, agreed with the Treasurer's suggestions as to raising the subscription, which was also supported by Mr. C. Sordes Ellis.

In moving the adoption of the Report of Council, Mr. David Howard remarked that only those who could remember the time when there was no organisation of professional chemists knew what it was to be without the Institute. The public now realised that there were other chemists than the pharmaceutical chemists, and, whether consulting practitioners, works chemists, or teachers, they could but admit that very important work had been done during the past year both by way of holding examinations for the hall-marking of young members of the profession, and of action taken to safeguard their interests. He alluded briefly to the recently published Report of the Committee appointed by the Treasury to enquire into the working of the National Physical Laboratory. It had not perhaps conceded all that the Institute asked, but it had met them to a considerable extent, and the profession was indebted to the Council for what they had done in that matter. The Examinations of the Institute were real, practical, and useful, and had exerted an enormous influence on chemical training in British universities and colleges.

The motion was seconded by Mr. G. T. Holloway, who said he knew that the Fellows and Associates warmly appreciated the work of the Institute in maintaining the status of the profession.

Scrutineers having been appointed to examine the votes for the election of the Officers, the Council, and Censors, the President delivered his Address.

He said that the Annual Report showed that the past year was one to which the Fellows and Associates could look back with satisfaction, as it bore evidence of distinct progress and healthy development. The membership had increased, there was a marked advance in the number of entries to the examinations, the Library had been extended, and the finances were in a more satisfactory state. On the occasion of every annual retrospect, however, they were reminded of the mortality of man. The year 1907 proved very fatal to chemists of the highest distinction throughout the world, terminating as it did the labours of Berthelot, of Mendeleeff, of Moissan, and of Perkin, all of whom would be remembered as amongst the greatest masters of chemical science. He referred to the rare intuitive genius of Perkin, and the extraordinary influence which his discoveries had exerted on both science and

industry, and said it was remarkable that he had transmitted so large a measure of his inspiration to the gifted family of chemists he had left behind. Of the other Fellows whom the Institute had lost by death, he made special mention of Dr. Dupré, for many years regarded as a distinguished leader of professional chemists; Dr. Macfadyen, the first Director of the Lister Institute; Dr. John Clark, President of the Society of Public Analysts; Mr. Samuel Hall, Treasurer of the Society of Chemical Industry; Mr. Montague Page; Mr. Richard John Friswell, a Past Vice-President and one of the most active workers for the Institute; and Mr. William Ashwell Shenstone, F.R.S., who had only recently served on the Council.

After referring to the splendid services of the retiring Officers and Members of Council, particularly mentioning Dr. Ed. Divers, F.R.S., and Mr. Edward Bevan, the retiring Vice-Presidents, and Prof. G. G. Henderson, the retiring Examiner, the President commented on the recent addition to the Board of Examiners of Prof. Herbert Jackson (to examine with Mr. Bertram Blount in the Intermediate Examination) and Prof. W. H. Perkin, F.R.S. (to examine in Organic Chemistry).

Continuing, the President dealt with the difficulties of students in deciding the most advisable method of preparing for admission to the profession of chemistry. He advised all serious students to aim at the Associateship of the Institute, and to shape their courses of studying according to its Regulations. Without the qualification of the Institute they would greatly restrict the field in which they could seek employment. The requirements of the Institute tended to broaden the base of chemical training, and could only usefully benefit the student in whatever branch of chemistry he might subsequently engage. He advised them to work for Degrees with high honours in chemistry concurrently with their preparation for the professional examinations of the Institute, so that they might be entitled to claim exemption from the Intermediate Examination. The Institute, by making a regulation to this effect, had put a high premium upon University study, and prevented unnecessary multiplication of examinations. He was sure that the leniency of the Examiners in the Universities did not extend so far as to place any but really satisfactory candidates in the first or Second Class Honours Divisions, and statistics had shown that they had been as successful in the Final Examinations of the Institute as candidates who had passed its Intermediate Examination. It was usually necessary for the candidate, after taking the Honours Degree or passing the Institute's Intermediate Examination, to obtain special training extending over at least a year before proceeding to the Final Associateship Examination. He was convinced that the usual three years' curriculum was wholly inadequate, for whilst the ground to be covered in the study of chemistry had attained colassal dimensions compared with what it was twenty-five years ago and was continually being extended, the students' time was no more protracted than before. The limited time at the disposal of the student gave him little opportunity to take proper advantage of the excellent equipment now to be found in the universities and colleges, and teachers were aware of the urgent necessity of increasing the minimum length of the curriculum prior to graduation, but no University appeared to have the courage to initiate this reform. In the matter of students, it was quality not quantity that universities required, for every science student was a net loss financially, and the work of the classes was too often hampered by a large proportion of undesirables.

On the motion of Prof. J. Millar Thomson, seconded by Mr. Bertram Blount, a cordial vote of thanks was accorded to the President for his Address.

Mr. Blount, in the course of his remarks, alluded to the evidence given by Prof. Frankland before the National Physical Laboratory Committee, and said that so far as the result of the action of the Institute on this matter had been satisfactory, it was greatly due to the fair and convincing manner in which the President had represented the views of the chemical profession.

The President having replied, the Report of the Scrutinerers was received. The following were elected Censors:—Mr. Russell Forbes Carpenter, Mr. David Howard, Sir William Ramsay, and Prof. J. Millar Thomson.

Mr. Percy A. E. Richards, Mr. Walter F. Reid, and Mr. G. T. Holloway were elected Hon. Auditors, and the Officers and Council were declared elected as follows:—

President—Percy Faraday Frankland, LL.D., Ph.D., F.R.S.

Vice-Presidents—Martin Onslow Forster, D.Sc., F.R.S.; Oscar Guttmann, M.Inst.C.E.; Egbert Grant Hooper; David Howard; Herbert Jackson; Sir William Ramsay, K.C.B., LL.D., F.R.S.

Hon. Treasurer—Alfred Gordon Salamon, A.R.S.M.

Members of Council—Leonard Archbutt; Julian Levett Baker; Adrian John Brown, M.Sc.; Russell Forbes Carpenter; Frederick Daniel Chattaway, M.A., D.Sc., F.R.S.; Harold Govett Colman, M.Sc., Ph.D.; John Henry Coste; Bernard Dyer, D.Sc.; Henry John Horstman Fenton, M.A., Sc.D., F.R.S.; Walter William Fisher, M.A.; Henry George Greenish; Otto Hehner; George Gerald Henderson, M.A., D.Sc.; William Richard Eaton Hodgkinson, Ph.D.; Arthur Robert Ling; William Macnab; George McGowan, Ph.D.; Gerald Tattersall Moody, D.Sc.; Henry de Mosenthal; Henry Droop Richmond; Kennedy Joseph Previté Orton, M.A., Ph.D.; John Edward Stead, F.R.S.; Francis Napier Sutton; Robert Rattray Tatlock; Oliver Trigger; John Augustus Voelcker, M.A., B.Sc., Ph.D.; Alexander Forbes Watson, B.Sc.

With a vote of thanks to the retiring Officers and Members of Council, moved by Dr. J. A. Voelcker, seconded by Mr. Salamon, and to which Dr. E. Divers and Col. C. E. Cassal responded, the meeting terminated.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 2, January 12, 1908.

Density of Graphite.—H. Le Chatelier and S. Wologdine.—Already noticed.

Transformation of Solutions of Yellow Phosphorus into Red Phosphorus.—Albert Colson.—The author has established the parallelism between the transformation of yellow into red phosphorus in the free state and when the substance is dissolved. The transformation occurs more quickly the higher the temperature. The time necessary to bring about the commencement of the transformation is approximately inversely proportional to the concentration of the solution when a given temperature is maintained. If "vapour tension" is substituted for "concentration" it is clear that the transformations in solution and in the free state are strictly comparable. The two processes are, however, not identical, and the presence of a solvent retards the transformation.

Constitution of Manganese Cast-Irons.—L. Guillet. Cast-irons containing small amounts of manganese when examined micrographically reveal the process of sorbite and carbide, while those containing more manganese consist of much carbide surrounded by a eutectic which the author has now found to be the eutectic mixed crystals—cementite. Manganese cast-irons, like nickel cast-irons, contain γ ferrite when the amount of manganese or nickel is large enough, but in manganese cast-irons a good deal

of carbide is present, increasing in amount as the percentage of manganese increases. A specimen containing 3·6 per cent carbon and 15 per cent manganese is made of practically pure eutectic. The addition of manganese to grey cast-iron produces ferrite before causing the disappearance of graphite.

Ammoniacal Cuprous Sulphate.—M. Bouzat.—By adding cuprous oxide, ammonium sulphate, and alcohol to aqueous ammonia a precipitate is obtained. After being dried at the ordinary temperature of the air it loses about 1 per cent of its weight when the temperature is raised to 60—80°. Its composition is then represented by $SO_4Cu_2{\cdot}4NH_3$. When it is quite dry it is stable in air, but if it contains small quantities of mother-liquor it instantly oxidises, turning green and generating heat. It is decomposed by water, giving a precipitate of cuprous oxide. It gives a precipitate of copper with dilute sulphuric acid, and a solution of cupric sulphate and ammonium sulphate.

Synthesis of 3-Campholene Lactone.—G. Blanc.—αα-Dimethyladipic ether when treated with sodium in toluene, gives a sodium derivative which by the action of ethyl bromacetate is converted into 3-dimethyl 3-cyclopentanone-2-carbonic-1-acetic ether. This ether is saponified to 3-dimethyl 3-cyclo-pentanone-2 acetic acid by boiling with hydrochloric acid. The ethyl ether of this acid yields a bitertiary glycol and a lactone which is β-campholene lactone.

Constitution of Isosparteïne.—Charles Moureu and Amand Valeur.—Isosparteïne appears to be derived from sparteïne by the transformation of a piperidine chain into a pyrolidine chain. The formula proposed for isosparteïne, which agrees with the value found for its molecular refraction, represents it as a bitertiary base, saturated, and not methylated at the nitrogen. All these properties belong to it in common with sparteïne.

No. 3, January 20, 1908.

Radio-lead.—B. Szilard.—The author has studied the conditions in which it is possible to separate radium D, E, and F from radio-lead when the latter undergoes certain chemical reactions. The re-crystallisation of the nitrate in a neutral solution separates the polonium (radium F) which remains in the solution, but has no effect upon the radium D and E which remain in the crystals. In an acid solution radium E is left in the solution. With the chloride the same separation is effected rapidly and completely. When radio-active lead carbonate is dissolved in concentrated sulphuric acid, and the filtered liquid is evaporated to dryness, the quantity of radium D in the residue is greater than that corresponding to the radio-active equilibrium of the radium E and F present. Nevertheless, there is only a slight concentration of the radium D in the product. Commercial urea gives a precipitate which contains a large part of the radium E and F in the solution but very little radium D, and ammonium carbonate gives the same result. These and other results show that it is easy to concentrate radium F, but much more difficult to concentrate radium D.

Synthesis of Ammonia.—M. Woltereck.—When mixtures of air and hydrogen are passed over iron sesquioxide ammonia is obtained, the most favourable temperature for the reaction being 300—350°. Better results are obtained when water vapour and air are passed over heated turf, and sugar carbon can also be employed. Thus small quantities of ammonia are formed during oxidations in presence of water, provided that the temperature does not exceed 700°.

Catalytic Power of Silica and Alumina.—J. B. Senderens.—Experiments upon the catalytic power of silica and alumina have shown that when silica is precipitated from sodium silicate or aluminium silicate at a moderate temperature it acts as a dehydrating catalytic agent towards alcohols, and gives pure ethylene compounds. But if the silicates are strongly heated for a long time the catalytic power tends to change, and the silica becomes a dehydrogenating agent. Exactly the same holds good for alumina.

Heat of Solution of Alkali Metals and Heat of Formation of their Monoxides.—E. Rengade.—The author's determinations of the heats of solution of the alkali metals give the following results :—(Na,Aq) = 44·1, (K,Aq) = 46·4, (Rb,Aq) = 47·25, (Cs,Aq) = 48·45. The heats of solution of their monoxides are :—(Na_2O,Aq) = 56·5, (K_2O,Aq) = 75·0, (Rb_2O,Aq) = 80·0, (CS_2O,Aq) = 83·2. This gives the following values for the heat of formation of the monoxides :—(Na_2,O) = 100·7, (K_2,O) = 86·8, (Rb_2,O) = 83·5, (Cs_2,O) = 82·7. These figures show that the affinity for oxygen decreases as the atomic weight increases.

Determination of Carbon Disulphide in Benzene.—Isidore Bay.—Phenylhydrazine gives with carbon disulphide a white crystalline precipitate of formula $CS_2(C_6H_5{-}NH{-}NH_2)_2$. The precipitation is complete after two or three hours. The precipitate is then filtered off through double weighed filter-papers, carefully washed with benzene, and dried in a vacuum. By this method carbon disulphide can be very accurately determined in commercial benzenes.

Transformation of α-Oxyacids into Aldehydes by Boiling an Aqueous Solution of their Mercuric Salts. Application to Preparation of *l*-Arabinose.—Marcel Guerbet.—By boiling for some hours mercuric lactate is decomposed into mercurous lactate, lactic acid, aldehyde, and carbon dioxide almost quantitatively according to the equation $2(C_3H_5O_3)_2Hg = (C_3H_5O_3)_2Hg_2 + C_3H_6O_3 + C_2H_4O + CO_2$. This reaction is not peculiar to lactic acid, but is common to all acids having an OH in the α-position. Thus the mercuric salt of gluconic acid, $CH_2OH{-}(CHOH)_4{-}CO_2H$, gives *l*-arabinose, $CH_2OH{-}(CHOH)_3{-}CHO$. The mercurous gluconate is rapidly decomposed into mercury and mercuric gluconate, which again undergoes the same change.

Simultaneous Production of 1.6 and 2.7 Dimethylanthracene.—James Lavaux.—In the following reactions the author finds that the product is not a single anthracene but a mixture of the two dimethylanthracenes 1.6 and 2.7 :—I. Action of CH_2Cl_2 on toluene in presence of $AlCl_3$ (Friedel and Crafts). II. Action of $CHCl_3$ on toluene in presence of $AlCl_3$ (Elbs and Wittich). III. Action of $C_2H_2Br_4$ on toluene in presence of $AlCl_3$ (Anschütz). IV. Action of $AlCl_3$ on toluene (Anschütz and Immendorff). V. Action of $C_6H_5{-}CH_2Cl$ on toluene in presence of $AlCl_3$ (Friedel and Crafts). VI. Action of $AlCl_3$ on xylyl chloride (Friedel and Crafts). VII. Dimethylanthracene from coal-tar (Zinck and Waschendorff). The first of these anthracenes fuses at 240° and the other at 244·5°, and they form a mixture which fuses exactly at 225°. This is the lowest melting-point which the author has found for different mixtures of the two substances, and must therefore be the melting-point of their eutectic. The two constituents can be separated by combining chemical and physical methods.

Syntheses by means of Methyl and Ethyl Adipates.—L. Bouveault and R. Locquin.—Already noticed.

Action of Nascent Hypoiodous Acid upon Acids of Formula $R{-}CH{=}CH{-}CH_2{-}CO_2H$.—J. Bougault.—Phenylisocrotonic acid, $C_6H_5{-}CH{=}CH{-}CH_2{-}CO_2H$, is transformed into benzoylacrylic acid,—

$$C_6H_5{-}CO{-}CH{=}CH{-}CO_2H,$$

by the action of iodine in presence of a very large excess of sodium carbonate. The oxidation of the acid by alkaline potassium permanganate gives benzoic acid and oxalic acid, and reduction by sodium amalgam gives phenyl-γ-oxybutyric acid, $C_6H_5{-}CHOH{-}CH_2{-}CH_2{-}CO_2H$. The reaction which gives rise to benzoylacrylic acid may be represented by the equation $C_{10}H_{10}O_2 + 2O = H_2O + C_{10}H_8O_3$. The intermediate product formed is possibly

C_6H_5—CHOH—CHI—CH_2—CO_2H. The same reaction applied to *p*-methoxyphenylisocrotonic acid, CH_3O—C_6H_4—CH=CH—CH_2—CO_2H, gives an anhydrous acid which the author has as yet prepared in small quantities only. By analogy it should be *p*-methoxybenzoylacrylic acid.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd instant, Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Colonel David Bruce, Miss Deane Butcher, Miss Cleghorn, Mrs. Dugald Clerk, Mr. V. Gordon, Mr. J. Hunter Gray, Miss Hassard, Mr. W. L. Preece, Dr. C. W. Saleeby, Dr. Hans Sauer, Mrs. Schilizzi, Miss Schilizzi, Mr. C. E. Wurtzburg, and Prof. H. A. Wilson, F.R.S., were elected Members. The Special Thanks of the Members were returned to Sir Andrew Noble, Bart., K.C.B., for his donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures; to Mr. Shelford Bidwell for his Donation of £5 5s. to the General Fund; to Mr. W. Hugh Spottiswoode for his present of a Manuscript Record containing the early Laboratory Experiments of the late John Peter Gassiot, F.R.S., who was formerly a Manager and Benefactor of the Institution; and to Mrs. Kemp for her gift of a portrait of the late Sir Benjamin Baker, K.C.B., F.R.S., a Vice-President of the Royal Institution.

NOTES AND QUERIES.

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

Heat of Combustion.—1. Has the heat of combustion of aluminium as $2Al+3O=Al_2O_3$ been experimentally determined? 2. If so, what is its calorific value expressed in calories per kilogrm. of substance (*i.e.*, Al), or in any other convenient measurement?—G. M.

MEETINGS FOR THE WEEK.

Monday, 9th.—Royal Society of Arts, 8. (Cantor Lecture). "Fuel and its Future," by Prof. V. B. Lewes.

Tuesday, 10th.—Royal Institution, 3. "Membranes—Their Structure, Uses, and Products," by Prof. William Stirling, M.A., LL.D., D.Sc., &c.

Wednesday, 11th.—Royal Society of Arts, 8. "The Use of Reinforced Concrete in Engineering and Architectural Construction in America," by Ernest R. Matthews, F.R.S.E.

Thursday, 12th.—Royal Institution, 3. "Early British History and Epigraphy," by Prof. Sir John Rhys, M.A., &c.

—— Royal Society of Arts, 4.30. (Indian Section). "Progress of Native States during the past Forty Years," by Sir David W. Keith Barr, K.C.S.I.

Friday, 13th.—Royal Institution, 9. "Transatlantic Wireless Telegraphy," by Chevalier G. Marconi, D.Sc., &c.

—— Physical, 8. "Certain Dynamical Analogues of Temperature Equilibrium," by G. H. Bryan. "Experiments on Artificial Fulgurites," by Miss D. D. Butcher. "Distribution in Electric Fields of the Active Deposits of Thorium and Actinium," by S. Russ.

Saturday, 14th.—Royal Institution, 3. "Electric Discharges through Gases," by Prof. J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

VOL. XCVII., No. 2520.

SOLIDIFICATION OF HELIUM.

ON the evening of the 5th inst. Sir James Dewar received the following telegram, announcing the solidification of the last of the so-called "permanent gases"—helium :—

"Professor Dewar, Royal Institution, London.

Converted helium into solid. Last evaporating parts show considerable vapour pressure, as if liquid state is jumped over.

KAMERLINGH OHNES.

Leiden, 5th, 9 p.m."

To this Sir James Dewar replied :—

"Professor Ohnes, Leiden University.

Congratulations. Glad my anticipation of the possibility of the achievement by known methods confirmed. My helium work arrested by ill-heath, but hope to continue later on.

DEWAR.

Royal Institution, 5th, 11 p.m."

THE OXIDATION OF FERROUS HYDRATE BY CUPRIC HYDRATE IN THE PRESENCE OF AMMONIA.

By HENRY R. ELLIS, B.Sc., F.C.S.,
and
W. HENRY COLLIER, F.C.S.

THE fact that ammonia does not produce a blue colour when added to copper sulphate solution if ferrous sulphate is present has been noted by Levol (*Ann. Chim. Phys.*, lxv., 320).

This reaction has also been studied by Felix Hermann recently (*Chem. Zentr.*, 1907, i., 1394), and also by the authors (*Proc. Chem. Soc.*, xxiii., 235).

In the paper then submitted to the Chemical Society it was shown that certain conclusions of Felix Hermann were incorrect; as these appear in the yearly report issued by the Chemical Society, the authors of the present paper have repeated their observations.

Hermann regards the non-appearance of the distinct blue coloration when NH_4OH is added to a solution of ferrous sulphate and copper sulphate, as being due to the reduction of cuprous salt which oxidises the iron; he also states that the ferric hydroxide produced is insoluble in dilute H_2SO_4, and since his precipitate dissolved in cold dilute H_2SO_4 he concluded that the original ferrous sulphate was regenerated.

This the authors have shown to be quite incorrect; *i.e.*, that ferric hydrate is soluble in cold dilute H_2SO_4, and, secondly, that the ferric salt remains as such, and is not reduced.

To ascertain the solubility of ferric hydrate in dilute H_2SO_4 the following experiments were carried out :—

1. Ferric hydrate was prepared by the addition of ammonium hydrate to a solution of ferric chloride, the precipitation was washed, and then added to $4N.H_2SO_4$, when it was immediately dissolved.

2. Another sample of the ferric hydrate was boiled with water for two hours, and after cooling was added to cold $4N.H_2SO_4$ and completely dissolved, but more slowly than before.

3. A third sample of ferric hydrate was dried for some time at 120° C., and was now partly insoluble in $4NH_2SO_4$; even on boiling the whole was not completely dissolved.

From this it is evident that the ferric hydrate is only difficult to dissolve in dilute H_2SO_4 when it has become partially dehydrated, and in the reaction between NH_4OH, $CuSO_4$, $FeSO_4$ such a condition is very improbable.

The precipitate in this reaction consists of ferric hydrate, ferrous hydrate, a cuprous body, and probably basic sulphates of copper and iron.

That this precipitate dissolves in dilute H_2SO_4 to produce ferrous and ferric sulphate is extremely easy to show. By using sufficient ammonia the whole of the iron is oxidised by the copper salt and ammonia, and dissolves as ferric sulphate with no ferrous sulphate. From the H_2SO_4 solutions cuprous chloride has been obtained by adding HCl.

Mixed solutions of $FeSO_4$ and of $CuSO_4$ were allowed to stand in closed flasks for varying times, with and without NH_4OH, the amount of which was also varied in different experiments. After standing, the solution was treated with dilute H_2SO_4 (20 cc. 4N), and titrated against N/10 $KMnO_4$.

The end-point was very distinct in all experiments carried out in the cold, but when the solutions were boiled the end-point was untrustworthy, and such experiments were not continued.

The following table will illustrate the experimental results :—

I. *Interaction in the Cold of Equivalent Quantities of* $FeSO_4$ *and* $CuSO_4$.

Time.	N/10 $FeSO_4$.	N/10 $CaSO_4$.	N/10 $KMnO_4$.
2 mins.	20	20	20
5 ,,	20	20	20
10 ,,	20	20	20
60 ,,	20	20	20
12 ,,	20	20	20

Therefore no reaction takes place under these conditions.

II. *The two Solutions Heated together on Water-bath out of contact with Air.*

Time.	N/10 $FeSO_4$.	N/10 $CuSO_4$.	N/10 $KMnO_4$.
1 mins.	20	20	19·3
	20	20	19·5
	20	40	19·5 (*a*)
	20	40	19·2
10 ,,	20	20	18·6
	20	40	18·275

(*a*) A brown precipitate was produced, due to hydrolysis of the iron salt.

Therefore the $FeSO_4$ is slowly being oxidised.

III. *Equivalent Quantities of* $CuSO_4$ *and* $FeSO_4$ *with varying quantities of* NH_4OH.

	Time.	N/10 NH_4OH.	N/10 $CuSO_4$.	N/10 $FeSO_4$.	N/10 $KMnO_4$.
		Cc.	Cc.	Cc.	Cc.
1.	15 mins.	20	20	20	18·8
		20	20	20	18·8
		20	20	20	18·9
2.	35 ,,	20	20	20	18·1
		20	20	20	18·2
		20	20	20	18·0
3.	115 ,,	20	20	20	16·0
		20	20	20	16·1
		20	20	20	16·0
4.	16 hrs. 45 mins.	20	20	20	15·9
		20	20	20	15·8
		20	20	20	15·9

Therefore iron is oxidised by the $CuSO_4$ and ammonia, but only about one-fifth of the total is so charged, and the oxidation does not continue after a certain time if air is excluded.

	Time.	N/10 NH_4OH. Cc.	N/10 $CuSO_4$. Cc.	N/10 $FeSO_4$. Cc.	N/10 $KMnO_4$. Cc.
5.	15 mins.	10	10	10	9·175
		20	10	10	8·7
		30	10	10	8·075
		40	10	10	6·1
		50	10	10	4·075
	4 hrs.	50	10	10	0·575
	15 „	50	10	10	0·6

IV. *Excess of* NH_4OH *and of* $CuSO_4$

When the bodies were present in the following proportion, 10NH_4OH, $CuSO_4$, and ½$FeSO_4$, the whole of the iron was oxidised in a few minutes, and on dissolving in dilute H_2SO_4 two drops of N/10 KMO_4 solution produced a permanent coloration.

Conclusions.

1. The failure of the ammonia test for copper in solution is brought about by the ferrous sulphate present, which reduces the copper to cuprous compounds
2. The whole of the iron can be oxidised by copper sulphate and ammonia in a short time.
3. The copper dissolves as cuprous compounds, and the ferrous and ferric hydrates dissolve without the ferric sulphate being reduced.
4. The reaction between iron and copper salts in presence of ammonia is different from the reaction in acid solution, when copper and cuprous salts will reduce ferric compounds on prolonged boiling.

The Chemical Laboratory,
The Polytechnic, Regent Street, W.

NOTE ON THE DETERMINATION OF FERROUS IRON.

By NICHOLAS KNIGHT.

Robert Manzelius, in the Geological Survey of Sweden (Sveriges Geol. Undersökning), calls attention to a universal defect in the estimation of ferrous iron in minerals and rocks. He finds that a considerable error arises from grinding the rock in the ordinary way to a fine powder owing to the oxidation of ferrous to ferric iron. If the specimen is reduced to a coarse powder instead of being *finely* pulverised, a more accurate result is attainable. This source of error has hitherto escaped the attention of analysts.

We have investigated specimens of siderite with a view to determine the oxidation effect when the mineral is finely pulverised. In each case only the ferric oxide was estimated, and the method of Berzelius as modified and improved by Bunsen was employed.

About a grm. of the specimen was weighed each time in a 200 cc. flask, which was fitted with a bulb tube and Bunsen valve. The substance was dissolved in a small quantity of hydrochloric acid, and a crystal of sodium carbonate was introduced to make an atmosphere of carbon dioxide. The flask was cooled as quickly as possible with water, and the ferric iron was precipitated with barium carbonate. The precipitated iron was at once filtered with suction, and washed twenty or thirty times with cold water. The ferric carbonate was dissolved in hydrochloric acid, the excess of barium removed with sulphuric acid, and the iron precipitated with ammonia. The ores contained only about 1¼ per cent of residue insoluble in hydrochloric acid. Two different specimens of the mineral were studied.

I. The specimen was run through a Taylor hand ore-crusher, and came out as a coarse powder. The mean of several fairly concordant results was 2·68 per cent Fe_2O_3. The coarse powder was next so finely ground in an agate mortar as not to feel gritty when placed between the teeth. It gave 3·26 per cent Fe_2O_3.

II. This specimen was enveloped in heavy paper, and reduced to a coarse powder in an iron mortar; 2·67 per cent of Fe_2O_3 was obtained. This coarse powder was finely ground in an agate mortar, when 3·11 of Fe_2O_3 per cent was obtained.

The oxidation is due to the heat caused by friction, and possibly in a lesser degree to the greater surface exposed to the air when the mineral is in a very finely divided state. The coarse powder is easily acted upon by the hydrochloric acid, and there is no necessity for making the determination with a very fine powder.

Our thanks are due to Mr. Robert H. Lott for making the analyses herein described.

Cornell College, February 12, 1908.

THE CHEMICAL ELEMENTS.

Periodicity, Weight, and Valency.

By GEO. WOODIWISS.

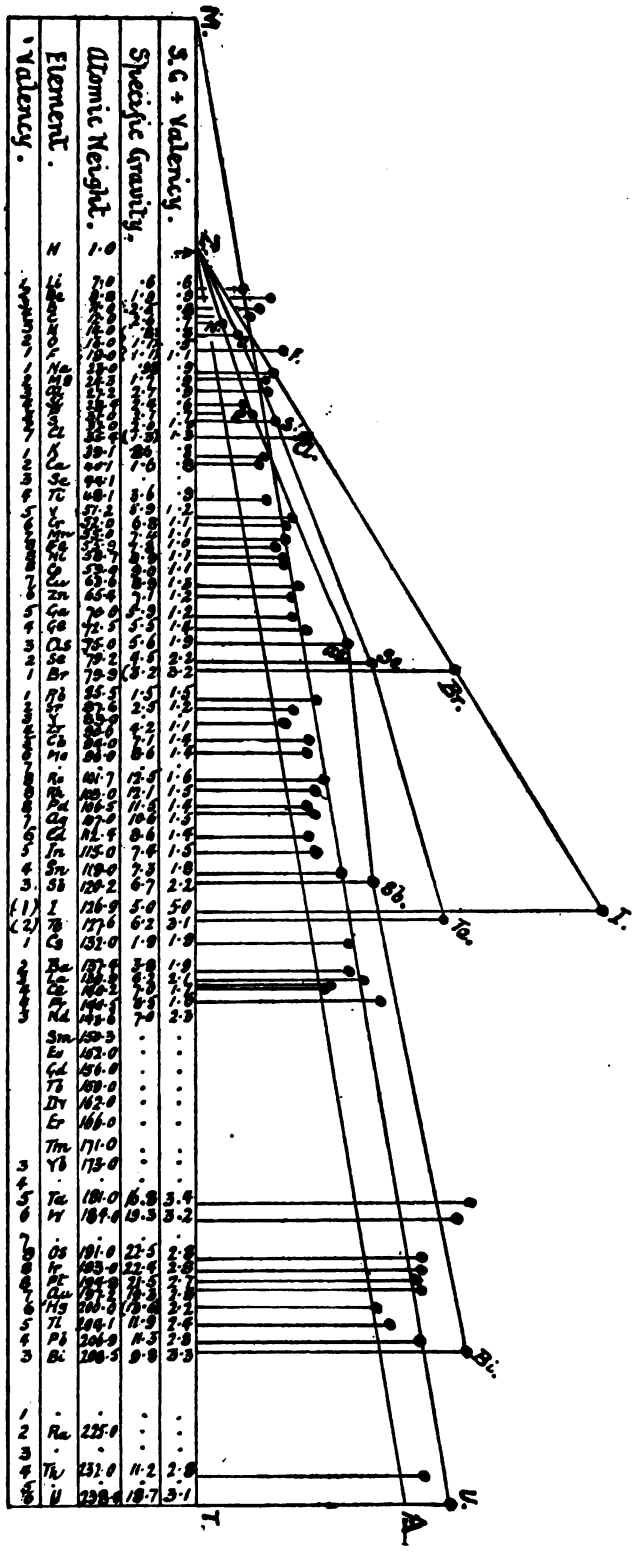
The atomic weight of copper is about three times that of sodium, the specific gravity is about nine times as great. Why should there be this great difference in relative weight in the two states? What is the order by which this difference takes place? At the first glance it would appear a very simple matter to obtain the relative weight of the elements in the solid state, but this is far from being the case; that is, under uniform conditions. In the first place, specific gravity is, and always must be, taken at a temperature wherein one element has an advantage over another in the amount of heat absorbed. Again, time, temperature, and pressure during solidification, and many other causes, tend to affect the ultimate result. Carbon, for instance, may crystallise from its solvent iron as graphite, or under increased pressure as the diamond. The diamond may be suitably heated, swell, and assume a coke-like mass. Each of these three states of the one element have a separate specific gravity. Phosphorus, platinum, sulphur, and others have allotropic forms. Silver in the molten state may absorb gases, large quantities of which are liberated on solidification, leaving cavities in the metal, and also probably affecting cohesion of the particles. Some elements at certain temperatures actually expand with reduction of heat. Traces of impurities and many others are the causes that may affect specific gravity. Given the elements in a perfectly pure state, solidified under exactly like conditions, and the ratio of weight at ordinary temperatures would at once be altered by alteration in temperature, for each element has a separate coefficient of expansion.

We must descend, therefore, to the lowest temperatures, to where the elements are totally devoid of heat, or rather, to where they are totally devoid of expansion, to obtain a truly comparative weight in the solid state. By Avogadro's theory we know that equal volumes of all gases under like conditions contain equal numbers of molecules. We therefore know that the molecular volume of all the various elements in the gaseous state is equal. On reviewing the ratio of weight in the solid state it is evident that this concordance has been upset; either there has been a change in the number of atoms to the molecule, or the molecular volume itself has changed for one element differently from that for another. When we consider the uniformity in volume of the molecules when charged with heat at the higher temperatures and the wonderful symmetry that nature delights in in all her laws, we must be prepared for regularity and symmetry in the atoms or molecules at the lower temperatures as well as at the higher. Allowing then a liberal margin for deviation, the accompanying diagram is constructed in an attempt to show that in all probability such is the case.

On the line M T are marked the elements at a distance from Z proportionate to their atomic weight. From M T perpendicular lines terminated by a dot are formed of a

length equal to the monovalent specific gravity; that is, $\frac{\text{specific gravity}}{\text{valency}}$. The valency employed is, perhaps, a new departure in periodicity, but is illustrated in a diagram (CHEMICAL NEWS, vol. xciii., p. 214). On the present diagram it is given by the bottom row of figures. It will be noticed these have a periodic rise and fall, commencing with an alkali and ending with a halogen thus, 1.2.3.4.3.2.1, 1·2·3·4·3·2·1, 1—8·8·8—1, 1—8·8·8—1. By this system of valency the copper group has a value of 7, and is therefore sharply separated from the sodium group, and the heavy metals generally are separated from the lighter ones. The most remarkable point, however, is—so far as the metallic elements are concerned—that the periodic rise and fall in specific gravity disappears, and an approximately regular increase is now in harmony with the regular increase in atomic weight. Atomic volume essentially depending upon specific gravity, it follows that the periodic rise and fall in atomic volume disappears, and that the periodic rise and fall in atomic volume is a function of valency. That is, so far as the metallic elements are concerned. With regard to the non-metallic and allied elements the case is different. To show this more clearly the line M U is drawn. In placing this line an endeavour is made to conform as nearly as possible to an average position indicated by the numerous dots. It will be noticed that most of the well known metals conform prettly closely to this line, the less well known metals and the non-metals generally being farthest away. We must not overlook the fact, however, that the specific gravity employed is taken at a temperature wherein absolute uniformity is not to be expected. It is evident that it is by no mere coincidence for the dots to fall on and about the line M U, and when we consider the uniformity in size of the molecule in the gaseous state, the enormous contraction that has taken place between that and the solid state, the great difference in boiling-points, melting-points, latent heats, &c., the close approximation to this line is remarkable. It is apparent that even at the intermediate temperature at which specific gravity is usually compared, there is an undoubted tendency for regularity in relative weight, and it is not at all improbable that were the elements totally devoid of expansion the weights would conform to some regular system of simple proportion.

In considering the alkali metals we find there is no indication of any system except a gradual increase in weight, as shown by the inclined straight line M U. Sodium has a deviation above and potassium below; but as there is a corresponding irregularity in vapour density, this may, perhaps, be attributable to some foreign cause. Taking, then, the ratio of weight of the alkali group as represented approximately by the straight line M U, then M U meeting M T at M we have at M a zero of weight for this group in the solid state. It is evident that the angle U M T may be made greater or less, but whatever alteration is shown thereby in the weight of one member of the group, a proportionate alteration is made for the rest of the group, and the ratio of weight is not altered; that is, providing always that the position of the zero M remains the same. If the ratio of weight of the group be altered then the zero must be altered to correspond. In a similar manner the zero of weight for the elements in the atomic state is at Z, and the angle, I Z T, may be varied to place the line I Z in various positions without any alteration to ratio of weight. But the line I Z cannot represent a ratio with the zero at M. If the angle I Z T is reduced until I Z is parallel with M U, then any weight represented by the line Z A is directly proportionate to the atomic weight. And as M U is parallel to Z A, it is evident that any weight represented by M U is equal to that of Z A plus a certain unknown quantity x, x being regulated by the distance of M U from Z A. Therefore the weight represented by M U is directly proportionate to atomic weight plus the unknown quantity x. We thus have specific gravity divided into two portions, one directly proportionate to atomic weight, the other a common quantity



x. The atomic volume may also be so divided and some remarkable calculations made, but it is not the purpose to enter into these here. Suffice that the zero of weight has moved from Z to M from the atomic to the solid state respectively, and that there must therefore be a corresponding change in ratio of weight.

It will be noticed the vertical lines are tangents of circles having a radius equal to the atomic weight of the elements. Thus, let hydrogen have a specific gravity of, say, 0·5, and the zero M be from the zero Z a distance of, say, 44 on the atomic weight scale, then a tangent at Z is 0·488, which is the distance apart of the lines M U and Z A. In the following table the Column A is atomic weight, B the tangent multiple, E the tangent at Z, F the calculated specific gravity, H the experimental specific gravity, K the difference between calculated and experimental specific gravity. The sodium gronp is taken with a valency or value of 1 and the copper group with a valency of 7.

		A.	B.	E.	F.	H.	K.
Li	1	(7·03	× 0·011	+ 0·488) =	0·57	0·59	− 0·02
Na	1	(23·05	× 0·011	+ 0·488) =	0·74	0·98	− 0·24
K	1	(39·11	× 0·011	+ 0·488) =	0·92	0·86	+ 0·06
Ru	1	(85·43	× 0·011	+ 0·488) =	1·43	1·5	− 0·07
Cs	1	(132·89	× 0·011	+ 0·488) =	1·96	1·88	+ 0·08
Cu	7	(63·60	× 0·011	+ 0·488) =	8·36	8·95	− 0·59
Ag	7	(107·92	× 0·011	+ 0·488) =	11·81	10·57	+ 1·24
Au	7	(197·23	× 0·011	+ 0·488) =	18·76	19·33	− 0·57

In answer to the original question, then, as to why the specific gravity of copper is about nine times that of sodium, whereas the atomic weight is only about three times as great, it may be stated that for the members of the sodium group and for the copper group the ratio of weight of the solid state has changed from that which held for atomic weight, and further that for the purpose of solidification the copper group takes a valency or value of seven times that of the sodium group.

The case for the non-metals and allied elements is different. For the non-metals generally the same zero appears for both the atomic and solid states, and as a consequence the atomic volume for each member of a group of elements is approximately the same as—

Chlorine	26·6
Bromine	25
Iodine	25·6
Oxygen	14·3
Sulphur	15·4
Selenium	17·6
Nitrogen	15·6
Phosphorus	14·7
Arsenic	15·9

South-Western Polytechnic.—The Eleventh Annual Distribution of Prizes and Certificates to the students of the Evening Classes and Day College will take place at this Institute on Friday, March 13th, 1908, when the Lord Alverstone, G.C.M.G., Lord Chief Justice of England, will present the awards. The Chair will be taken at 8 o clock p.m., by W. Hayes Fisher, Esq., Chairman of the Governing Body. There will be a selection of orchestral music at 7.30 p.m., under the direction of Mr. Seymour Dicker, Head of the Music Section.

ON THE VOLUMETRIC ESTIMATION OF POTASSIUM AS THE COBALTI-NITRITE.

By W. A. DRUSHEL.

The use of sodium cobalti-nitrite for the qualitative detection of potassium is well known, and its use as a quantitative reagent has been described by R. H. Adie and T. B. Wood (*Journ. Chem. Soc.*, lxxvii., 1076; Sutton's "Vol. Anal.," 9th Ed., p. 62), whose results are fairly accurate and favourably comparable with results obtained by the platinic chloride gravimetric method. In the process worked out by these investigators a solution of a potassium salt containing the equivalent of 0·5 per cent to 1 per cent of K_2O is acidified with acetic acid and precipitated by an excess of sodium cobalti-nitrite. The mixture is allowed to stand at least a few hours, preferably over night, and is then filtered through a perforated crucible fitted with an asbestos felt. The precipitate is washed with 10 per cent acetic acid. According to Sutton it is important that the precipitation should be made in a solution containing the equivalent of 0·5 per cent to 1 per cent of K_2O, since in solutions of lower concentration the precipitate comes down in a condition in which it is apt to run through the filter in washing. The precipitate is then decomposed by boiling in dilute sodium hydroxide, and the cobalt is removed as the hydroxide by filtration. The nitrites, which are a measure of the potassium in the precipitate, are estimated by titrating with standard potassium permanganate. Adie and Wood found by analysis that the composition of the precipitated potassium salt is represented by the formula $K_2NaCo(NO_2)_6 \cdot H_2O$. According to their method a cubic centimetre of strictly $N/10$ potassium permanganate is equivalent to 0·000785 grm. K_2O.

The object of this investigation was to determine the best conditions for precipitating and filtering the potassium cobalti-nitrite, and to shorten the work of estimating the potassium by oxidising directly with potassium permanganate without the preliminary decomposition of the precipitate and removal of cobalt recommended by Adie and Wood. In a series of preliminary experiments the precipitated cobalti-nitrite was oxidised by an excess of potassium permanganate, the excess of permanganate reduced by standard oxalic acid, and the remaining oxalic acid titrated to colour. In this treatment trivalent cobalt is reduced to the bivalent condition, and from the formula of potassium sodium cobalti-nitrite it would appear that the oxygen thus made available should be equivalent to one-twelfth of that necessary to oxidise the nitrites. The results of these experiments are given in Table I.

TABLE I.

No.	K_2O taken.	$KMnO_4$ used in titration of nitrites after removal of cobaltic hydroxide.	$KMnO_4$ equivalent to cobaltic hydroxide.	$KMnO_4$ used in direct titration.
	Grm.	Cc.	Cc.	Cc.
1.	0·0235	32·4	2·5	—
2.	0·0235	32·25	2·5	—
3.	0·0235	32·65	2·55	—
4.	0·0353	48·35	3·88	—
5.	0·0353	49·00	3·95	—
6.	0·0235	—	—	30·00
7.	0·0235	—	—	29·65
8.	0·0235	—	—	29·4
9.	0·0353	—	—	43·65
10.	0·0353	—	—	44·4

Portions of a potassium chloride solution of known strength were treated with an excess of sodium cobalti-nitrite and filtered on perforated crucibles fitted with asbestos felts. (The sodium cobalti-nitrite was prepared according to the directions given by Adie and Wood, *loc. cit.*, also given in Sutton's "Volumetric Analysis," 9th Ed., p. 62). The precipitates were first washed with

a 10 per cent acetic acid solution, then once with water. In Experiments 1 to 5 the precipitate was decomposed by boiling with sodium hydroxide and the nitrites estimated according to the method of Adie and Wood, giving the results in the second column of Table I. The cobaltic hydroxide filtered off on asbestos was reduced by heating nearly to boiling in a measured amount of standard oxalic acid containing a little sulphuric acid. The excess of oxalic acid was estimated by titrating with standard potassium permanganate, and from this the equivalent of the cobaltic hydroxide in terms of permanganate was found by subtraction, giving the results in the third column of the table. In Experiments 6 to 10 the precipitated potassium salt together with the crucible and asbestos felt, after stirring the precipitate and felt loose from the crucible, was placed in a beaker containing a measured amount of standard permanganate, taking care to use an excess, diluted to about ten times its volume, and heated nearly to boiling. After five to eight minutes, or when the manganese hydroxide formed gave the solution a dark colour, it was acidified with 5 cc. to 20 cc. of sulphuric acid (1 : 7). After a few minutes a measured excess of standard oxalic acid was run in from a burette, the temperature being kept a little below the boiling-point until the solution became clear, and then titrated to colour with permanganate. The whole amount of permanganate used less the equivalent of the oxalic acid used is the amount necessary for the oxidation of the precipitate. The results are given in the fourth column.

From the results of Table I. it appears that the oxidising value of the cobaltic hydroxide in terms of permanganate is nearly one-twelfth of that required for the oxidation of the nitrites, while the amount of permanganate necessary in the presence of the cobalt is nearly eleven-twelfths of that required for the oxidation of the nitrites after the removal of the cobalt. The factor used, therefore, in calculating the results from the direct titration should be twelve-elevenths of that given by Adie and Wood; that is, in titrating the precipitate without first separating the cobalt one cubic centimetre of strictly *n*/10 potassium permanganate is equivalent to 0·000856 grm. K_2O.

Unless the potassium salt solution is of the proper concentration the precipitate is very difficult to filter and wash, and shows a tendency to pass through the felt. By repeated experiments it was found that this difficulty, as well as the necessity for allowing the precipitate to stand over night, is avoided by evanorating the mixture nearly to dryness on the steam bath after adding the sodium cobalti-nitrite solution in considerable excess. Upon cooling the pasty residue it becomes hard and dry. It is then treated with cold water to dissolve the excess of sodium cobalti-nitrite, and the insoluble portion is collected on the filter. This precipitate may be freely washed with cold water without showing a tendency to pass through the filter, and is so insoluble that less than 0·5 of a mgrm. of the dried precipitate will dissolve in a litre of water at the room temperature during twenty-four hours standing with occasional shaking. This mode of treatment was found to work well and was used in all the subsequent experiments.

The method as worked out and used in all the experiments except those of Table I. is as follows:—The solution of a potassium salt, containing not more than 0·2 grm. K_2O and free from ammonium salt, was treated with a rather large excess of sodium cobalti-nitrite solution acidified with acetic acid, and evaporated to a pasty condition over the steam bath. It was then cooled and treated with 50 cc. to 100 cc. of cold water, and stirred until the excess of sodium cobalti-nitrite was dissolved. It was allowed to settle and decanted through a perforated crucible fitted with an asbestos felt. The precipitate was washed two or three times by decantation, after which it was transferred to the crucible and thoroughly washed with cold water. In the meantime a measured excess of standard potassium permanganate was diluted to ten times its volume and heated nearly to boiling. Into this the precipitate and felt were transferred and stirred up, after which the crucible was also put into the solution, since particles of the precipitate stick persistently to the sides of the crucible. After the oxidation had proceeded five or six minutes manganese hydroxide separated out and the colour of the solution darkened. At this point 5 cc. to 25 cc. of sulphuric acid (1 : 7) were added, and the solution, after stirring, was allowed to stand a few minutes. Then a measured amount of standard oxalic acid, containing 50 cc. strong sulphuric acid per litre, was run in from a burette, taking care to add an excess. The temperature was maintained a little below the boiling-point until the solution became colourless and the manganese hydroxide had completely dissolved. It was then titrated to colour by permanganate in the usual manner. From the whole amount of permanganate used the permanganate equivalent of the oxalic acid used was subtracted and the remainder multiplied by the factor calculated for the strength of permanganate used, 0·000856 being the factor for strictly *n*/10 potassium permanganate.

To make the *n*/10 oxalic acid solution, exactly 7·1066 grms. of pure recrystallised ammonium oxalate were dissolved in about 700 cc. of cold distilled water contained in a litre flask. To this solution were then added 50 cc. of strong sulphuric acid. The contents of the flask were cooled to 15° C. and made up to the mark with distilled water. The potassium permanganate solution was made approximately decinormal and standardised in the usual way. This standard was checked by standardising under conditions as nearly as possible like those under which the solution was used. A measured portion was diluted ten times, heated nearly to boiling, acidified with dilute sulphuric acid, and allowed to stand a few minutes. It was then bleached with a measured amount of oxalic acid, using it in slight excess, and titrated to colour. The two methods agreed very well, the difference in permanganate seldom being greater than one-tenth to two-tenths of a cubic centimetre in 25 cc.

TABLE II.

No.	K_2O taken. As KCl.	K_2O found. Gravimetrically.	K_2O found. Volumetrically.	Error in K_2O. Gravimetrically.	Error in K_2O. Volumetrically.
	Grm.	Grm.	Grm.	Grm.	Grm.
1.	0·0237	0·0240	0·0238	+0·0003	+0·0001
2.	0·0237	0·0243	0·0242	+0·0006	+0·0005
3.	0·0354	0·0359	0·0355	+0·0004	—
4.	0·0474	0·0478	0·0471	+0·0004	−0·0003
5.	0·0048	0·0048	0·0050	—	+0·0002
6.	0·0024	0·0024	0·0023	—	−0·0001
7.	0·0005	—	0·0006	—	+0·0001
8.	0·0015	—	0·0017	—	+0·0002
9.	0·0355	—	0·0355	—	—

In the first six experiments of this series the precipitate was dried at 115° C. and weighed. It was then treated with permanganate by the method previously described. Experiments 6, 7, and 8 show that very small amounts of potassium may be estimated with a fair degree of accuracy.

In Table III. the effect of the presence of members of the calcium group was investigated. Calcium and magnesium apparently do not interfere, while barium and strontium tend to give high results.

TABLE III.

	$CaCl_2$ taken.	$MgCl_2$ taken.	$BaCl_2$ taken.	$Sr(NO_3)_2$ taken.	K_2O taken.	K_2O found.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
1.	0·2000	0·2000	—	—	0·0005	0·0007	+0·0002
2.	0·3000	0·5000	—	—	0·0237	0·0234	−0·0003
3.	0·5000	1·0000	—	—	0·0829	0·0824	−0·0005
4.	0·5000	1·0000	—	0·5000	0·0711	0·0737	+0·0026
5.	0·5000	1·0000	0·5000	0·5000	0·0474	0·0493	+0·0019
6.	0·5000	1·0000	0·5000	—	0·0237	0·0251	+0·0014
7.	0·5000	1·0000	—	—	0·0711	0·0713	+0·0002

The method may also be used in the presence of phosphoric acid and is therefore applicable to the estimation of K_2O in fertilisers. In Table IV. are the results obtained in nine fertilisers by the platinic chloride method and the cobalti-nitrite volumetric method. In columns one and two are the duplicate results obtained by two analysts of the Connecticut Agricultural Experiment Station, and in column three are the results by the volumetric method. The water-soluble phosphoric acid present in these samples is given in the fourth column.

TABLE IV.

No.	Per cent K_2O in mixed fertilisers. K_2O by platinum chloride method.		K_2O by volumetric cobalti-nitrite method.	Per cent water-soluble P_2O_5 in sample.
1.	5·22	5·18	5·18	4·16
2.	6·53	6·56	6·56	3·10
3.	2·23	2·24	2·24	7·82
4.	8·68	8·64	8·78	0·94
5.	6·37	6·42	6·38	6·62
6.	6·08	6·13	6·13	5·61
7.	4·08	4·02	4·02	3·15
8.	4·62	4 66	4·67	2·43
9.	1·68	1·67	1·77	6·03

Ten grms. of the fertiliser were placed in a 500 cc. flask and 300 cc. of water were added. The contents were boiled for thirty minutes and ammonia water was added to slight alkalinity. Enough ammonium oxalate was added to precipitate all the calcium, and, after cooling, the solution was made up to the mark on the neck of the flask and well shaken. The solution was then filtered through a dry filter into a dry flask. Two 50 cc. portions of the filtrate were transferred with a pipette to platinum dishes, one portion being used for the gravimetric estimation by the platinum chloride method and the other for the volumetric estimation by the cobalti-nitrite method. After evaporating these portions to half their volume over the steam-bath, 1 cc. sulphuric acid (1 : 1) was added and the evaporation was continued as far as possible over the steam-bath, and finally over a low flame. After the danger of spattering was over the flame was increased and the charred organic matter was burned off, finally, over the blast lamp. The potassium sulphate was dissolved by adding a little water and heating over the steam-bath, and the potassium was estimated as previously described.

The volumetric method may be summed up thus: The potassium is precipitated as potassium sodium cobalti-nitrite by an excess of sodium cobalti-nitrite and the mixture is evaporated on the steam-bath. The precipitate is separated by filtration through asbestos and oxidised by hot standard potassium permanganate. The excess of permanganate is bleached by an excess of standard oxalic acid, and the solution is then titrated to colour by permanganate. The amount of potassium oxide is found by multiplying the oxygen value of the amount of potassium permanganate used by the factor 1·09.

This method has the advantages over the platinum chloride method, that no expensive reagents are used and that the time required for a determination is materially reduced. The method is considerably shorter than that of Adie and Wood and does not require the potassium solution to be of any definite concentration to work well.

In closing, the author desires to acknowledge his indebtedness to Dr. R. G. Van Name for many helpful suggestions during the progress of the work.—*American Journal of Science*, xxiv., p. 433.

Faraday Society.—Sir Oliver Lodge will deliver his Presidential Address to the Society on Tuesday, March 24th, next. The subject of the Address will be "Some Aspects of the Work of Lord Kelvin."

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, February 20th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

THE PRESIDENT announced that letters have been received from those gentlemen recently elected Honorary and Foreign Members, acknowledging the honour which the Society desired to pay them.

Certificates were read for the first time in favour of Messrs. Albert Edward Findley, B.Sc., 1, Welford Road, Handsworth, Birmingham; George Edward Holden, 23, Durnford Street, Middleton, Manchester; Percy Hulme Hornby, 111, Nine Elms Lane, S.W.; Herbert Mansfield, B.Sc., A.I.C., 70, Stapleton Hall Road, Stroud Green, N.

Certificates have been authorised by the Council under Bye-Law I. (3) in favour of Messrs. Bidhu Bhushan Dutt, M.A., Presidency College, Calcutta; Atul Chandra Gañguli, B.A., Ravenshaw College, Cuttack, India; Arthur Horrobin, Ajmer, Rajputana, India; Pañchanan Neogi, Rajshahi College, Rajshahi, Bengal.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

Vice-Presidents to retire—Prof. A. Smithells and Prof. W. P. Wynne.

Ordinary Members of Council to retire—Mr. E. C. C. Baly, Dr. Bernard Dyer, Mr. E. Grant Hooper, and Dr. G. T. Moody.

As President—Sir William Ramsay.

As Vice-Presidents who have filled the office of President—Prof. H. E. Armstrong, Prof. A. Crum Brown, Sir William Crookes, Sir James Dewar, Dr. A. G. Vernon Harcourt, Prof. R. Meldola, Dr. H. Müller, Prof. W. Odling, Prof. J. Emerson Reynolds, Sir Henry E. Roscoe, Dr. W. J. Russell, Prof. T. E. Thorpe, and Prof. W. A. Tilden.

As Treasurer—Dr. Alexander Scott.

As Secretaries—Dr. M. O. Forster and Prof. A. W. Crossley.

As Foreign Secretary—Dr. Horace T. Brown.

As Vice-Presidents—Prof. J. Campbell Brown, Prof. J. J. Dobbie, Prof. F. S. Kipping, Dr. R. Messel, Sir A. Pedler, and Prof. W. H. Perkin.

As New Ordinary Members of Council—Mr. J. L. Baker, Mr. A. C. Chapman, Prof. J. B. Cohen, and Dr. J. T. Hewitt.

Dr. A. Harden, Dr. H. Forster Morley, and Dr. J. A. Voelcker were elected Auditors to audit the Society's Accounts.

A ballot for the election of Fellows was held, and the following were subsequently declared elected:—Edward Philip Andreae, Ph.D.; Guy Barr, B.A., B.Sc.; Robert Barton, jun.; Marie Joseph Arsène Braun, Ph.D.; Harry James Brown; Walter Brown, jun.; John Arthur Carpenter, B.A.; Hans Thacher Clarke; Archibald Edgar Collens; William Henry Collier; David Cowan Crichton, M.A., B.Sc.; Cyril Dickinson, B.Sc.; Edwin Mortimer Eagles, M.A.; Joseph Valentine Francies; Robert Cecil Gale; John Maxwell Heron; Thomas Percy Hilditch; Arnold Merrick; Capel Darcy Morewood; Alfred William Oke, B.A., LL.M.; George Neville Pingriff, B.A.; Douglas Robert Pinnock; Arthur Robert Runeckles; Andrew L. Scott; William Bayliss Shaw; Puran Singh; John Armstrong Smythe; Charles Sedgley Spiers; Arthur Stead, B.Sc.; Adolph Octavius Trechmann; Thomas Marshall Tyson; Harry Jackson Unwin; Alfred Wade; Herbert Walker; Herbert Edmeston Watson, B.Sc.; John Watson, B.Sc.; David Thomas Williams; Joseph Henry Williams; Harry Percy Wilson; William Henry Withey, B.A.; Francis Charles Benjamin Wood; Joseph Yates.

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

*32. "*Organic Derivatives of Silicon.* Part VI. *The Optically Active Sulphobenzylethylpropylsilicyl Oxides.*" By FREDERIC STANLEY KIPPING.

The sulphonic acids obtained by resolving *dl*-sulphobenzylethylpropylsilicyl oxide with one of the active methylhydrindamines (*Trans.*, 1907, xci., 209) have been further studied, and the results clearly show that the two acids are optically active, enantiomorphously related compounds having the constitution $(SO_3H\cdot CH_2\cdot C_6H_4\cdot SiEtPr)_2O$; although they contain two asymmetric silicon groups, their specific rotations are very small, the values obtained for the sodium salts being $[\alpha]_D \pm 5{\cdot}8—5{\cdot}9°$.

The crystalline *dA*/*d*B- and *lA*/*l*B-methylhydrindamine derivatives differ very widely in outward properties from the *dA*/*l*B- and *lA*/*d*B- compounds, which have a very gelatinous or horny nature, but all four salts have a specific rotation $[\alpha]_D \pm 15—16°$ in methyl-alcoholic solution.

The *dA*/*l*B- and *lA*/*l*B-menthylamine salts are practically indistinguishable from one another or from the salt of the *dl*-acid, and this is also true in the case of the corresponding three *d*-bornylamine derivatives; the cinchonidine and cinchonidine hydrogen salts of the two active acids differ slightly in melting point.

dl-Sulphobenzylethylpropylsilicyl oxide is decomposed by hot concentrated sodium hydroxide, giving *p*-toluenesulphonic acid.

*33. "*The Preparation of Conductivity Water.*" By HAROLD HARTLEY, NORMAN PHILLIPS CAMPBELL, and REGINALD HOLLIDAY POOLE.

The efficiency of different methods of preparing conductivity water has been investigated in order to find a trustworthy way of obtaining water with a specific conductivity not greater than 1 gemmho ($1{\cdot}0\times10^{-6}$ reciprocal ohms) in a chemical laboratory under ordinary conditions. By combining several devices in use in other laboratories, a still has been constructed which in one operation gives a fair yield of water with a conductivity of 0·75 gemmho at 18°, starting from ordinary distilled water with a conductivity of 5 gemmhos without any preliminary chemical treatment. The distillation can be carried out in a chemical laboratory where nothing is done to keep the air specially free from impurities.

DISCUSSION.

Dr. T. M. LOWRY congratulated the authors on being able to produce water of such low conductivity under ordinary laboratory conditions. The still described by Mr. Bousfield (*Trans.*, 1905, lxxxvii., 740) gave almost equally good water (after boiling in a platinum flask, values as low as 0·45 gemmho had been obtained), and had the advantage that it could be left running without attention for a month at a time, but the quality of the water deteriorated when the still was worked in an impure atmosphere, unless special precautions were taken to protect the distillate. It was now generally recognised that the air rather than glass or metal vessels was the most dangerous source of contamination; "gemmho" water could be stored for many months without deterioration in the large green bottles in which the Welsbach solutions were imported, and which could be purchased through the ordinary trade channels; on the other hand, water of lower conductivity did not usually repay the trouble involved in its preparation, since it deteriorated so rapidly in contact with air that it was likely (by giving a false impression of its actual purity) to introduce rather than eliminate an error in conductivity measurements.

Dr. PHILIP asked whether, in view of the fact that a Jena glass flask was found suitable for storing the pure water, the metal parts of the condenser might not be replaced by Jena glass apparatus.

In answer to Dr. Philip, Mr. HARTLEY said that very good results had been obtained with a Jena glass condenser, but a block tin tube was better, as it produced more rapid condensation, and could be soldered into the condensing vessel, avoiding the use of corks which required frequent renewal.

*34. "*Derivatives of Para-diazoiminobenzene.*" By GILBERT THOMAS MORGAN and FRANCIS MARY GORE MICKLETHWAIT.

It has been shown that the explosive diazoimino-derivative obtained by Hantzsch from phenyl-*p*-phenylenediamine (*Ber.*, 1902, xxxv., 895) belongs to the same group of compounds as the stable arylsulphonyl-*p*-diazoimides prepared by the authors. A series of substances connecting this unstable *p*-diazoimine with the *p*-diazoimides has been obtained by a study of the diazo-derivatives of 2 : 4 : 6-trinitrophenyl-*p*-phenylenediamine, 2 : 4-dinitrophenyl-*p*-phenylenediamine, 4-nitrophenyl-*p*-phenylenediamine, and 2-nitrophenyl-*p*-phenylenediamine.

The first of these bases, which contains a substituent comparable in acidic character to the acyl groups in the arylsulphonyl-*p*-diamines, furnishes a stable *p*-diazoimino-derivative similar in its properties to the arylsulphonyl-*p*-diazoimides, and produced under comparable conditions by the action of sodium acetate on the diazo-salt of 2 : 4 : 6-trinitrophenyl-*p*-phenylenediamine.

The diazo-salts of 2 : 4-dinitrodiphenyl-*p*-phenylenediamine give rise to a diazoimine only when treated with potassium hydrogen carbonate, but not with aqueous sodium acetate. The product is more explosive than the trinitro-derivative.

The diazo-salts of 2- and 4-nitrophenyl-*p*-phenylenediamine do not yield diazoimines either with an alkali acetate or carbonate, but only on treatment with ammonia is the condensation product obtained. In this respect, these bases behave like phenyl-*p*-phenylenediamine itself.

These results show that the ease of formation and the stability of the derivatives of the hypothetical *p*-diazoiminobenzene are determined by the acidic nature of a substituent attached to one aminic nitrogen.

DISCUSSION.

Dr. GEORGE YOUNG pointed out that five-atom carbon-nitrogen rings differ markedly in their nature, and especially in regard to their stability, from heterocyclic nuclei containing either a greater or smaller number of atoms in the ring. Hence arguments based on a comparison of the *p*-diazoiminobenzenes with compounds such as *o*-diazoiminobenzene or Wolff's derivative of tetronic acid, which contain five-atom rings, cannot be decisive as between the benzenoid constitution discussed by Dr. Morgan, in which there is a seven-atom and the quinonoid formula with its three-atom heterocyclic grouping.

Dr. MORGAN, in reply to Dr. Hewitt, said that in conjunction with Mr. E. G. Couzens he had made many attempts to prepare diazoimides of the meta-series from the benzenesulphonyl-*m*-diamines of benzene, toluene, *m*-xylene, and mesitylene. Being entirely unsuccessful, they inferred that the diazoimide condensation was not wholly a matter of internal salt formation, and that the change occurred only when this factor was reinforced by the tendency for ring formation which characterises the ortho- and para-derivatives as distinguished from the meta-series. The picryl-*p*-phenylenediazoimine closely resembled the para-diazoimides, and it seemed only reasonable to suppose this compound also owed its existence to the combined operation of these salt and ring-forming tendencies.

With regard to the point raised by Dr. CAIN in reference to the validity of analogies concerning the constitution of ortho-, para-, and peri-derivatives based on experimental evidence obtained from the last of these three series, it seemed to him that this testimony was greatly to be preferred to that derived from a comparison instituted between substances so very dissimilar as *p*-aminophenol and *a*-aminotetronic acid.

*35. "*The Affinity Constants of Bases as Determined by the Aid of Methyl-orange.*" By VICTOR HERBERT VELEY.

The author has extended the work of which a pre-

liminary account has already appeared (*Proc.*, 1907, xxiii., 284).

Results were given for the hydrochlorides of (i.) bases not containing an alkyl grouping; (ii.) aliphatic amines; (iii.) aminoacetic acids; and (iv.) uric acid derivatives. As regards hydrazine in (i.), and all cases of (iii.), it was shown that the results obtained by the methyl-orange method are concordant with those obtained by the electric conductivity method, although the dilutions were about forty to eighty times greater. The tentative conclusion was drawn that either there is a limiting value of V in the Arrhenius equation $K_h/K_w = (1-x)V/x^2$, or that the hydrolytic reaction becomes reversible. As regards cases of (iv.), the general agreement of the results obtained by the methyl-orange method with those of the solubility method was considered, although the increase of hydrolysis relative to dilution is less than that required by Arrhenius' formula.

36. "*The Action of Thionyl Chloride and of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives.*" By George Barger.

In the chloro-compounds, formed by heating the methylene ethers of catechol derivatives with phosphorus pentachloride, the most labile chlorine atoms are those introduced into the methylene group. By the action of water or of glacial acetic acid at low temperatures, this pair of chlorine atoms is replaced by an oxygen atom, with the formation of a cyclic carbonate. The "dichlorpiperonal" of Fittig and Remsen (*Annalen*, 1871, clix., 144) is therefore the cyclic carbonate of 3:4-dihydroxybenzylidene chloride (I.), and does not possess an aldehyde group as implied by the present formula (II).

$$O{:}C\!<\!\overset{O}{\underset{O}{>}}\!C_6H_3\cdot CHCl_2. \qquad Cl_2{:}C\!<\!\overset{O}{\underset{O}{>}}\!C_6H_3\cdot CHO.$$

I. II.

Similarly, the supposed chloro-acid, obtained by Fittig and Remsen from piperonylic acid in an impure condition, is in reality the cyclic carbonate of protocatechuoyl chloride or carbonyldioxybenzoyl chloride, $O{:}C{:}O_2{:}C_6H_3\cdot COCl$.

Heating with excess of thionyl chloride to 180° has the same effect as phosphorus pentachloride and water, so that cyclic carbonates are formed directly from the methylene ethers.

3:4-*Carbonyldioxybenzoyl chloride* boils at 166—167°/12 mm., and crystallises from a mixture of benzene and light petroleum in stout crystals melting at 68°. Several derivatives were described.

37. "*A Study of the Diazo-reaction in the Diphenyl Series.*" By Gilbert Thomas Morgan and Francis Mary Gore Micklethwait.

The arylsulphonylbenzidines, $RSO_2\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, furnish yellow, crystalline diazonium salts giving rise, on treatment with aqueous sodium acetate, to dark brown crystalline compounds which are either monohydrated nitrosoamines, $R\cdot SO_2\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot NO,H_2O$, or dihydrated diazoimides (I.):—

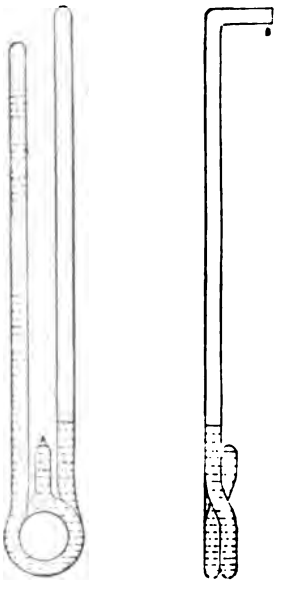
$$\begin{array}{l} C_6H_4\cdot N_2 \\ \quad | \quad\quad | \\ C_6H_4\cdot N\cdot SO_2R,2H_2O \end{array} \qquad \begin{array}{l} C_6H_4\cdot N_2 \\ \quad | \quad\quad | \\ C_6H_4\cdot NH \end{array}$$

I. II.

In this respect, these acylbenzidines differ from benzidine, which gives rise to a diazoimide (II.). The diazonium salts of the arylsulphonylalkylbenzidines, $RSO_2\cdot N(C_2H_5)\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, although distinctly less coloured than those of the unalkylated bases, have nevertheless not been obtained in a colourless condition. There is accordingly no reason for supposing that the diazonium salts of the alkylated bases are differently constituted from those which still contain the labile acidic hydrogen atom (*).

38. "*A Simple Manometer for Vacuum Distillation.*" By Norman Leslie Gebhard.

The manometer described consists essentially of a barometer tube bent in the form depicted in the figure. The simple trap A prevents effectually any air from being forced back into the barometer tube and thus affecting the readings. In order to remove any air thus trapped, it is merely necessary to incline the apparatus so that the



mercury expels the air into the open arm again; this is, however, only necessary at the end of an operation, as the apparatus is capable of yielding accurate readings in spite of the presence of air in the trap.

39. "*Researches on the Anthraquinones.*" By William Henry Bentley and Charles Weizmann.

An account was given of the condensations of: (1) phthalic anhydride and pyrogallol trimethyl ether; (2) hemipinic anhydride and veratrole; (3) hemipinic anhydride and pyrogallol trimethyl ether in presence of aluminium chloride. These reactions yield respectively: (1) *trimethoxybenzoylbenzoic acid*, m. p. 169°; (2) *tetramethoxybenzoylbenzoic acid*, m. p. 193—194°; (3) *hydroxytetramethoxybenzoylbenzoic acid*, m. p. 190°. These acids on further condensation with concentrated sulphuric acid yield respectively: (1) *dihydroxymonomethoxyanthraquinone*, m. p. 235—236°; (2) *hydroxytrimethoxyanthraquinone*, m. p. 226°; (3) *trihydroxydimethoxyanthraquinone*, m. p. 230°. By employing phosphoric oxide in place of sulphuric acid, it was found possible to obtain tetramethoxyanthraquinone (m. p. 239°) from tetramethoxybenzoylbenzoic acid.

40. "*The Formation of 4-Pyrone Compounds from Acetylenic Acids.*" Part I. By Siegfried Ruhemann.

The author finds that ethyl phenylpropiolate condenses with the ketones of formula $R\cdot CH_2\cdot CO\cdot R'$ in presence of sodium ethoxide to form 4-pyrone derivatives thus:—

$$C_6H_5\cdot C{:}C\cdot CO_2Et + CH_2\cdot R\cdot CO\cdot R' = C_6H_5\cdot C\!\underset{O-CR'}{\overset{CH\cdot CO}{\gtrless}}\!C\cdot R + C_2H_6O.$$

Up to the present, acetone and acetophenone have been used, and 2-phenyl-6-methyl-4-pyrone,—

$$C_6H_5\cdot C\!\underset{O\cdot C(CH_3)}{\overset{CH\text{——}CO}{\gtrless}}\!CH,$$

and 2:6-diphenyl-4-pyrone,—

$$C_6H_5\cdot C\!\underset{O\cdot C(C_6H_5)}{\overset{CH\text{——}CO}{\gtrless}}\!CH,$$

respectively have been obtained.

Along with diphenyl-4-pyrone, there is formed in this reaction a colourless compound, $C_{25}H_{20}O_3$, which yields a violet solution with concentrated sulphuric acid, and is produced according to the equation $C_6H_5{\cdot}C{:}C{\cdot}CO_2Et + 2C_6H_5{\cdot}CO{\cdot}CH_3 = C_{25}H_{20}O_3 + C_2H_6O$.

$C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}C(CO{\cdot}C_6H_5){:}C(CH_3){\cdot}C_6H_5$ is the formula suggested for this substance.

41. "*The Action of Mustard Oils on the Ethyl Esters of Malonic and Cyanoacetic Acids.*" By Siegfried Ruhemann.

Ethyl sodiomalonate reacts with phenyl thiocarbimide, thus:—

$$CHNa(CO_2Et)_2 + C_6H_5{\cdot}NCS = C_6H_5{\cdot}N{:}C(SNa)CH(CO_2Et)_2,$$

and this additive product, with acids, yields diethyl thiocarbanilinomalonate, $C_6H_5{\cdot}NH{\cdot}CS{\cdot}CH(CO_2Et)_2$. This, on hydrolysis with dilute caustic potash, loses 1 molecule of carbon dioxide, forming *thiocarbanilinoacetic acid*, $C_6H_5{\cdot}NH{\cdot}CS{\cdot}CH_2{\cdot}CO_2H$, which melts at 91—92°, and at the same time evolves carbon dioxide to yield thioacetanilide. The colourless sodium compound of diethyl thiocarbanilinomalonate forms a *benzyl* derivative, which is also colourless, and has the formula $C_6H_5{\cdot}N{:}C(S{\cdot}CH_2{\cdot}C_6H_5){\cdot}CH(CO_2Et)_2$.

Ethyl sodiobenzylmalonate and phenyl thiocarbimide do not yeld a compound of formula $C_6H_5{\cdot}N{:}C(SH){\cdot}C(CH_2{\cdot}C_6H_5)(CO_2Et)_2$. This fact would point to a different way of representing the product of the union between ethyl sodiomalonate and phenyl thiocarbimide, but, for the present, the author adheres to the former view.

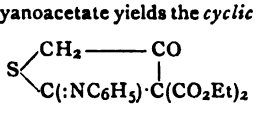
Ethyl sodiocyanoacetate also combines with phenyl thiocarbimide, and furnishes *ethyl thiocarbanilinocyanoacetate*, $C_6H_5{\cdot}NH{\cdot}CS{\cdot}CH(CN){\cdot}CO_2Et$. This compound is colourless, as are its *sodium* and *ammonium* salts as well as its *benzyl* derivative, $C_6H_5{\cdot}N{:}C(S{\cdot}CH_2{\cdot}C_6H_5){\cdot}CH(CN){\cdot}CO_2Et$, but on drying at 100° or on crystallisation from hot solvents it turns yellow. This behaviour is regarded as pointing to the existence of the substance in two tautomeric forms:—

$$C_6H_5{\cdot}N{:}C(SH){\cdot}CH(CN){\cdot}CO_2Et$$

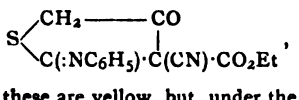
and—

$$C_6H_5{\cdot}NH{\cdot}CS{\cdot}CH(CN){\cdot}CO_2Et,$$

The action of ethyl chloroacetate on the sodium derivatives of diethyl thiocarbanilinomalonate and of ethyl thiocarbanilinocyanoacetate yields the *cyclic* compounds:—



and—



respectively; these are yellow, but, under the influence of potassium hydroxide, change into colourless isomerides. The nature of these transformations is still under examination.

42. "*The Triazo-group.* Part II. *Azoimides of Propionic Ester and of Methyl Ethyl Ketone.*" By Martin Onslow Forster and Hans Eduard Fierz.

On comparing the behaviour of the α- and β-triazo-derivatives of ethyl propionate towards alkali, it was found that, whilst the first-named resembled triazoacetic ester, ethyl β-triazopropionate rapidly parts with hydrazoic acid.

α-Triazopropionic acid, $CH_3{\cdot}CHN_3{\cdot}CO_2H$, is a colourless oil, having a rancid odour, and forms crystals which melt at 0°; the *silver* salt, $C_3H_4O_2N_3Ag$, crystallises from hot water in lustrous needles. The *ethyl* ester, $C_5H_9O_2N_3$, prepared from ethyl α-bromopropionate and sodium azide, boils at 46° under 2 mm. pressure, and has sp. gr. 1·065 compared with water at 23°; the *amide*, $C_3H_6ON_4$, crystallises from benzene in rectangular plates, melting at 79°.

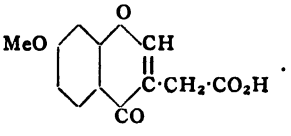
Ethyl-β-triazopropionate, $N_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5$, prepared from the iodo-ester and sodium azide, boils at 58° under 4 mm. pressure; aqueous ammonia eliminating hydrazoic acid, it has not been possible to prepare the amide and the free acid from this ester.

3-Triazobutanone-2, $CH_3{\cdot}CO{\cdot}CHN_3{\cdot}CH_3$, produced on agitating the corresponding chloro-derivative of methyl ethyl ketone with aqueous sodium azide, boils at 46° under 2 mm. pressure, and has sp. gr. 1·057 at 18°; the *semicarbazone*, $C_5H_{10}ON_6$, crystallises in snow-white plates, and melts at 94°.

1-Triazobutanone-2, $N_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$, boils at 56° under 2 mm. pressure, and has sp. gr. 1·084 at 18°; it resembles the foregoing ketone and acetonylazoimide in its behaviour towards alkali and sulphuric acid. The *semicarbazone*, $C_5H_{10}ON_6$, crystallises in needles, and melts at 101°.

43. *Brazilin and Hæmatoxylin.* Part VIII. *Synthesis of Brazilinic Acid, the Lactones of Dihydrobrazilinic and Dihydrohæmatoxylinic Acids, Anhydrobrazilic Acid, &c. The Constitution of Brazilin, Hæmatoxylin, and their Derivatives.*" By William Henry Perkin, jun., and Robert Robinson.

The authors have continued and elaborated the work of which a preliminary account has already appeared (*Proc.*, 1907, xxiii., 291). Further confirmation of the constitution of the members of this group is afforded by the synthesis of *anhydrobrazilic acid*, which has been proved to possess the formula:—



PHYSICAL SOCIETY.

Ordinary Meeting February 28th, 1908.

Dr. Charles Chree, F.R.S., President, in the Chair.

A paper by Mr. S. W. J. Smith and Mr. H. Moss, entitled "*On the Contact Potential Differences determined by means of Null Solutions*," was read by Mr. Smith.

When a mercury jet breaks in the surface of an electrolyte there is in general an E.M.F. between the jet and a still mercury electrode immersed in the electrolyte. If the contact potential difference between the still mercury and the solution is π_s, that between the jet and the solution being π_d, the observed E.M.F. is $E_p = \pi_s - \pi_d$. This E.M.F. is found to be equal to the polarising E.M.F., E_m, required to produce the maximum surface-tension between mercury and the electrolyte.

Since $E_m = \pi_s - \pi_m$, where π_m is the potential difference between the Hg and the electrolyte when the surface-tension is a maximum, it follows that $\pi_m = \pi_d$. Apart from special assumptions nothing more concerning these potential differences can be deduced from the purely experimental result $E_m = E_p$.

From the latter it is seen that E_p can be predicted if E_m is known. If $E_m = 0$ then $E_p = 0$. Hence a mercury jet will show no potential difference against still mercury when both are in contact with an electrolyte for which the "natural" surface-tension is also the maximum. A solution for which $E_p = 0$ is called by Palmaer a "null solution." Without observing the electro-capillary curve he found by trial two solutions for which $E_p = 0$. Although he concluded from his experiments that $\pi_s = \pi_d = 0$, it is clear that, without special assumptions, the only necessary conclusion is $\pi_s = \pi_d = \pi_m$.

The primary object of the paper is to show that in

general Palmaer's deduction is not only unnecessary but wrong.

If an experimental method can be found of obtaining from any electrolyte MX (for which E_m is positive) a solution for which $E_m = 0$, then it will be possible to obtain an indefinite number of null solutions. Such a method has been found. It consists in the addition to the electrolyte of a particular small quantity of M_2S (throughout the experiments M = Na or K, although it seems certain that the process could be generalised).

A number of null solutions were found, including one which gave results practically identical with those obtained by Palmaer. It is shown, however, that the potential difference Hg | null solution is a variable. For example, Hg | null KI can differ by about a quarter of a volt from Hg | null KCl, although in each case $\pi_s = \pi_m = \pi_d$.

The only assumption made in interpreting the results is that equal surface-tensions mean equal potential differences in those parts of the electro-capillary curves (of salts of K and Na of equal ionic concentration) which are of identical form. This assumption is admitted in all the theories that have been proposed.

Mr. S. Skinner congratulated the authors upon the accurate series of experiments which they had carrried out.

Dr. W. Watson expressed his interest in the paper, referring especially to the action of dissolved oxygen present in the solutions.

Mr. F. E. Smith referred to the fact that in the paper values for the contact potential difference were given to four places of decimals, and asked if any significance could be attached to the last two figures. He pointed out that the results obtained from drop electrodes were very different from those obtained by Billitzer using a different method. He asked if experiments had been made with jets of various sizes and under various pressures, and whether the form of the curves had been sufficiently studied.

Mr. Lewis asked if the authors had used other substances besides Na_2S, and if they had taken account of chemical actions which might take place at the electrodes.

Dr. Erskine Murray referred to experiments he had made some years ago on contact potential differences between metals in which the oxygen of the air behaved in a manner analogous to the dissolved oxygen in the author's solutions.

Mr. S. W. J. Smith, replying to Mr. F. E. Smith, said that Palmaer's value for the contact potential difference between mercury and *n*/10 KCl solution was quoted from his paper. With regard to Billitzer's views, they laboured for the present under the disadvantage that other observers had tried, but failed, to reproduce the effects which he describes. The form of the electro-capillary curve had been carefully studied. Van Laar had formulated a theory based upon the fact that the curve can be considered to consist within the limits of experimental error of portions of two parabolas. His interpretation of the significance of the point at which the curve changes from one parabola to the other had in reality no experimental support. The question of the character of the jet, amount of immersion, &c., had been carefully studied, and certain relations between the E.M.F. and the time of contact with the liquid had been arrived at. His (Mr. Smith's) point of view differed from that of Paschen in that he believed the experimental evidence to show that the E.M.F. between a Paschen electrode and an electrolyte was not in general zero. He cited a case in which apparently the potential difference between a Paschen jet and one electrolyte ($ZnSO_4$) differs by nearly half a volt from that between a Paschen jet and another electrolyte ($CuSO_4$). It was only when the electro-capillary maxima for two electrolytes were equal that the Paschen E.M.F.'s for the electrolytes were the same. An electro capillary maximum could not be obtained for $CuSO_4$ solution, probably because of deposition of copper on the mercury, just as a maximum could not be obtained from concentrated H_2SO_4 on account of the evolution of hydrogen. Paschen's experiments did not prove that the potential difference between an electrolyte and a mercury jet breaking in its surface is zero. It was possible that a certain fraction (in some cases the whole, *e.g.*, in null solutions) of the steady potential difference might arise practically instantaneously.

In reply to Mr. Lewis, Mr. Smith remarked that they used Na_2S because it was deducible from electro-motive data—in agreement with chemical—that the solubility of mercury sulphide was extremely small even compared with that of calomel. In reference to Mr. Lewis's suggestion that certain interactions might take place between the mercury, the dissolved salt, and the Na_2S independently of the oxygen, he said that although he had found that the amount of Na_2S required (in the way the experiments were performed) was not chemically equivalent to the amount of oxygen in solution, yet the amounts of Na_2S and oxygen were found to be roughly proportional to one another in experiments they had performed with the help of Mr. W. F. Higgins. He indicated to the meeting directions in which further experimental evidence was being sought. The electro-motive method of tracing minute chemical change was both delicate and simple.

A paper on "*An Experimental Examination of Gibbs' Theory of Surface Concentration regarded as the Basis of Adsorption, and its Application to the Theory of Dyeing*," was read by Mr. W. C. M. Lewis.

The object of the paper was to investigate experimentally Gibbs' theory of surface concentration; this concentrating of a solute in the surface-layer of a solution being dependent on variations in surface-tension. The following is a particular form of the more general equation, viz.:—

$$\Gamma = \frac{-c}{RT}\frac{d\sigma}{dc},$$

where Γ = the excess mass of solute per sq. cm. surface, c = the bulk concentration of the solution, T = the absolute temperature, R = the gas constant, and σ = the surface-tension. Assuming surface-tension effects to be the basis of adsorption, measurements were made of the various quantities in the above equation. The material at the surface of which adsorption took place consisted of a pure hydrocarbon oil. The material adsorbed was bile-salt in aqueous solutions of different concentrations. The interfacial tension σ was measured by the drop-pipette method, a curve being obtained showing the variation of tension with concentration. Γ was measured in two ways —(1) at the surface of oil-drops of radius about 1 mm., and (2) at the surface of drops of radius about 10^{-4} mm., *i.e.*, emulsion particles. Determinations by both methods agreed within the limits of experimental error. Similar experiments were made with certain dye-stuffs. The general result was that the actual values found for Γ exceeded the calculated by about fifty times the latter, the conclusion being that there is a real discrepancy of considerable magnitude. As regards the discrepancy noted, no suggestion is as yet offered, but the author stated that it might be connected with possible concentration changes at the surfaces.

Mr. S. W. J. Smith remarked with reference to the author's opinion that possible concentration changes at the surface of the mercury might have some bearing upon contact potentials, that Warburg had developed a theory of electro-capillarity based upon this assumption. It had been shown that mercury drops falling through a solution of a salt produced changes of concentration, just as in the author's experiments concentration changes were produced in a solution by rising drops of oil. There were at least two different interpretations of the mercury experiments.

Mr. A. Campbell asked if the absorption of moisture from the air by cellulose was a case of adsorption, and also if the amount of adsorption in dyeing depended upon the temperature.

Mr. Lewis said there was little doubt that the deposition of moisture on cellulose was a case of adsorption. Adsorption is accompanied by an evolution of heat, and a rise of temperature decreases adsorption.

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).

Ordinary Meeting, March 2nd, 1908.

Dr. J. LEWKOWITSCH in the Chair.

THE Honorary Secretary, Mr. JULIAN L. BAKER, read an Obituary Account of the late Chairman, Mr. R. J. Friswell.

The Honorary Secretary then read the following paper, "*The Preparation of Para-Toluidine from Mixed Toluidines by Means of Para-Toluidine Hydrate*," by the late R. J. Friswell.

A paper has recently been published (*Trans. Chem. Soc.*, 1907, xci., 1797) by J. W. Walker and Miss Beveridge describing a hydrate of para-toluidine. The problem of preparing pure para-toluidine is of great importance in the coal-tar products industry, inasmuch as this base is the material employed in the production of the well-known colouring principle primuline, and is likewise a constituent of several other commercially valuable artificial colouring matters. This mixture of bases obtained by the reduction of the crude nitro-toluene contains 35 to 40 per cent of the more valuable para-toluidine, and this was separated by churning the crude product with small fragments of ice. The plant employed in this operation consisted of a machine with a rotating ice-breaker and a beater, which took the form of a covered-in cylindrical tank in which the ice and bases could be pounded together. A change in the sound produced by the stirrers showed when the reaction was complete, and the product, which had now the consistence of a stiff paste, was blown into a filter-press, and in this way a solid compound of para-toluidine and water was obtained and freed from ortho-toluidine, which, under these conditions, does not form a hydrate. The press-cakes of para-toluidine hydrate were then melted up and the base freed from water and distilled. In this way pure para-toluidine could be easily prepared at a moderate cost. This method was devised by the author in 1889, and since then large quantities of pure para-toluidine have been prepared by it.

"*The Chloramin Reactions of the Proteins, and Technical Applications.*" By C. F. CROSS, E. J. BEVAN, and J. F. BRIGGS.

Monochloramin, NH_2Cl, is formed by the interaction of ammonia and chlorine; more conveniently, and in fact quantitatively, by the interaction of ammonia and hypochlorites (F. Raschig, *Ber.*, 1907, xl., 4586). Reacting with a second molecule, hydrazine is synthesised, $NH_2ClNH_3 = H_2N{\cdot}NH_2HCl$, and this typical reaction has been extended to aromatic amines (*Zeit. Angew. Chem.*, 1907, xx., 2065).

The authors find that the amine groups of the nitrogenous colloids (proteins) react similarly, forming characteristic chloramines which are relatively stable. The combined chlorine reacts with hydriodic acid thus: $XNHCl + 2HI = XNH_2 + HCl + I_2$, and hence volumetric iodometric methods are available for estimating these chloramines.

Gelatin (hydrated) gives maximum and constant numbers by reaction with the pure halogen, fixing 9 per cent of its weight (dry) of chloramin Cl, equivalent therefore to 16 per cent "active Cl." On this is based a much simplified method of estimating gelatin in "tub-sized" papers. The gelatin chloramin, washed, dehydrated, and dried, has been kept ten weeks without the loss of "active chlorine."

The tissue proteins of flax react to form chloramins in the hypochlorite liquors of the linen bleacher. The chlorine fixed is proportional to the nitrogen contents of the flax in the successive stages of purification of the goods, yarns or fabrics. Thus fixed to form chloramins these resist "souring" and washing. Trade samples of "creamed" flax yarns have been found to contain as much as 0·1 per cent of such "active chlorine."

Hydrolysed chloramines are present in the standing "bleach liquors," and a method has been devised for their estimation, based on their differential resistance to hydrogen peroxide. They have the peculiar property of combining with cellulose in such a way as to resist washing. These results are of fundamental importance to the textile bleaching industry. The chloramin reaction is of service in histological investigations in localising proteins and amino compounds.

The nitrogenous colloids in reacting to form chloramins appear to retain their colloidal characteristics, and the results of these investigations promise to contribute to the solution of problems of the colloidal state, including those of dyeing and photographic action.

FARADAY SOCIETY.

Ordinary Meeting, February 25th, 1908.

Mr. T. M. LOWRY in the Chair.

DR. V. H. VELEY, F.R.S., read a paper on "*Hydrolysis as Illustrated by Heats of Neutralisation.*"

In this paper it is pointed out that a correlation of hydrolysis values, and basic constants deduced therefrom, with those of heats of neutralisation, presents interesting and important issues. As regards the former, determinations at different temperatures by equally accurate methods are wanted to test the validity of the Nernst equation, $Q = RT^2 \frac{d \log^{10} K}{dt}$; as regards the latter, no data are available in many cases.

Relationships of a general character are discussed for the hydrochlorides of nitrogen containing bases, and certain sodium salts of phenols and carboxylic acids. The effect on thermoneutrality and basic constants by the introduction of a second amino-grouping is considered, and it is shown that if attached to nitrogen it produces an *increase*, but a *decrease* if attached to carbon, hydrazin being an exception. Similar arguments are adduced as to the effect of the substitution in the benzenoid amines by various elements and groupings, and it is shown generally that the order of strength of such derivatives is $p > m > o$ in the majority of cases. The great increase in thermoneutrality and basic constants (almost complete disappearance of hydrolysis) caused by the addition of hydrogen to pyridine and quinoline appears to point to a total difference of chemical structure.

Finally, it is pointed out that determinations are required of hydrolysis values at considerable dilution of certain metallic chlorides, as determinations are either completely wanting, or, if obtained, are discordant, and a hope is expressed that the record, however imperfectly presented by the author, may lead to a further interest in the subject.

Dr. G. SENTER thought there was some doubt as to the connection between hydrolysis and heats of neutralisation —the greater the one the less the other—arrived at in the paper.

Dr. A. C. CUMMING asked how the author got over the difficulty of impurities in the water working at such extreme dilutions.

Dr. V. H. VELEY agreed that there were factors other than neutralisation involving heat changes. By his method the effect of impurities was eliminated.

A paper by Dr. JOSEPH KNOX, entitled "*A Study of the Sulphur Anion and of Complex Sulphur Anions*," was communicated by Dr. A. C. CUMMING.

The solubility of HgS (red and black) in Na_2S, K_2S, and BaS solutions has been determined, and has been found to depend on the formation of the complex anion, HgS_2''. By its greater solubility in these solutions the black modification of HgS has been shown to be the unstable form. The temperature-coefficient of the solubility in Na_2S between 25° and 33° is small and negative. The effect of adding NaOH to the Na_2S is to increase greatly the solubility of HgS, owing to the

diminished hydrolysis of Na_2S. In the presence of a large excess of NaOH the HgS dissolved becomes practically equivalent to the Na_2S, pointing to the formula Na_2HgS_2 for the complex. The formula has been confirmed by E.M.F. measurements, and by an investigation of the complex by the method of Bodländer (*Zeit. Physik. Chem.*, 1902, xxxix., 307). The constant for the formation of the complex anion from the ions $Hg^{\cdot\cdot}$ and S'' is—

$$k = \frac{[HgS_2'']}{[Hg^{\cdot\cdot}]\,[S'']^2} = 5{\cdot}1 \times 10^{54}.$$

From a solution saturated with both Na_2S and HgS a crystalline double sulphide of sodium and mercury—$2NaS,5HgS,3H_2O$—has been isolated and analysed.

The solubility of HgS in Na_2S_2 solutions is about half that in the corresponding Na_2S solutions, and the same complex anion HgS_2'' probably predominates here too.

From the study of the complex formation between HgS and Na_2S it is concluded that Na_2S in dilute solution is practically completely hydrolysed into NaOH and NaHS, and this conclusion is confirmed by independent dilatometric experiments on the catalysis of the decomposition of diacetone-alcohol by dilute Na_2S solutions (*cf.* Küster, *Zeit. Anorg. Chem.*, 1905, xliii., 53).

With the aid of the various constants obtained in the investigation, the constitution of the more important sulphide solutions used analytically in sulphide precipitations has been determined, and the approximate concentrations of the S'' and other ions in such solutions are tabulated.

By measuring the E.M.F. of the metals in solutions of Na_2S of known S''-ion concentration, the solubility products of HgS, Ag_2S, CuS, and PbS have been determined: $[Hg^{\cdot\cdot}]\,[S'']$ = 2·8 × 10−54, $[Ag^{\cdot}]^2\,[S'']$ = 3·9 × 10−50, $[Cu^{\cdot\cdot}]\,[S'']$ = 1·2 × 10−42, $[Pb^{\cdot\cdot}]\,[S'']$ = 2·6 × 10−15.

Dr. F. MOLLWO PERKIN referred to the bearing of the paper on analytical problems.

Dr. G. SENTER asked whether the author in his experiments had reached equilibrium in both directions.

Dr. A. C. CUMMING, in reply, said that Dr. Knox had done so in some cases.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

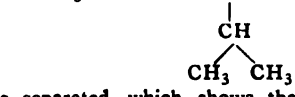
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 4, January 27, 1908.

Abnormal Mobility of the Ions of the Rare Earths.—Jules Roux.—The mobilities of the ions of the rare earths are much greater than those of monovalent and divalent ions, and also greater than the negative trivalent ions, except in the case of the samarium ion, the mobility of which is of the same order of magnitude as monovalent ions. This indicates that possibly the rare earths can be separated either by diffusion or by electrolysis. The mobility of the lanthanum ion increases from 111 at 18° to 131 at 25°.

Radio-activity of Plombières Waters.—André Brochet.—The author has determined the radio-activity of the Plombières water, and has obtained numbers which are considerably higher than those found by Chéveneau and Laborde. He has also shown that the emanation extracted from the water of the Capucin spring loses half its activity in four days. There appears to be no connection between the radio-activity of waters and their temperature.

Dissociation of Double Chlorides of Dimercuric Ammonium and Ammonium by Water.—H. Gaudechon.—The compounds $NHg_2Cl.NH_4Cl$ and $NHg_2Cl.3NH_4Cl$, in presence of water at the ordinary temperature, behave like true double salts, which confirms Rammelsberg and Pesci's hypothesis relating to their constitution. Thermochemical data, however, show that in the compound $NHg_2Cl.NH_4Cl$ the group NH_4Cl unites to the group NHg_2Cl with more energy than is usual in the case of double salts. Possibly the molecule contains complex radicles. The decomposition of $NHg_2Cl.NH_4Cl$ is limited by a very low concentration of NH_4Cl in the solution. In boiling water the NHg_2 radicle tends to decompose, giving NH_3, $HgCl_2$, and HgO.

Formula of Fenone.—L. Bouveault and M. Levallois.—Fenone, when treated with sodamide, gives an amide, $C_9H_{17}CONH_2$, from which, by the action of NaBr, diapophenyl urea, $CO{<}^{NH-C_9H_{17}}_{NH-C_9H_{17}}$, is obtained. This urea is decomposed by boiling sulphuric acid into the hydrocarbon, C_9H_{16} + H_2O, apofenene. Hence, probably the NH_2 group is attached to a tertiary carbon atom. From apofenene the symmetrical acetone acid, $C_9H_{16}O_3$ or—



can be separated, which shows that in all probability Semmler's formula for fenone is correct.

Essence of Magnolia Kobus.—Eug. Charabot and G. Laloue.—This essence is obtained by the distillation of the branches of the Japanese tree. The principal constituent is anethol, and the essence also contains about 15 per cent of citral.

NOTES AND QUERIES.

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

Heat of Combustion.—(Reply to G. M.).—The heat of combustion of Al has been determined by Dr. Strauss, Physicist to F. Knapp, Essen (see Minet, "Production of Aluminium and its Industrial Uses," p. 209). His result is given as 7140 cals. per grm., which works out as 386,988 cals. for Al_2+3O. Thomsen gives 380,200 for the same.—H. R. ELLIS.

MEETINGS FOR THE WEEK.

MONDAY, 16th.—Royal Society of Arts, 8. (Cantor Lecture). "Fuel and its Future," by Prof V. B. Lewes.

TUESDAY, 17th.—Royal Institution, 3. "Membranes—Their Structure, Uses, and Products," by Prof. William Stirling, M.A., LL.D., D.Sc., &c.

—— Royal Society of Arts, 8. (Shaw Lectures on Industrial Hygiene). "Child Workers and Wage Earners," by Miss Nettie Adler.

WEDNESDAY, 18th.—Royal Society of Arts, 8. "Impressionist Painting—its Genesis and Development," by Wynford Dewhurst, R.B.A.

—— Microscopical, 8. Presidential Address. "On Seeds, with Special Reference to British Plants," by Lord Avebury. Exhibition of Mounted Specimens of some of the Rarer Species of Fresh-water Polyzoa, by C. F. Rousselet.

THURSDAY, 19th.—Royal Institution, 3. "Standardisation in various Aspects—(1) Mechanical Engineeering," by R. T. Glazebrook, F.R.S., &c.

—— Royal Society of Arts, 8. (Howard Lecture). "The Navigation of the Air," by H. S. Hele-Shaw, F.R.S., &c.

—— Chemical, 8.30. "Constitution of Electro-negative 'Thiocyanates,'" by A. E. Dixon and J. Taylor. "Improved Form of Pycnometer," W. R. Bousfield. "Quantitative Conversion of Aromatic Hydrazines into Diazonium Salts," by F. D. Chattaway. "Action of Heat on ω-Hydroxycarboxylic Acids—Part IV., Racemic αα-Dihydroxyadipic Acid and Meso-αα-dihydroxyadipic Acid," by H. R. Le Sueur. "Spontaneous Crystallisation of Sodium Sulphate Solutions," by H. Hartley, B. M. Jones, and G. A. Hutchinson. "Quantitative Relations of Salts of Thallium and its Separation from Silver," by J. F. Spencer and Miss M. Le Pla. "Constitution of Hydroxyazo-compounds—Action of Diazomethane and of Mercuric Acetate," by C. Smith and A. D. Mitchell.

FRIDAY, 20th.—Royal Institution, 9. "Recent Earthquakes," by Prof. John Milne, F.R.S., &c.

SATURDAY, 21st.—Royal Institution, 3. "Electric Discharges through Gases," by Prof. J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

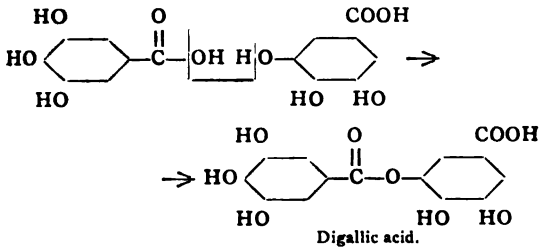
Vol. XCVII., No. 2521.

PRELIMINARY NOTE ON THE CONSTITUTION OF GALLOTANNIC ACID AND OF TANNINS IN GENERAL.

By STEWART J. LLOYD, Chicago University.

For some time the author has been investigating the structure of gallotannic acid and some of its derivatives, and although the experimental work has not yet been carried far enough to justify its publication in detail, the main results are perhaps sufficiently definite to be of service to other workers in the same field.

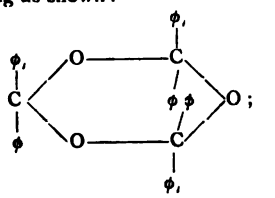
Until the discovery, in 1890, by Llavetsky, that natural gallotannic acid was optically active, it was considered, and quite justly, by chemists to be identical with digallic acid which is prepared by the condensation of two molecules of gallic acid.



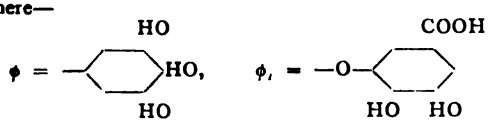
Digallic acid.

As, however, digallic acid contained no asymmetric carbon atom, attention was immediately drawn to the discrepancy, and differences were soon found in the physical, chemical, and physico-chemical properties of the two substances. Owing to the extraordinary difficulty of obtaining gallotannic acid pure, its optical activity was for a time attributed to the presence of a foreign substance, but the careful work of Rosenheim and Schidrowitz proved it to be inherent in the acid itself (*Journ. Chem. Soc.*, 1898, p. 878). The molecular weight, too, of gallotannic acid could not be obtained even approximately, the numbers varying from 400 to 2400.

From careful measurements in various solvents of the molecular weights of certain crystalline compounds of gallotannic acid, notably the pentacetyl derivative, and from various other experimental data, the conclusion has been reached by the author that natural gallotannic acid is composed essentially of three digallic groups united in a six-element ring as shown :—



where—



The analogy with the trithioketones and thioaldehydes described by Baumann and Tromm is quite striking (*Ber.*, xxiv., p. 1419). The optical activity follows, of course, from the formula, and we should expect a structurally inactive *cis*-form as well. There are several tannins from different plants resembling gallotannic acid very closely, so closely indeed that chemical identity has frequently been claimed for them. An investigation of these may result in the discovery of the substance in question.

Whether or not the other group of tannins, of which oak-bark tannin is the best known member, and which reduce to pyrocatechin instead of to pyrogallol, possess an analogous structure, has not yet been learned. The rather difficult investigation of this department of organic chemistry should however be somewhat facilitated by the knowledge of the existence in it of carbon-oxygen rings.

THE FALSIFICATION OF NITRO-COTTON WITH MERCURIC CHLORIDE AND ITS DETECTION.

By JAMES MOIR, D.Sc.

Mercuric chloride is frequently added to wet collodiou cotton, ostensibly to prevent its becoming mouldy, but sometimes also to make it pass the official heat test, even when it is really defective.

Ordinary tests for mercury fail because $HgCl_2$ cannot be extracted (except by volatilisation) owing to its affinity for organic matter. I have therefore invented the two following simple processes :—

(a). *Combination of Hargreaves and Rowe's Method with E. A. Mann's Method.*—The moist cotton, along with a piece of (ignited) silver foil is placed in a flask immersed in boiling water, and air is aspirated through it, and then through potash bulbs containing 2 per cent sulphuric acid. After two hours the $HgCl_2$ which has escaped the silver is deposited thereon by using the foil as anode in electrolysing the dilute sulphuric acid from the bulbs (two hours with about 4 volts required). The foil is dried and sublimed on to a microscope slide, as in the other methods.

(b). *Conversion into Non-volatile Compound.*—The cotton is extracted with hot very weak KI solution, and the extract (containing K_2HgI_4) concentrated to a small bulk and electrolysed. Iodine separates on the platinum basin used as cathode, and the whole of the mercury collects on the gold or silver foil anode after two or three hours, and is worked up as above. The latter method is the quickest and most sensitive I have tried as yet, and has the advantage of having no danger of explosion attached to it.—*Journal of the Chemical, Metallurgical, and Mining Society of South Africa*, viii., No. 7.

PENTAVALENT BISMUTH.

By E. B. HUTCHINS, jun., and VICTOR LENHER.

Peculiar interest has been attached to investigations of a higher state of valence than that of three with bismuth. Its many analogies to the other members of the fifth group of the periodic system have caused the pentavalent condition to be sought for repeatedly. Pentavalent arsenic and pentavalent antimony are well known ; both the oxides and types of the halides exist with these elements. With bismuth as the element having the highest atomic weight in this series, pentavalent derivatives might reasonably be expected.

Since 1818, when Brandes and Bucholz (*Schweigger's J. Chem. Phys.*, xxii., 27) prepared an oxide of bismuth containing more oxygen than the trioxide, many attempts have been made to prepare the pentoxide, a bismuthic acid or a bismuthate. Gutbier (*Zeit. Anorg. Chem.*, xlviii., 162 ; xlviii., 298 ; xlix., 432 ; l. 210) has recently reviewed the various methods which other investigators have used, and with his own work has questioned the acidic character of the higher oxides of bismuth. The authors have repeated most of the methods given for the preparation of these

oxides, and have obtained products by the various reactions whose analyses corresponded to the tetroxide, potassium bismuthate, and impure bismuthic acid. It appears that although none of the higher products of oxidation of bismuth except the tetroxide are stable, yet under the proper conditions, it is possible to have a higher state of oxidation than the valence of three.

Very little attention has, however, been directed to the study of other derivatives than the oxygen type. Muir fused together sulphur and bismuth trichloride and obtained $BiSCl$ but not $BiSCl_3$ (*Journ. Chem Soc.*, xxxix., 22). He also treated Bi_2O_3 with chlorine with the view of obtaining $BiOCl_3$ analogous to $POCl_3$, but obtained only $BiCl_3$. Rauter states that when he treated bismuth pentoxide with silicon tetrachloride he obtained bismuth trichloride as the product (Liebig's *Annalen*, cclxx., 251).

In order to ascertain the action of chlorine on bismuth trichloride at very low temperatures, some of the dry powdered salt and some clear crystals were introduced into a test-tube which was placed in a Dewar bulb containing liquid air. Chlorine gas was passed into the tube, and it at once assumed the solid state. When a large excess of the solid chlorine had collected in the tube, it was withdrawn from the bulb and the solid chlorine allowed to melt. The trichloride was then well shaken with the liquid chlorine and the two returned to the liquid air bulb, where it was kept for an hour. The trichloride remained unchanged in appearance during the entire course of the experiment. After the chlorine had been allowed to spontaneously evaporate, analysis of the powdered material showed it to contain 33·2 per cent of chlorine. From this experiment it is evident that bismuth pentachloride is not formed by the action of solid or liquid chlorine upon the trichloride. Other similar experiments were conducted in which the trichloride was kept in contact with chlorine at $-15°$ for several hours. In no case was the chloride changed in appearance by the action of the chlorine, nor could an excess of chlorine above that required for the trichloride be detected by analysis.

A small quantity of impure bismuth pentoxide was maintained at a temperature of $-10°$ and dilute hydrochloric acid added. The pentoxide dissolved at that temperature with the evolution of chlorine gas. Experiments looking to the formation of double halides of pentavalent bismuth likewise proved fruitless. A hydrochloric acid solution of bismuth trichloride was saturated with chlorine at $-10°$ and solid ammonium chloride added; the solution was then concentrated over sulphuric acid. Colourless crystals separated which on analysis proved to be $BiCl_3,2NH_4Cl$. This salt is described by Deherain (*Comptes Rendus*, liv., 726).

$CsICl_2$, the perhalide of Wells and Penfield (*Am. Journ. Sci.*, xliii., 27), was dissolved in water and a molecular quantity of bismuth trichloride added; chlorine was passed through the hot solution, when a yellow crystalline salt separated at once. Analysis showed this substance to contain 35·05 per cent cæsium, 37·0 per cent of bismuth, and 27·8 per cent of chlorine. The compound is therefore $2BiCl_3,3CsCl$, which has been described by Brigham (*Am. Chem. Journ.*, xiv., 181). In a similar manner bromine was added to a hot solution of cæsium tribromide and bismuth tribromide in hydrobromic acid. In this experiment a finely divided yellow precipitate was obtained which was quite insoluble in hydrobromic acid, but readily soluble in hydrochloric and nitric acids. Analysis showed this to be a new salt corresponding to the formula $2BiBr_3,3CsBr$, as it contained 46·9 per cent bromine, 27·0 per cent cæsium, while the theoretical for $2BiBr_3,3CsBr$ is 46·8 per cent bromine, 27·1 per cent bismuth, and 26·1 per cent cæsium.

It is evident from the preceding work and from the experiments of others that while bismuth can exist in a higher state of valence than three with oxygen, thus far the halogens have not been combined with bismuth in any higher ratio than that of the valence of three.—*Journal of the American Chemical Society*, xxix., No. 1.

A METHOD FOR THE VOLUMETRIC ESTIMATION OF TITANIUM

By H. D. NEWTON.

About forty years ago, F. Pisani (*Comptes Rendus*, lix., 298) stated that titanic acid could be estimated by reduction with zinc in hydrochloric acid solution, the action being hastened by gentle heat, and, after the reduction was complete, pouring off the undissolved zinc, washing, and titrating with potassium permanganate. Pisani, while stating that the above procedure gave excellent results, gave no test analyses. Marignac (*Zeit. Anal. Chem.*, vii., 112) applied Pisani's method, shortly after its publication, to the estimation of titanic acid in the presence of niobic acid. Marignac's procedure differed slightly, however, from Pisani's, in that the titanic acid was reduced out of contact with the air, by means of a long bar of zinc extending well up into the neck of the flask, the zinc being removed after the reduction was completed and the solution titrated directly in the flask. The test analyses given are good, though the results are low, especially when large quantities of titanic acid are used.

Somewhat later, Wells and Mitchell (*Journ. Am. Chem. Soc.*, xvii., 878) modified Pisani's method, as improved by Marignac, by using sulphuric acid solutions and protecting the solution from oxidation during cooling and titration by means of a stream of carbon dioxide. The experimental results are still below the theory, the greater portion of the error being attributed by the authors to the oxidising action of the air, which gained access to the liquid in spite of the precautions taken.

The work to be described is a result of an attempt to eliminate the oxidising action of the air by reducing and cooling under an atmosphere of hydrogen, and converting the equivalent of titanium sesquioxide to ferrous sulphate by introducing an excess of ferric salt. A cold solution of a ferrous salt, as is well known, is very slowly acted upon by atmospheric oxygen (Peters and Moody, *Am. Journ. Sci.*, xii., 367).

The reaction between the salts of titanium and iron takes place according to the following equation:—

$$Ti_2(SO_4)_3 + Fe_2(SO_4)_3 = 2Ti(SO_4)_2 + 2FeSO_4.$$

For this work, the titanium solutions were made by treating re-crystallised potassium titanofluoride with concentrated sulphuric acid, evaporating the mixture to the fuming point of the acid, and diluting to a known volume. The resulting solutions were standardised by the basic acetate method, slightly modified in the present case, owing to the absence of any iron in the solutions used (Gooch, *Am. Chem. Journ.*, vii., 283).

Measured portions of these solutions were drawn into a flask of about 100 cc. capacity, a definite amount of zinc having a known iron content was added, the solution finally made up to such volume as to contain about ten per cent of concentrated sulphuric acid, this strength of acid being sufficient to hold the titanic acid in solution and yet be without oxidising action on the reduced oxide. A rubber cork, through which passed a delivery tube and small separating funnel, was inserted into the mouth of the flask. Gentle heat was applied, while an atmosphere of hydrogen was constantly kept above the liquid until all the zinc was dissolved and the solution cooled, a process which generally took about an hour. An excess of ferric sulphate was passed through the separating funnel and followed at once by cold, freshly distilled water until the flask was filled to the neck. The contents of the flask were then poured into a litre flask containing more cooled distilled water, and the whole immediately titrated with tenth-normal potassium permanganate.

In Table I. are given results obtained by the foregoing procedure. In Table II. are recorded similar experiments in which larger amounts of titanic acid were taken.

These experiments show that it is possible to reduce titanic acid by means of zinc in a small flask and to

determine the titanium with success, by reducing in an atmosphere of hydrogen, adding an excess of ferric sulphate, and titrating the resulting, and equivalent, ferrous salt with potassium permanganate. The factor for metallic iron divided by 0·689 gives the factor for titanium dioxide.

TABLE I.

Titanium sulphate.	$KMnO_4$.	TiO_2 taken.	TiO_2 found.	Error.
Cc.	Cc.	Grm.	Grm.	Grm.
30	6·50	0·0520	0·0523	+0·0003
30	6·52	0·0520	0·0524	+0·0004
30	6·45	0·0520	0·0519	−0·0001
30	6·50	0·0520	0·0523	+0·0003
30	6·48	0·0520	0·0521	+0·0001
30	6·42	0·0520	0·0518	−0·0002
30	6·50	0·0520	0·0523	+0·0003

TABLE II.

25	19·95	0·1596	0·1599	+0·0003
25	19·93	0·1596	0·1598	+0·0002
25	19·95	0·1596	0·1599	+0·0003
25	19·90	0·1596	0·1595	−0·0001
25	19·95	0·1596	0·1599	+0·0003
25	19·95	0·1596	0·1599	+0·0003
25	19·90	0·1596	0·1595	−0·0001
25	19·85	0·1596	0·1591	−0·0005
25	19·95	0·1596	0·1599	+0·0003
25	19·88	0·1596	0·1594	−0·0002
25	19·95	0·1596	0·1599	+0·0003
25	19·95	0·1596	0·1599	+0·0003

In conclusion, I wish to thank Prof. F. A. Gooch for advice and assistance given during the progress of this work.—*American Journal of Science*, xxv., p. 130.

THE ATOMIC WEIGHT OF CHLORINE.*

By WILLIAM A. NOYES and H. C. P. WEBER.

THE ratio of the atomic weights of oxygen and of chlorine is one of extreme importance, on account of the number of atomic weights based either directly or indirectly upon the atomic weight of chlorine.

During the last few years alone, since the determination of the ratio silver to chlorine by Richards and Wells (*Journ. Am. Chem. Soc.*, xxvii., 459), the atomic weights of a considerable number of the common elements have been determined, basing them on the value of chlorine. These values have been calculated on the oxygen basis, assuming that the ratio silver : oxygen :: 107·93 : 16 is correct. Guye and Ter-Gazarian have called attention to a possible source of error in the chlorate ratio of Stas, correction for which would bring the value of silver down to 107·89 (*Comptes Rendus*, cxliii., 411). The newly accepted value 14·01 for nitrogen also points to the lower value of 107·89. Very nearly at the close of this work conclusive evidence has been presented by Richards and Forbes (*Journ. Am. Chem. Soc.*, xxix., 808) and by Richards and Jones (*Journ. Am. Chem. Soc.*, xxix., 826) that the value 107·93 for silver is too high. The only direct comparison between hydrogen and chlorine which we have is that of Dixon and Edgar (*Phil. Trans.*, ccv., 169, Series A.; CHEMICAL NEWS, xci., 263)—the determinations by Deutsch (Dissertation, 1905) in the laboratory of Professor Guye, were scarcely of sufficient accuracy to be considered as atomic weight determinations. In this determination hydrogen was made to burn in an excess of chlorine. The hydrogen was weighed absorbed in palladium and the chlorine in the liquid form in a glass bulb. The hydrogen and chlorine were caused to unite in a large globe of glass containing a small quantity of water to absorb the hydrochloric acid formed. Corrections were applied for the quantity of chlorine remaining uncombined by titrating the amount of iodine liberated by it from a solution of potassium iodide. A further correction was applied for the amount of chlorine used up in liberating oxygen from water, by determining the amount of oxygen set free.

The fact that there was only one such direct determination of the ratio between chlorine and hydrogen, together with the opportunity afforded of carrying out the determination with hydrogen prepared in the same apparatus used for generating the hydrogen in the recent determination of the ratio of hydrogen to oxygen, made a new determination seem to be worth while.

The method we have used, besides being a direct comparison between hydrogen and chlorine, involves the principle of complete synthesis with the determination of the weights of all the substances reacting and of the reaction products formed. Briefly stated, the method consists in weighing the hydrogen absorbed in palladium, and the chlorine in the form of potassium chlorplatinate. The hydrogen is passed over the heated potassium chlorplatinate, from which it removes chlorine to form hydrochloric acid. The hydrochloric acid formed is condensed in a third section of the apparatus and weighed. We have thus the weight of hydrogen used, the weight of chlorine removed, and the weight of hydrochloric acid formed. In this manner two series of ratios, each independent of the other, are obtained.

Working in this manner and with hydrogen prepared under the same conditions and at the same time as that used in the determination of the ratio hydrogen to oxygen by one of us, we believe that we have very favourable conditions for bridging the gap—

$$Ag \rightarrow \mathbf{Cl} \subset \mathbf{H} \rightarrow O.$$

Purification of Materials and Weighing.

Hydrogen.—The hydrogen used in these experiments was prepared and purified in the same manner as described in a previous paper on the atomic weights of hydrogen (Noyes, *Journ. Am. Chem. Soc.*, xxix., 1720; see also CHEMICAL NEWS, xcvii., p. 56 *et seq.*). The gas was taken from the generating apparatus at intervals covered by the period of the work on hydrogen. Consequently all remarks concerning its character and purity as used in the hydrogen-oxygen ratio apply to these determinations. As in that work so in this, two methods of generating the hydrogen were employed. In the last series of determinations the hydrogen was obtained by the electrolysis of a solution of barium hydroxide.

Platinum.—The platinum used in the preparation of potassium chlorplatinate was originally obtained in the form of platinum sponge. The preliminary purification consisted in dissolving this in aqua regia and evaporating to remove nitric acid. The separation from other platinum metals was carried on according to the method of Schneider and Seubert as described in Graham Otto's "Lehrbuch," 5th Ed., iv., 1153.

The solution of chlorplatinic acid was boiled for half an hour with excess of caustic soda, acidified, and the platinum precipitated as potassium chlorplatinate. The chlorplatinate so obtained was reduced with sodium formate. The platinum black was then heated with dilute hydrochloric acid to remove iron and washed until it commenced to go through as colloidal platinum. It was then re-dissolved and the process repeatedly gone through until the mother-liquors from the chlorplatinate precipitation were practically colourless and free from other platinum metals. As the same platinum was continually used and underwent a large number of successive solutions and reductions during the preliminary work, it seems safe to assume that it was sufficiently pure.

Potassium Chlorplatinate.—During the preliminary work it was soon discovered that the preparation of chlorplatinic acid by the use of aqua regia was unsatisfactory. The removal of nitric acid by the process of repeated evaporation was tedious and at best uncertain. To overcome this difficulty and eliminate nitric acid

* From *The Journal of the American Chemical Society*, xxx., No. 1.

entirely, a process of dissolving the platinum electrolytically in purified hydrochloric acid was devised. This proved quite satisfactory, and will be described in the following paper. After solution of the platinum in hydrochloric acid had been effected, the solution, which contained approximately 120 grms. of platinum and measured 500 cc., was evaporated to about one-half its volume in a glass-stoppered wash-bottle. At the same time a current of chlorine was passed through the boiling solution. The chlorine used for this purpose was prepared by the action of pure potassium permanganate upon chemically pure hydrochloric acid which had been previously boiled with a small quantity of permanganate to insure its freedom from bromine compounds. The solution of chlorplatinic acid thus obtained had a beautiful bright colour matching almost exactly that of a 0·1 per cent solution of methyl orange. It contained about 100 grms. of hydrochloric acid in excess, and after filtration and dilution to one litre was used directly for the precipitation of potassium chlorplatinate. For this purpose a solution of potassium chloride was prepared, using an excess of one-third above the theoretical quantity dissolved in one litre of water. The excess of potassium chloride as well as the excess of hydrochloric acid in the chlorplatinic acid were deemed necessary to check hydrolytic decomposition. For the same reason the precipitation of potassium chlorplatinate was carried out with as concentrated solutions as practicable. The precipitation itself was carried out by pouring the platinum solution into the potassium chloride in a fine stream, the precipitate meanwhile being agitated thoroughly by a current of air. In some cases as much as four hours were spent in precipitating 300 grms. of potassium chlorplatinate. The potassium chlorplatinate so obtained was of a pale yellow colour, resembling precipitated sulphur, and was microcrystalline. It was filtered from the mother-liquor by means of a suction-pump, washed with water, and finally with alcohol and ether. After having been removed from the hardened filter, it was heated for some time in a large platinum dish on an electric air-bath until the greater part of the moisture retained had been driven off. The quantity necessary for one determination was then transferred to a hard glass tube. This tube was placed in a cylindrical air-bath which could be raised to a temperature of 400°. The potassium chlorplatinate was gradually raised to this temperature, a current of air, dried successively by sulphuric acid and phosphorus pentoxide, passing over it continuously. The behaviour of the salt under these conditions served as a criterion of its purity. At the exit of the current of gas, a wash-bottle was placed containing a drop of methyl orange. At first a small quantity of moisture and hydrochloric acid passed off. Finally, however, a point was reached where no further hydrochloric acid could be detected in the issuing gas stream. At this point the heating was stopped, usually after the chlorplatinate had been heated to 400° for about seven hours, or more. It seems that the chlorplatinate, when pure, will stand the temperature of 400° indefinitely in a non-reducing atmosphere, without suffering any change chemically. No appreciable quantity of hydrochloric acid could be detected after the hydrochloric acid and water held mechanically had once been driven off. This all, provided the salt was pure to start with. In the first trials, in which the chlorplatinate had been prepared by the use of aqua regia, its behaviour was entirely different. In these cases decomposition set in in the neighbourhood of 250° and seemed to go on progressively throughout the whole mass of the salt.

After having been dried in this manner, the chlorplatinate was transferred to the final apparatus with little or no exposure to the air, through an opening which was sealed off after filling. In this it was subjected to final drying at 350° and evacuation, as described under the manipulations.

Potassium Chloride.—As a starting point for the preparation of pure potassium chloride, the purest commercial article obtainable was taken. This was first re-crystallised from a solution made slightly alkaline with potassium hydroxide to remove traces of ammonia which were present. The salt was then re-dissolved in water and chlorine passed through the hot solution for several hours, after which it was concentrated and the potassium chloride allowed to crystallise out. Following this the salt was re-crystallised five times from water, precipitated three times by alcohol, and finally precipitated from aqueous solution by purified hydrochloric acid gas. The crystals in these varied processes were separated from the mother-liquors by centrifugal drainage.

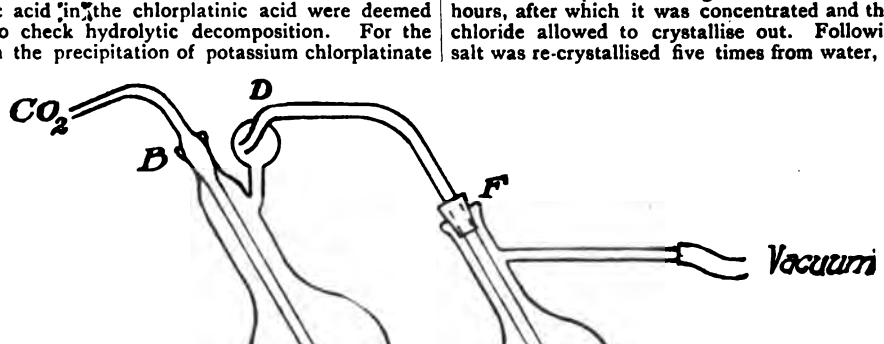


Fig. 1

This potassium chloride certainly contained less bromine than 1 in 50,000. To test for bromine the following process, a modification of that described by Andrews, was adopted (*Journ. Am. Chem. Soc.*, xxix., 275).

The flask A is fitted with a ground glass joint at B which ends in an extremely fine capillary at C. The side tube D has a trap to prevent spray from being carried over. An ordinary distilling flask is affixed to the end of this side tube with a rubber stopper in such a manner as to bring the side tube well into the bulb of the flask E. The flask A is charged with 200 cc. of distilled water, 20 cc. of N/5 potassium iodate, and 20 cc. of 2 N nitric acid. The flask E contains about 5 cc. of a 4 per cent solution of potassium iodide (which must not liberate iodine upon being acidified). The flasks are then connected by means of the stopper at F and vacuum applied. The capillary tube which is ground into the flask at B is connected with a carbon dioxide generator, and after vacuum has been applied, should yield a fairly steady stream of bubbles through the liquid, so as to insure regular boiling and at the same time not appreciably to diminish the vacuum. It is desirable to have a pure neutral gas such as carbon dioxide or nitrogen passing through the capillary, since traces of reducing substances in the air used would vitiate the results. The gas passing through the capillary, besides insuring regular boiling, acts as a diluent for the

steam formed and as such checks the reaction $H_2O + Br_2 = 2HBr + O$.

The flask containing the potassium iodate and nitric acid mixture is then heated on the water bath until 100 cc. have distilled into the flask containing the potassium iodide. If the resulting distillate is coloured by the presence of free iodine, the process is repeated after adding water to make up for the quantity distilled off, until a satisfactory blank is obtained. Then 3—5 grms. of the potassium chloride to be tested are dissolved in a little water and added to the flask containing the iodate and the volume of the solution made up to 250 cc. again. The distillate containing the free iodine corresponding to the amount of bromine distilled over, is then titrated with a solution of thiosulphate corresponding to 1 mgrm. of bromine per cubic centimetre. To 5 grms. of potassium chloride which had been treated until blank distillates were obtained the following quantities of bromine were added and found :—

Added ..	1	0·5	0·3	0·1	mgrm.
Found ..	1	0·52	0·36	0·12	mgrm.

The potassium chloride used for precipitating potassium chlorplatinate contained less than 0·1 mgrm. bromine in 5 grms. or 1 : 50,000. This amount, it is safe to assume, was further reduced in the preparation of potassium chlorplatinate.

Hydrochloric Acid.—The hydrochloric acid used in the preparation of pure hydrochloric acid was free from sulphuric and nitric acid. It was treated by allowing chlorine to bubble through it for one day. Following this, air was bubbled through the acid saturated with chlorine until the chlorine was expelled and the acid was again colourless. Usually the air was left passing through the acid over night, a reduction of about one-fifth in the volume of the acid, due to evaporation, taking place with the removal of the excess of chlorine. During the manipulations in preparing chlorplatinic acid, it was further subjected to the action of chlorine twice, namely, during electrolysis of the platinum and on evaporation of the platinum solution.

Chlorine.—All the chlorine used was generated by the action of pure potassium permanganate on hydrochloric acid which had been previously boiled with a small quantity of potassium permanganate.

Water.—The water used was obtained by re-distilling distilled water with alkaline permanganate, rejecting the first part of the distillate until it no longer contained ammonia.

Balance and Weights.—The balance and weights were identical with those described under the atomic weight of hydrogen (Noyes, *Journ. Am. Chem. Soc.*, xxix., 1723). The air of the balance case was dried by means of a current of air as described in the previous paper. Each piece of apparatus was weighed with a corresponding counterpoise approaching it within 1 cc. in volume and 30 grms. in weight. In the case of the hydrogen the counterpoise was within 0·3 cc. of the volume and 2 grms. of the weight of the palladium tube.

All pieces were rinsed with distilled water after having been used in a determination. Having been wiped dry, they were suspended for some time in a desiccator through which a current of dry air was passing, before being transferred to the dry air of the balance. For the hydrogen apparatus twelve to twenty-four hours were allowed in order to attain constant surface conditions. The current of air through the balance was stopped fifteen to twenty minutes before a weighing was made. Duplicate weights were taken at intervals of an hour or more and rarely differed by more than 0·05 mgrm.

Weights.—The weights were calibrated to vacuum standard here in the Bureau of Standards. The small correction necessary on account of the difference in volume between the brass and platinum weights was included in a table with the corrections for the errors of the weights.

(To be continued).

THE USE OF TIN AS A CATHODE FOR THE RAPID QUANTITATIVE ELECTROLYTIC DEPOSITION OF ZINC, COPPER, SILVER, CADMIUM, AND NICKEL.*

By LAURENCE T. SHERWOOD and GELLERT ALLEMAN.

The high price of platinum, together with other minor considerations, led to an investigation in the Laboratory of the Department of Chemistry, Swarthmore College, in order to determine if metallic cathodes, other than platinum, could be used for the quantitative electrolytic deposition of various metals, and, if so, to determine the exact conditions productive of the best results. While it is intended to continue this investigation, using other metallic cathodes, especially tungsten, this article has to deal entirely with the tin cathode, and the deposition on it of the five elements named in the title.

Attention is directed to the fact that all the results obtained are published in the tables—none having been rejected.

While not so generally applicable as platinum, it was found that for the estimation of the metals enumerated, tin could be substituted for the more expensive material. The attempt has not yet been made to use this cathode in determining any other of the metals, but judging from the work thus far it seems quite possible that it may be used for all of those which are deposited in the metallic state.

Platinum has been regarded as about the only suitable cathode material because of its insolubility and immunity from corrosion, and, of course, these were anticipated as the chief defects of tin. The solvent action of electrolytes was especially feared, but with certain precautions, which

Diagram 1

Diagram 2

will be mentioned under the special considerations, there was no loss of tin during the determination even with such powerful solvents as sulphuric acid and potassium cyanide. Corrosion of other natures gave no trouble whatever.

The following general facts regarding the care of the dishes may be worth mentioning :—

Solutions which have not a solvent action may, during the progress of an analysis, be heated in them upon a sheet of asbestos (thickness exceeding a quarter inch) or upon an electric stove without fear of oxidising the tin.

On account of the low melting-point of tin the dish cannot, of course, be held in the free flame nor set upon hot asbestos or an electric stove, if empty.

The surface should be kept bright by an occasional scouring with fairly coarse sea-sand.

For reasons which will appear later it is preferable, but not necessary, to keep separate dishes for depositions of each particular metal.

The first dishes were made of Kahlbaum's tin, cast in an

* From the *Journal of the American Chemical Society*, xxix., No. 7.

TABLE I.

$ZnSO_4.7H_2O = Zn$, in grm.	NaOH, in grms.	Volume in cc. when diluted.	Approximate temperature at start.	Current N.D.$_{100}$ = A.	Volts.	Time, in minutes.	Zn deposited, in grms.	Error in per cent of Zn in $ZnSO_4.7H_2O$.
0·2496	8	100	65°	5	5	30	0·2490	0·05
						30	0·2495	0·01
						30	0·2501	0·05
						25	0·2502	0·06

TABLE II.

$ZnSO_4.7H_2O = Zn$, in grm.	NaOH, in grms.	Volume in cc. when diluted.	Approximate temperature at start.	Current N.D.$_{100}$ = A.	Volts.	Time, in minutes.	Zn deposited, in grms.	Error in per cent of Zn in $ZnSO_4.7H_2O$.
0·2496	8	100	65°	3	7	30	0·2494	0·02
						30	0·2501	0·05
						30	0·2492	0·03
						30	0·2494	0·02
						30	0·2494	0·02
						25	0·2582	0·13
						25	0·2536	0·37
						25	0·2515	0·18
						25	0·2507	0·10
						25	0·2505	0·08
0·2500	8	100	65°	3	7	25	0·2508	0·07
						25	0·2498	0·02
						25	0·2517	0·16
						25	0·2495	0·04
						25	0·2502	0·02
						25	0·2417	0·75
						25	0·2448	0·47
						25	0·2476	0·22
						25	0·2486	0·13

TABLE III.

$ZnSO_4.7H_2O = Zn$, in grm.	$CH_3.COONa$, in grms.	30 per cent acetic acid, in cc.	Volume in cc. when diluted.	Approximate temperature at start.	Current, N.D.$_{100}$ = A.	Volts.	Time, in minutes.	Zn deposited, in grm.	Error in per cent of Zn in $ZnSO_4.7H_2O$.
0·2500	3	0·2	100	20°	3	18·5—11·5	15	0·2509	0·08
								0·2496	0·03
								0·2499	0·01
								0·2489	0·10
								0·2491	0·08

TABLE IV.

$ZnSO_4.7H_2O = Zn$, in grm.	$CH_3.COONa$, in grms.	30 per cent acetic acid, in cc.	Volume in cc. when diluted.	Approximate temperature at start.	Current, N.D.$_{100}$ = A.	Volts.	Time, in minutes.	Zn deposited, in grm.	Error in per cent of Zn in $ZnSO_4.7H_2O$.
0·2500	3	0·2	100	20°	2	12·5—9·5	15	0·2494	0·05
								0·2483	0·15
								0·2505	0·05
								0·2491	0·08
								0·2504	0·04
								0·2474	0·23
								0·2488	0·11
								0·2509	0·08
								0·2484	0·14
								0·2483	0·15
								0·2497	0·03
								0·2513	0·12
								0·2490	0·09
								0·2489	0·10
								0·2517	0·16
								0·2496	0·03
								0·2516	0·15
								0·2480	0·18

NOTE.—Speed of rotator was 700 revolutions per minute.

TABLE V.

$ZnSO_4.7H_2O = Zn$, in grm.	$CH_3.COONa$, in grms.	30 per cent acetic acid, in cc.	Volume in cc. when diluted.	Approximate temperature at start.	Current N.D.$_{100}$ = A.	Volts.	Time, in minutes.	Zn deposited, in grm.	Error in per cent of Zn in $ZnSO_4.7H_2O$.
0·2500	3	0·2	100	20°	2	18—13	17	0·2500	0·00
0·2500	3	0·2	100	65°	2	14—11	17	0·2493	0·06
							17	0·2500	0·00
							17	0·2497	0·02
							16	0·2496	0·03
							16	0·2490	0·09
							18	0·2498	0·02
							16	0·2496	0·03
							17	0·2495	0·04

iron mould of the shape represented by cross-section diagram No. 1, and cut down on a lathe to a suitable weight (70 to 80 grms.). The dimensions were :—Diameter of top, 8 cm. ; diameter of bottom, 7 cm. ; height, about 3·3 cm. The total inside surface was approximately 115 sq. cm., which was equivalent to about 100 sq. cm. when 100 cc. of liquid was rotating inside. Most of the work on zinc was done with these dishes, but they were unsatisfactory both in their form and on account of pores in their surfaces due to imperfections in the castings. The dish which has thus far given the best results has a form indicated by cross-section diagram No. 2.

These were spun by J. Bishop and Son, from sheet block tin (No. 18 B. and S. gauge) bought of Messrs. Eimer and Amend. The diameter of the top was 9 cm. ; the total surface about 125 sq. cm., which was equivalent to about 100 sq. cm. when 100 cc. of liquid was rotating within. They weighed about 65 grms. Owing to the softness of tin, the edge of the dish where it is grasped hy the forceps in weighing should be as thick as consistency will permit.

To economise time the rotating anode was used in practically all the investigations. The forms used consisted of platinum wire respectively 1·4 mm. and 1·1 mm. in diameter (Nos. 17 and 19, B. and S. gauge), bent into spirals. The former size was slightly preferable. The spirals were depressed in the centre, conforming somewhat to the shape of the dish. Their diameter was 3·5 cm. The anodes were inserted in the motor shaft. The motors supplied by the Electro-Dental Manufacturing Co., of Philadelphia, were wound to run on a 110 volt lighting circuit, and had a speed of 500 to 700 revolutions per minute. While they answered practically all purposes it is recommended if this form of rotator is used that the maximum speed be at least 1000 revolutions per minute. A lamp resistance could be put in the circuit to diminish this speed to any desired. Within the range of speeds used there was hardly a perceptible difference in the character of the metallic deposits.

Zinc.—Methods outlined by Exner were adapted for this metal, first using a platinum dish, and later tin (*Journ. Am. Chem. Soc.*, xxv., 900). With a few exceptions, probably due to some slightly different conditions, his methods served very well. A few experiments showed also that Classen's method, using ammonium oxalate and tartaric acid as electrolytes (*Ber.*, xii., 1622), could probably be used with the tin cathode. However, not enough tests were made to decide conclusively.

Table I. records a series of determinations with a platinum dish. The results in Table II. were obtained by almost the same method on the tin cathodes described in diagram No. 1. Sodium hydroxide dissolves tin slowly when no current is passing through it, and the following procedure is therefore recommended. Prepare the sodium zincate by adding the specified amount of sodium hydroxide (in solid form) to the zinc sulphate solution in a beaker. (It is perhaps worth mentioning that Jena glass should be used in preparing the zincate solution, since the strong alkali is apt to dissolve material from the ordinary glass beaker).* Place the dish on its support, and add 30 or 40 cc. of hot water ; *close the circuit*, having the rhesostat adjusted so that about 1 ampère will flow as soon as the electrolytes are added ; introduce the hot zincate solution, dilute to a suitable volume, adjust the electrodes, start the rotator, and allow the full current to pass in. If this procedure is followed, tin will not be dissolved. With the sodium acetate method it is unnecessary to observe the precaution of having the circuit closed before the electrolyte is added.

The deposits on tin exactly resembled those on platinum. They were crystalline, but could easily be washed in the usual manner, and weighed. After weighing, the loose material was wiped and brushed out, and another determination made by depositing on the remaining coating. Moreover, when once coated with zinc, no precautions were necessary to protect the tin from the solvent action of the sodium hydroxide. The adherent coating was very thin, and several depositions could be made before cleaning all the zinc off. To remove the adherent zinc, use dilute hydrochloric or sulphuric acid, or nitric acid with a specific gravity, 1·52. Nitric acid more dilute than this attacked the tin rapidly. After cleaning, the tin surface usually had to be scoured bright with sea-sand. Of course the dishes lost a little weight in cleaning, but with reasonable care they last indefinitely. Dishes in constant use for a year lost less than 2 grms.

In all the determinations of Table II. only two dishes were used, and neither of them was cleaned of the adherent zinc after the series was begun. It is quite possible that by depositing upon the porous zinc surface which was formed after the first few determinations a source of error was introduced, which may account for the inconsistent results in the latter part of the series and throughout Table IV. This point was not thoroughly investigated, but the better results in the first determinations seemed to indicate that that was the case. The irregular results in both Tables II. and IV. are also probably due to the pores and imperfections in the dishes used. Series V. was run on the better form of dish described by diagram No. 2, and the results are consistent. Four or five determinations were made without cleaning off the adherent zinc. It is not advisable to run more than this number in succession.

The time set down by Exner for these depositions was ten to fifteen minutes (see also paper by Ingham, *Journ. Am. Chem. Soc.*, xxvi., 1272). Failure to comply with some conditions made it necessary to take a longer time with the sodium hydroxide electrolyte. The bulk of the metal came down in the first few minutes, but traces remained until the time stated had expired. The time required on tin was the same as that on platinum. As rapidity was not a special object in this investigation no great effort was made to reduce the time, although it should not be difficult to do so. Five ampères, the current used on platinum, gave too loose a deposit on the tin, but no longer time was required with 3 ampères.

Tables III. and IV. record series on platinum and tin respectively with the sodium acetate electrolyte. This method was adapted with practically no change from Exner's conditions. The deposits in both cases were crystalline, and rather loose, but there was no difficulty in washing and weighing them.

The series recorded in Table V. was run by Mr. R. L. Hill, of this laboratory. He used the tin dishes represented in diagram No. 2, and was careful not to run more than four or five determinations on a particular dish without cleaning off the adherent coating of zinc. He also used a slower rotator (550 R. P. M. instead of 700 R. P. M) and a slightly smaller anode, which may account for the extra time required.

(To be continued).

* It must be remembered that Jena glass contains zinc, however, and is somewhat attacked by alkaline solutions. Porcelain would probably be safer.—Ed. *Journ. Am Chem Soc.*

A Remarkable Colour Photograph.—At the present time, when colour photography is in the air and new methods are being exploited on every side, it is interesting to see a good reproduction of a really fine example of general colour photography from nature by the three colour process. The *Photographic News*, one of the most enterprising of publications devoted to the needs of the amateur photographer, is usually well to the front in all up-to-date matters concerning the art of the camera, and is now the first photographic weekly in the world to publish a *fac simile* reproduction in natural colours from nature. This is given in a recent issue of the *Photographic News* as a special mounted supplement, and is a splendid example of colour photography by Mr. H. J. Comley, of Stroud. The picture is a fine example of a perfect rendering of a still-life study of fruit and glass. The wonderful texture and colour of a group of oranges, the transparency of the glass, and the tones of a basket and some crumpled paper are portrayed with a realism that is almost startling.

REVISIONS OF THE THEORY OF ELECTROLYSIS.*

By HENRY S. CARHART, LL.D.

No subject in the whole domain of theoretical electricity possesses more interest to the electro-chemist than the theory of the decomposition of aqueous solutions of salts and acids through the agency of an electric current. For more than a hundred years scientific attention has been converged on it, for it has presented problems both of unusual interest and of unusual difficulty. Its development has not been one of uninterrupted progress, but rather one of leaps and bounds, alternating with seasons of suspended animation. Even with the noteworthy additions of the past twenty years, it cannot be said that all difficulties have yet been resolved. We are in little danger of so completely clearing up the entire field that nothing shall be left for posterity.

An historical review of this subject, biassed it may be by perspective and distorted by the disproportionately large visual angle under which we view recent events, may yet give us more respect for the achievements of the past and less unreserved satisfaction with the advances of our own times.

The earliest record of observed electrolysis dates back of the invention of Volta's dry pile and "crown of cups." The decomposition of water by electrical means was described by Van Troostwijk and Deimann in 1789. It was accomplished by sending a series of electric discharges through water in a narrow glass tube between gold wires whose ends were an inch and a-half apart. The tube was placed vertically, and when the end of the upper wire became uncovered the spark caused the explosive reunion of the mixed gases. These experimenters concluded, contrary to the opinion of many of their scientific contemporaries, that both the hydrogen and the oxygen were obtained from the decomposition of water, and that water consisted of a union of these two gases only. They cited both the synthesis and the analysis taking place in their experimental tube as proofs of their view. But the question as to the manner in which electricity acts to effect the decomposition remained unanswered. They did not obtain the two gases separately, but mixed in the glass tube. An enormous number of discharges were said to be necessary to produce an appreciable volume of mixed gases —14,600 for one-third of a cubic inch.

A little later, Ritter found that 50 or 60 discharges from a Leyden jar through a solution of silver nitrate between silver wires gave a visible deposit of metallic silver on the negative electrode. By reversing the poles this deposit disappeared, and at the same time a new deposit formed on the other wire.

It is therefore obvious that the scientific world was prepared to accept electrolytic decomposition when Volta disclosed his invention of the dry pile and the voltaic battery, or "crown of cups." This disclosure was made in a letter to Sir Joseph Banks, President of the Royal Society of London, dated March 20th, 1800. Before this letter was published in the *Philosophical Transactions* its contents had become known to London physicists, and Nicholson and Carlisle had decomposed water by means of Volta's pile. Carlisle made the acute observation that when a drop of water was placed on the upper plate of the pile to improve the contact between it and the wire of the external circuit, gas was given off; and Nicholson recognised the presence of hydrogen when the wire used was steel. These and similar facts induced them to send the electric current from a pile of thirty-six pairs through river water between brass wires in a glass tube half an inch in diameter. A fine stream of gas bubbles was at once given off from the negative electrode. One-fifteenth of a cubic inch was obtained in an hour and a-half, and when this was mixed with an equal volume of air the mixture exploded on the approach of a lighted wax taper.

Although these observers expected the decomposition of water, they were not prepared for the astonishing fact that, while the hydrogen appeared at the exposed end of one of the wires, the oxygen appeared only at the end of the other, nearly 2 inches distant. This phenomenon was to its discoverers inexplicable. They made the very relevant and acute remark that this new phenomenon "appears to show perhaps a general law of the action of electricity in chemical processes." The explanation of this remarkable fact has ever since engaged the attention and best endeavours of science.

It is worthy of attention also that Nicholson and Carlisle observed that chemical action takes place in a voltaic cell when it functions as a source of current. In other words, they recognised that a voltaic cell is also an electrolytic cell. This is the first of many facts which tell against Volta's contact theory of the electro-motive force of a voltaic cell. Volta himself asserted that the chemical actions going on in a voltaic cell have practically no essential significance.

In this same celebrated year of 1800 Cruikshank decomposed lead acetate between silver wires. A minute or two after connection was made he observed lustrous metallic lead crystals on the negative electrode, while gas was released at the positive. Cruikshank called attention to the fact that only liquids containing oxygen conduct electricity, and he appears to have concluded that electricity seizes on the oxygen and transports it invisibly to the positive pole. Not so far removed from this conception is the present view that the oxygen conveys an electric charge rather than that the charge conveys the oxygen.

The separate appearance of the two products of decomposition at the electrodes was the most noteworthy, and at the same time the most inexplicable fact of electrolysis to all the chemists and physicists of the day. An unknown correspondent in *Nicholson's Journal* expressed himself as follows:—

"I should like to inquire how it can happen in any system that the two components of water can be caused to appear at such a distance from each other. Does the hydrogen from the dissociated particles of water at the zinc side of the pile fly from it at the instant when the oxygen is liberated there? If that is so, why does not one see the gas bubbles on the way? Or does the oxygen migrate from the silver side to the zinc side? Or are there two streams at once?"

It should be remembered that Volta attached an extra zinc plate to the silver at the positive end and an extra silver plate to the zinc at the negative end, both in the case of his dry pile and crown of cups or voltaic battery. Hence, in the early literature the zinc side means the positive and the silver the negative.

Sir Humphry Davy was early in the field of electric research, and at once distanced all his English *confrères* by the number and importance of his detail discoveries. In particular at the outset he obtained oxygen and hydrogen in different tubes separated in the circuit by the interposition of his own person as a conductor, and he proved conclusively that the two gases are evolved in the same relative proportion in which they exist as elements in water. But Sir Humphry Davy added little to the theory of electric action in electrolysis. Near the close of one of his papers published in December, 1800, he remarks:—

"On these facts I shall not presume to speculate. . . . Many observations must be collected, probably, before we shall be able to ascertain whether water is decomposed in galvanic processes. Supposing its decomposition, we must assume that at least one of its elements is capable of rapidly passing in an invisible form through metallic substances, or through water and many connected organic bodies, and such an assumption is incommensurable with all known facts. But a short period has elapsed since philosophers beheld with wonder solid and fluid substances

* Presidential Address delivered at the Seventh General Meeting of the American Electro-chemical Society. From the *Smithsonian Report* for 1906, p. 147.

assuming new modes of existence in different gases. Do not the new phenomena of galvanism authorise us to hope that at no very distant time they will behold even those gases undergoing novel changes, and existing in new and now unknown forms?"

The diffuseness and lack of concreteness of ideas in those early days of the science, before the time of Ohm's law, are strikingly illustrated in the following extract from a syllabus of a course of lectures delivered by Davy in the theatre of the Royal Institution in January, 1802:—

"The agency of the galvanic influence which occasions chemical changes in water, and communicates shocks to the living body, is probably in some measure distinct from that agency which produces sparks and the combustion of bodies. The one appears, all other circumstances being similar, to have little relation to surface in compound circles, but to be great in some unknown proportion as the series are numerous. The intensity of the other seems to be as much connected with the extension of the surface of the series as with their number."

Davy was not at that time able to distinguish between electro-motive force or electric pressure and strength of current.

The long contest waged between the supporters of the contact theory of electric action in a voltaic couple and the chemieal theory is briefly alluded to in this same syllabus, without any clear intimation of the position taken by Sir Humphry himself:—

"M. Volta has supposed that an electric current is always produced by the mere contact of certain different conductors of electricity. But many of the British philosophers have denied this position, accounting for galvanism from the destruction of the equilibrium of electricity in galvanic circles in consequence of the chemical agencies of the different bodies composing them."

On November 20, 1806, Davy read before the Royal Society a Bakerian lecture on "Some Chemical Agencies of Electricity." In this lecture he takes a decided position against the chemical theory of electrical excitation held by many British philosophers. He says:—

"The general ideas advanced in the preceding pages are evidently directly in contradiction to the opinion advanced by Fabroni, and which, in the early stages of investigation, appeared extremely probable, namely, that chemical changes are the *primary* causes of the phenomena of galvanism.

"Before the experiments of M. Volta on the electricity excited by the mere contact of metals were published, I had to a certain extent adopted this opinion; but the new facts immediately proved that another power must necessarily be concerned."

In this same lecture we find suggestions by this distinguished philosopher harmonising with the celebrated theory of Grotthus; but no credit is due to Davy for these suggestions, because Grotthus published his theory in the year 1805 in Rome under the title, "Memoire sur la decomposition de l'eau, et des corps qu'elle tient en Dissolution a l'aide de l'Électricité Galvanique." A second edition followed the next year, and the memoir was also published in the *Annales de Chimie* in 1806. Sir Humphry says:—

"It is very natural to suppose that the repellant and attractive energies are communicated from one *particle to another particle* of the same kind, so as to establish a conducting chain in the fluid; and that this is really the case seems to be shown by many facts. . . .

"In the case of the separation of the constituents of water, and of solutions of neutral salts forming the whole of the chain, there may possibly be a succession of decompositions and recompositions throughout the fluid."

Ostwald says ("Elektrochemie," p. 307) that the different theories proposed to explain the separate evolution of the products of electrical decomposition vied with one another in improbability, and no one of them was free from the most serious objections. When at length one view met with general acceptance it was not so much because of its unconditional excellence as because it was at least relatively the best of all.

Here the account of Grotthus himself relating to the origin of his theory. He says:—

"Volta's pile, which made the genius of its inventor immortal, is an electrical magnet, of which each element—that is, each pair of plates—has both a positive and a negative pole. The consideration of this polarity has suggested to me the idea that a similar polarity might form between the molecules of water when it is acted on by this same electrical agent; and I must confess that this was for me a gleam of light."

Freiherr von Grotthus was a most interesting character. At the age of a year and a-half the death of his father left him to the care of his mother, and he lived with her on her landed estate in Lithuania, near the borders of the Baltic province of Kurland, till his seventeenth year. The taste for science developed in him at an early age, but it was stifled in the most brutal and unsympathetic manner by his teacher, who had neither the taste nor the intelligence for the studies to which the genius of Grotthus inclined. In the year 1803, at the age of eighteen, he went to Leipzig to study, and after six months there he betook himself to Paris, where he listened to the lectures of the most distinguished philosophers of the time. The threatened war between France and Russia compelled him to leave Paris, and he hastened to Naples, where he remained till the end of the year 1805. Through his fortunate acquaintance there with a distinguished English physician named Thomson, who was the owner of a small galvanic apparatus, our young natural philosopher was enabled to repeat the experiments of Professor Pacchiani, which were then exciting much attention. The result was his theory of electrolysis, first published in 1805, when its author was not more than twenty years of age, a theory which held sway for nearly three-quarters of a century, and which has for ever linked his name with the history of electrochemistry.

Under more favourable conditions of birth, education, and surroundings Grotthus might have become one of the most distinguished investigators of his time. But in the autumn of 1807 he felt compelled to return to his ancestral estate, and to busy himself with the duties of manager. Here in the country, in a remote angle of Lithuania, for the most part without literary associates, and lacking often the most essential means of research, he wrung from nature some of her well-concealed secrets and wrote nearly all his contributions to science.

For years he suffered unspeakably from an incurable organic malady. The trouble increased from day to day, and finally reached such an acute stage that he was brought to the rash decision to sever voluntarily the thread of life. He died in 1822 at the age of thirty-seven.

The Grotthus theory of the mechanism of electrolysis does not respond, as we now know, to the facts of later discovery. But since for the first time it made comprehensible the physical possibility of the phenomena of electrolytic decomposition it has enduring value.

Grotthus conceived that a species of polarisation is set up in the water by electrical agency, so that the positively charged elements are turned toward the negative electrode and the negatively charged ones in the other direction. Also, that at the moment of separation of the oxygen and hydrogen from each other a division of their natural charge of electricity takes place, in some way not explained. Attractions and repulsions follow; also the continuous movement of two streams of charged particles in opposite directions, through the process of molecular interchanges, or the exchange of partners whose conjugal bond is chemical affinity. Grotthus does not appear to have got the conception that a current in an electrolyte is the convection of positive and negative charges in opposite

directions, but his theory was directed toward the explanation of the most obvious and novel fact, that the products of the decomposition appear at widely distant points. He distinctly remarks that the process, as he conceives it, involves decomposition at the electrodes only, where the current passes between the electrode and the electrolyte. He says :—

"I conclude, therefore, that if it were possible to produce in water a current of galvanic electricity so that it should describe in it a complete circuit, all the molecules of the liquid which are in this circuit would at the same instant be decomposed and again reformed; whence it follows that the water, although it underlies the action of galvanism, would still always remain water."

Grotthus had no consistent idea of the relation between the charges carried by the components of a molecule and the passage of a current. The current appeared to him only to align the molecular components, and the resulting molecular cleavages and re-formations were due to the attraction and repulsion between the electric charges or their polarity. His conception was crude and imperfect compared with the corresponding concepts of the present time. But it showed at least that the phenomena of electrolysis take place by a conceivable process. If it did not satisfy all intellectual demands, it quieted clamor and bridged the gulf between the known and the inexplicable. It was indeed a gleam of light that has never been effaced, and we owe an everlasting debt of gratitude to the farmer philosopher of Lithuania.

Grotthus gave a vivid picture of the chief phenomenon of electrolysis, the appearance of the separated constituents at the electrodes only. The knowledge of his time scarcely reached beyond this one fact. It was not long, however, before new observations were made which could with difficulty be fitted into his picture.

The essential fact which the theory of Grotthus was incompetent to answer satisfactorily was that the smallest electro-motive force may produce a current through an electrolyte, and the strength of this current follows Ohm's law.

Grotthus assumes that the application of an electromotive force to the electrodes gives rise to a polarised condition of the molecules, and that at the instant of the separation of the hydrogen and oxygen, for example, a separation of their natural charge of electricity takes place, either through contact or friction; so that one part becomes electro-positive and the other electro-negative. This perhaps means that the normal condition of an electrolyte is one of equilibrium with rigidly combined molecules. Grotthus did not appear to conceive of the cleavage of a polarised molecule until current passed.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 5, February 3, 1908.

Heat of Formation of Anhydrous Oxides of Lithium, Calcium, Strontium, and Barium.—M. de Forcrand.—The following are the results the author has obtained for the heat of formation of the oxides of calcium, lithium, strontium, and barium : — *Monoxides.* — $Ca + O = CaO$, +151·90 cals.; $Li_2 + O$ Li_2O, +143·32 cals.; $Sr + O = SrO$, +137·60 cals.; $Ba + O = BaO$, +125·86 cals. *Dioxides.*— $Ca + O_2$ CaO_2, +157·33 cals.; $Li_2 + O_2 = Li_2O_2$, +152·65 cals.; $Sr + O_2 = SrO_2$, +152·10 cals.; $Ba + O_2 = BaO_2$, +145·71 cals. The great resemblance in the numbers found for strontium and lithium, especially in the case of the dioxides, is very striking.

Complex Salts of Iron in which the Iron is Masked.—P. Pascal.—When freshly precipitated ferric pyrophosphate is added to a solution of sodium pyrophosphate, the solubility of the ferric salt is independent of the temperature and of the concentration of the sodium salt. When the solution is saturated the constituents are present in the proportion $(P_2O_7)_3Fe_4 : 3P_2O_7Na_4$. The iron in this solution does not give the ordinary iron reactions except as regards reducing agents, *e.g.*, oxalic acid, ammonium hydrosulphide. Thus, a new complex, to which the author has given the name ferripyrophosphate appears to be present. The sodium salt has the formula $Fe_2(P_2O_7)_3Na_6{\cdot}9H_2O$. A ferropyrophosphate, $Fe_2(P_2O_7)_3Na_8$, can be prepared by using metaphosphoric instead of pyrophosphoric acid.

New Derivatives of Camphenylone.—L. Bouveault and G. Blanc.—Sodamide gives with camphenylone a compound which is decomposed by water into soda and $C_9H_{14}O + NH_3$, dihydrocampholene amide. This amide, when treated with bromine in presence of sodium methyl alcoholate and methyl alcohol, is transformed into urethane,—

$$C_8H_{15}—CO—NH_2 + Br_2 + 2CH_3ONa = C_8H_{15}—NH—COOCH_3 + CH_4O + 2NaBr.$$

From the urethane an amine, $C_8H_5NH_2$, apocamphenylamine, can be isolated. Its chlorhydrate gives apocamphenylol with sodium nitrite,—

$$C_8H_{15}NH_2.HCl + NO_2Na = NaCl + N_2 + C_8H_{15}OH + H_2O.$$

By the oxidation of this new alcohol β-isopropylcyclopentanone is formed. Therefore apocamphenylamine is β-isopropylcyclopentylamine, and Wagner's formula for camphenylone is probably correct.

Order of the Addition of Ammonia to the Organic α-Oxides of Asymmetric Structure.—K. Krassousky.—Taking the oxides of propylene, isobutylene, and trimethylethylene as typical asymmetric oxides the author has investigated the action of ammonia on them. As a general result it was found that the hydroxyl group preferably unites with the atom of carbon to which the least hydrogen is attached.

No. 6, February 10, 1908.

Alcoholysis of Linseed Oil.—A. Haller.—By the fractional distillation of the ethers obtained by the action of alcohol on this oil in presence of ether four different fractions can be separated. From these fractions the following ethers can be isolated—methyl palmitate, methyl stearate, and methyl arachate. Arachic acid occurs only in very small quantities in the oil.

New Series of Ammoniacal Ferric Salts in which the Iron is Masked.—P. Pascal.—When ammonia is added to a solution of ferric pyrophosphate the liquid is coloured red, and a crystalline precipitate forms. Where the two liquids meet a layer of a red substance, with light yellow masses above it, can be detected, and in the upper part of the liquid long silky crystals are formed. All these substances are ammoniacal ferric salts in which the iron is masked. The crystalline precipitate contains sodium pyrophosphate, precipitated by the ammonia, and varying proportions of ammonia and iron. The ratio of the iron to the ammonia is fixed, and when excess of ammonia is present the precipitate may be regarded as formed of a combination of sodium phosphate and ferric pyrophosphate of formula $n(P_2O_7Na_4.10H_2O) + Fe_2(P_2O_7)_3Na_6 + 3NH_3 + pH_2O$. For n and p the author has obtained the following values:— $n_1 = 4$, $p_1 = 8$; $n_2 = 2{\cdot}5$, $p_2 = 15$; $n_3 = 18$, $p_3 = 25$. When the liquid is only slightly alkaline the yellow precipitate may be represented by the formula $n(P_2O_7Na_4.10H_2O) + Fe_2(P_2O_7)_3Na_6 + 2NH_3 + pH_2O$, in which n and p have the following values:—$n_1 = 18$; $p_1 = 50$; $n_2 = 9$, p_2 60. The red substance appears to have the formula $(P_2O_7)_3Fe_4 + 2P_2O_7Na_4 + 4NH_3 + 68H_2O$. When left for a long time in dry air it loses water and ammonia, and forms a brick-red powder, soluble in water, of formula $5[(P_2O_7)_3Fe_4 + 2P_2O_7Na_4] + 4NH_3 + 160H_2O$.

Magnesium Silicide.—Paul Lebeau and Robert Bossuet.—The metallo-graphic examination of silicon compounds of magnesium seems to show that only one magnesium silicide exists containing less than 40 per cent of silicon. To prove this, the authors isolated the crystals of the silicide by eliminating the magnesium as magnesium organic compound, and determined the amount of magnesium and silicon they contain. The results obtained agree closely with the formula $SiMg_2$. Thus the direct action of magnesium on silicon leads to the formation of only one definite compound, having the formula $SiMg_2$. This compound crystallises in the magnesium, but can be separated by removing the metal as magnesium organic compound. This silicide of magnesium is completely dissociated *in vacuo* or in a current of hydrogen at 1200°.

Physical Modifications of Gelatin in presence of Electrolytes and Non-electrolytes.—J. Larguier des Bancels.—In presence of various neutral salts gelatin dissolves in water at the ordinary temperature. Different neutral salts have very different solvent powers on gelatin. At the same concentration the salts of divalent metals have more solvent power than those of monovalent metals. The nitrate of a metal has a more energetic action than the chloride. In presence of electrolytes gelatin dissolves in mixtures of certain non-electrolytes and water, *e.g.*, in mixtures of alcohol or acetone and water. Other things being equal, these mixtures are more favourable to solution than pure water. A minimum quantity of pure water must be present, but when once this quantity has been reached the gelatin dissolves more rapidly the more non-electrolyte there is in the mixture. In order to separate the dissolved gelatin it is only necessary to eliminate the salts introduced into the liquid.

Rapid Determination of Potassium Bichromate in Milk.—M. Gouère.—The method depends upon the following reactions:—

$$K_2Cr_2O_7 + 6KI + 14HCl = Cr_2Cl_6 + 8KCl + 3H_2O + 6I.$$
$$2S_2O_3Na_2 + 5H_2O + I_2 = S_4O_6Na_2 + 2NaI + 5H_2O.$$

The milk is dried and ignited, the ash is taken up with water and potassium iodide, and pure hydrochloric acid are added. Then titrated hyposulphite is added until only a faint blue coloration is seen, without any tinge of yellow.

Preparation of Dithymol. Action of Bromine on Dithymol.—H. Cousin and H. Hérissey.—By dissolving thymol in alcohol, adding water and filtering, and then adding a solution of ferric chloride, a precipitate of dithymol is formed. It may be purified by re-crystallising from alcohol at 60°. When hydrated dithymol is suspended in chloroform and the theoretical quantity of bromine is added, a dibromo compound, $C_{20}H_{24}Br_2O_2$, is obtained in the form of pale yellow prismatic crystals. If this dibrominated compound is dissolved in chloroform and more bromine is added, a quinone corresponding to the dibromo-compound is precipitated by the addition of alcohol to the solution.

γ-Oxytetrolic Acid.—M. Lespieau and M. Viguier.—γ-Oxytetrolic acid, $CH_2OH—C\equiv C—CO_2H$, is a white crystalline compound prepared by adding propargyl alcohol to ethyl magnesium bromide, avoiding too great a rise of temperature. When the evolution of ethane has ceased carbon dioxide is passed in, and finally hydrochloric acid and ether are added. The raw product is purified by dissolving it in boiling benzene, from which it crystallises on cooling. The addition of bromine to this acid dissolved in ether gives an acid of formula $CH_2OH—CBr=CBr\ CO_2H$, and a lactone, $CH_2—CBr=CBr—CO$ (O).

Action of Alcohols on Sodium Benzylate.—Marcel Guerbet.—Ethyl and propyl alcohols condense with sodium benzylate, giving benzyl ethyl and benzyl propyl alcohols respectively, $C_6H_5—CH_2—CH_2—CH_2OH$ and $C_6H_5—CH_2—C_3H_6OH$, and the acids resulting from the oxidation of these alcohols. Benzyl alcohol, on the other hand, when heated with its sodium derivative does not give phenyl benzyl carbinol ($C_6H_5—CHOH—CH_2—C_6H_5$), but stilbene ($C_6H_5—CH=CH—C_6H_5$), dibenzyl ($C_6H_5—CH_2—CH_2—C_6H_5$), toluene, and benzoic acid. Probably, however, phenyl benzyl carbinol is first formed, and afterwards decomposes into stilbene and dibenzyl.

Method of Preparing Cyclic Aldehydes.—M. Savariau.—The author has shown that the condensation of chloral with cyclic organo-magnesium compounds gives secondary trichlor-alcohols, which may be transformed into acid alcohols by the action of alkalis, and then into cyclic aldehydes:—

$$C_6H_5—MgBr \rightarrow C_6H_5—CHOH—CCl_3 \rightarrow \begin{cases} C_6H_5—CHOH—CO_2H. \\ C_6H_5—CHO. \end{cases}$$

Moreover the trichlor-alcohols can be directly decomposed into aldehydes and chloroform by boiling with alkaline carbonates:—

$$C_6H_3(CH_3)_2—CHOH—CCl_3 = CHCl_3 + C_6H_3(CH_3)_2—CHO.$$

Berichte der Deutschen Chemischen Gesellschaft.
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Reaction between Phenols and Phosphorus Pentachloride.—W. Autenrieth and Alfred Geyer.—When three molecules of phenol, cresol, or β-naphthol and one molecule of phosphorus pentachloride react together, hydrochloric acid is evolved, and a phosphorous ester dichloride of general formula $Cl_2P(OR)_3$ is obtained, according to the equation $Cl_2PCl_3 + 3HO.R = Cl_2P(OR)_3 + 3HCl$. These phosphite dichlorides are comparatively stable in absence of moisture. Water decomposes them into the phosphoric ester of the phenol and hydrochloric acid, $Cl_2P(OR)_3 + H_2O = 2HCl + OP(OR)_3$.

Ammonium Syngenite.—J. D'Ans.—In order to determine whether ammonium syngenite contains one molecule of water or two, the author subjected the pure salt to a pressure of some thousand atmospheres in a hydraulic press, thus freeing it almost entirely from its mother-liquor. The salt was then powdered, and again pressed between filter-paper. When dried in a desiccator it gave up 80 per cent of water. At 170° it gave up 6·02 per cent of water, and on ignition it lost 47·66 per cent $(NH_4)_2SO_4$. These results show conclusively that the formula is $CaSO_4.(NH_4)_2SO_4.H_2O$.

Rhodium.—A. Gutbier and A. Hüttlinger.—The authors have investigated the halogen salts of rhodium in the course of a research which has for its aim the determination of the atomic weight of rhodium. They find that sodium hexachlor-rhodiate crystallises with twelve molecules of water. Cæsium and rubidium pentachlor-rhodiates cannot be prepared by heating rhodium with cæsium or rubidium chloride in a current of chlorine, but may be obtained by decomposing the potassium salt, or by the direct union of soluble rhodium dichloride with the alkaline chloride. They are slightly soluble in water and contain one molecule of water. Potassium pentabrom-rhodiate can be prepared by heating a mixture of very finely-divided rhodium and potassium bromide in a current of bromine. The decomposition of a solution of this bromo-salt with ammonium, cæsium, or rubidium bromide yields the corresponding brom-rhodiate. These bromo-salts contain no water. The potassium and ammonium salts are fairly soluble in water, the cæsium and rubidium salts are difficultly soluble. All these rhodium compounds give up their halogen as halogen hydride when they are heated in a current of hydrogen.

Colorimetric Method of Determining the Molecular Weight of Carbohydrates.—Leonhard Wacker.—*p*-Phenylhydrazine sulphonic acid and other hydrazines possess the property of giving a red soluble derivative with the aldehydes and alcohols of the aliphatic series in aqueous solution or suspension in presence of air and of an excess

of caustic alkali. The colour of the derivative varies very little with different carbohydrates, and it has been found that the intensity of the coloration of molecular weights is constant; *i.e.*, the intensity decreases as the molecular weight increases. The velocity of the reaction is inversely proportional to the molecular weight, and is proportional to the concentration. If the red coloration appears instantly, aldehydes of low molecular weight are present. With polyatomic alcohols and carbohydrates the colour appears after about fifteen minutes. Concentrated solutions of acetone, lactic, and citric acids, urea, and albuminoids also give the reactions.

Barium Percarbonate.—R. Wolffenstein and E. Peltner. — When carbon dioxide acts upon an excess of barium dioxide the gas is absorbed, and barium percarbonate results according to the equation $BaO_2 + CO_2 = BaCO_4$. When more carbon dioxide is passed in, hydrogen peroxide is rapidly evolved, and the percarbonate is decomposed as shown by the equation $BaCO_4 + H_2O + CO_2 = BaCO_3 + H_2O_2 + CO_2$. Probably the bicarbonate, $Ba<^{HCO_4}_{HCO_3}$, is formed as an intermediate product. Thus the formation of hydrogen peroxide from barium peroxide takes place in two stages. Barium percarbonate is a light yellow substance which decomposes when warmed and when allowed to stand in air. With dilute acids it gives hydrogen peroxide, and hence it is in all probability a true salt of percarbonic acid.

Percarbonic Acid Salts.—Richard Wolffenstein and Erich Peltner.—The authors have prepared four sodium salts of percarbonic acid:—Sodium dioxide carbonate, Na_2CO_4; sodium dioxide bicarbonate, $Na_2C_2O_6$; sodium trioxide carbonate, Na_2CO_5; sodium trioxide bicarbonate, $NaHCO_4$. Sodium dioxide carbonate is prepared by the action of carbon dioxide on sodium dioxide hydrate at a low temperature. It loses oxygen rapidly even in a desiccator and attempts to re-crystallise it have not as yet been successful. The bicarbonate of sodium dioxide results when Na_2CO_4 is saturated with carbon dioxide. It is considerably more stable than the carbonate. The third salt, sodium trioxide carbonate, is obtained when carbon dioxide acts upon sodium trioxide hydrate. This hydrate has already been described by Tafel under the name natryl hydrate, and is formed when alcohol acts upon sodium peroxide, $C_2H_5OH + O{:}Na.ONa = C_2H_5.ONa + O{:}Na.OH$. Prolonged action of carbon dioxide upon natryl hydrate gives the bicarbonate, $NaHCO_4$. All these salts are exceedingly easily decomposed by water. They behave like true percarbonic acid salts, and not like carbonic acid salts with hydrogen peroxide of crystallisation.

Action of Carbonates on Tetrathionates. — A. Gutmann.—The author has already shown that with dilute alkalis tetrathionates give thiosulphates and sulphites. Hence it was to be expected that when tetrathionates are boiled with carbonates or ammonia decomposition would occur in the same way. This, however, is not the case, thiosulphate and sulphate being formed, with evolution of carbon dioxide. Very small quantities of sulphite result with sodium carbonate but not with potassium carbonate. Sulphide is never formed. The reactions occur according to the equations $4S_4O_6Na_2 + 5CO_3Na_2 = 7S_2O_3Na_2 + 2SO_4Na_2 + 5CO_2$ or $4S_4O_5 = 7S_2O_2 + 2SO_3$.

Platinum Blue.—K. A. Hofmann and G. Bugge.—Platinous chloride-dis-acetonitrile, $Cl_2Pt(CH_3{\cdot}CN)_2$, gives with silver nitrate solution a precipitate of silver chloride and an intensely blue coloured solution. The coloured product of this reaction has now been isolated and has been identified as platinous acetamide, $Pt(NH{\cdot}CO{\cdot}CH_3)_2{\cdot}H_2O$.

Reactions of Mercury Cyanide.—K. A. Hofmann and H. Wagner.—According to many observers mercury cyanide does not conduct an electric current in aqueous solution, gives no mercury oxide with caustic potash, and no silver cyanide with silver nitrate. The authors have found, however, that although it gives no, or very few, ions in aqueous solution it does react with silver salts, *e.g.*, the acetate or nitrite. With caustic potash it yields a compound $(HgCy_2)_2{\cdot}KOH{\cdot}H_2O$, which is very soluble in water, and from which silver nitrate at once precipitates pure silver cyanide.

MISCELLANEOUS.

Society of Dyers and Colourists.—**Award of the Perkin Medal.**—At the Annual Meeting of the Society, to be held in the Hall of the Technical College, Bradford, on Friday, April 3rd, 1908, at 4.30 p.m., an Address will be given by the President, Prof. Raphael Meldola, F.R.S., F.I.C., on "The Founding of the Coal-tar Colour Industry." Prof. Meldola, who is a Past-President of the Chemical Society, was elected by the Council to the Presidency of the Society upon the death of the late Sir William H. Perkin. At the same meeting the first awards of the Perkin Medal will be made to Prof. Graebe and Prof. Liebermann for their "Synthesis of Alizarin, 1868." The Perkin Medal, which will be awarded once in each successive period of from three to five years, has been established as a recognition of investigations, discoveries, or inventions of high scientific or industrial importance applicable to or connected with the tinctorial industries.

The British Association, Winnipeg Meeting.—The Council of the British Association for the Advancement of Science has nominated Prof. J. J. Thomson, F.R.S., Cavendish Professor of Experimental Physics in the University of Cambridge, to be President of the meeting of the Association which is to be held at Winnipeg next year. The investigations carried on by Prof. Thomson in the Cavendish Laboratory, and by the distinguished men of science who first worked under him and received inspiration from his researches, laid the foundation for the new views held by chemists and physicists as to the electronic constitution of matter and the remarkable properties of radio-active substances. In 1894 Prof. Thomson was awarded one of the Royal Medals of the Royal Society, and to this was added, in 1902, the Hughes Medal, in recognition of his contributions to the advancement of electrical science, especially in connection with the phenomena of electric discharge through rarefied gases. Two years ago he was the recipient of the Nobel Prize for Physics. It is understood that provision will be made by the Canadian Government, in the estimates for the coming financial year, for a grant of 25,000 dollars (£5000) by the Dominion Parliament towards the expenses of the Association's visit to Winnipeg. The City of Winnipeg itself proposes to make a grant of 5000 dollars (£1000). The week of the meeting will probably be from August 25th to September 1st, 1909.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Royal Society of Arts, 8. (Cantor Lecture). "Fuel and its Future," by Prof V. B. Lewes.

TUESDAY, 24th.—Royal Institution, 3. "The Egyptian Sudan—its History, Monuments, and Peoples, Past and Present," by E. A. Wallis Budge, M.A., &c.

—— Royal Society of Arts, 4.30. "The Mineral Resources of Western Australia," by the Hon. C. H. Rason.

—— Faraday Society, 8. Presidential Address, "Some Aspects of the Work of Lord Kelvin," by Sir Oliver Lodge.

WEDNESDAY, 25th.—Royal Society of Arts, 8. "Recent Improvements in Decorators' Materials," by A. S. Jennings.

THURSDAY, 26th.—Royal Institution, 3. "Standardisation in various Aspects—(2) Electrical Engineering," by R. T. Glazebrook, F.R.S., &c.

—— Royal Society of Arts, 8. (Howard Lecture). "The Navigation of the Air," by H. S. Hele-Shaw, F.R.S., &c.

FRIDAY, 27th.—Royal Institution, 9. "Radio-active Change in the Earth," by Hon. R. J. Strutt, F.R.S., &c.

—— Physical, 5. (At the Northampton Polytechnic Institute, Clerkenwell). "Notes on the Plug Permeameter," "Use of Shunts and Transformers with Alternate Current Measuring Instruments," "Wattmeters," by C. V. Drysdale.

SATURDAY, 28th.—Royal Institution, 3. "Electric Discharges through Gases," by Prof. J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

VOL. XCVII., No. 2522.

NEO-ERBIUM.

By K. A. HOFMANN and O. BURGER.

THE decomposition of the old erbium earth carried out by Marignac (*Archives Genève*, 1878, lxiv., 87), Nilson (*Ber.*, 1880, 1430), and Cleve (*Comptes Rendus*, 1879, lxxxix, 708, and xci., 382), led to the separation of the accompanying elements: scandium, ytterbium, thulium, and holmium from erbium proper, Cleve's neoerbium. Krüss and Nilson (*Ber.*, 1887, 2134) questioned the elementary nature of this substance with atomic weight $R^{III} = 166{\cdot}25$, because they found that according to its mineralogical origin the earth exhibited a relative intensity of the absorption bands which varied within wide limits.

But, as it is now known (Muthmann and Stützel, *Ber.*, 1899, xxxii., 2653; Forsling, *Bih. Sv. Akad. Verb.*, xviii., 1, 4) that the presence of several absorbent or even colourless constituents exercises an influence which cannot be controlled on the relative strengths of the bands and lines, such reasons can no longer hold good. Nevertheless more recently (*Zeit. Anorg. Chem.*, 1893, iii., 369) Krüss, by fractional precipitation with aniline, separated an almost pure erbium preparation, obtained by Nilson, into earths of different equivalent weights, and hence he concluded "that we are not justified in regarding erbium earth as a single oxide Er_2O_3."

We have worked up Nilson and Krüss's material in order to find out definitely how far the decomposition could be carried, and in order to get a preparation which would be as simple as possible and in which the most interesting property of this class of substance, namely, the selective absorption and emission of light, would appear simpler than before.

It was found that the neo-erbium earth obtained by Nilson and Cleve's method still contained impurities, which, however, for the most part appeared to be thulium, holmium, and dysprosium. By the further purification described below the atomic weight was raised from the value $R^{III} = 166{\cdot}25$, previously obtained, to 167·43, and the absorption spectrum was simplified. Nevertheless the earth showed no indication of decomposition in Krüss and Nilson's sense of the word, although separating agents were tried which otherwise are exceedingly effective.

The spectra of the pure earth will be described at the end of this article.

Amongst methods of purifying, fractionation with aniline hydrochloride (Krüss, *Zeit. Anorg. Chem.*, 1893, iii., 353) was rejected, after it had been found that the removal of holmium could not be effected thus. For this purpose treating the salt with concentrated potassium sulphate solution was best; from the easily soluble parts the holmium lines 640 and 536 disappeared almost entirely, and the samarium lines completely. The removal of strongly basic earths was effected by the evaporation of nitrate solutions with excess of sodium nitrite to dryness on the water-bath. When the residue was taken up with water most of the erbium hydroxide was left. In this respect erbium resembles thorium (*cf.*, Erdmann, *Lehrbuch*, 1902, 603), although in other analytical properties they are not alike.

After the rest of the terbium earths had been removed with the difficultly soluble parts by the partial crystallisation of the formate, the arc spectrum, taken by Prof. G. Eberhard, revealed only small quantities of thulium, neo-holmium, and dysprosium, besides traces of yttrium and ytterbium. By very gradual fractional precipitation with dilute ammonia it was possible to remove the absorption lines of thulium entirely, and thus to exclude also the traces of ytterbium.

To separate dysprosium and neoholmium the method suggested by Urbain (*Comptes Rendus*, cxlii., 785), the partial crystallisation of the ethyl sulphates was very useful. The easily soluble crystals of the mother-liquor contained no more dysprosium, and showed traces of holmium lines only in very concentrated nitrate solutions. The crystals and liquor were identical as regards spectrum and equivalent weight.

Although the methods of fractional precipitation with ammonia, decomposition of the nitrites and partial solution in ammonium carbonate (C. James, CHEMICAL NEWS, xcv., 181) were repeatedly applied to this material, there was no indication of any further decomposition. The method of separating the yttrium earths, discovered by Auer v. Welsbach (*Monatshefte*, 1906, xxvii., 942), by the crystallisation of the ammonium double oxalate, is, as we can show, exceedingly effective for separating holmium and erbium. Our material behaved like a single substance.

After all impurities had been removed by ordinary reagents for purifying—sulphuretted hydrogen, ammonia, oxalic acid—we determined the equivalent weight by the sulphate method, observing the precautions enumerated by B. Brauner (*Proc. Chem. Soc.*, xvii., 63; and *Journ. Chem. Soc.*; lxxi., 1243). For vessels we used platinum crucibles of perfectly constant weight, and heated them in electric resistance furnaces. Further orientation experiments led to similar results to those which Brill (*Zeit. Anorg. Chem.*, xlvii., 464) had obtained with different rare earths by means of a micro-balance.

The normal composition of the sulphate was reached very slowly at 400°, quickly at 475°, and lasted to 630°. Constant weight was reached in the shortest time at 580°. The oxide was weighed before being converted into sulphate and after decomposition of the sulphate at 1100°, which gave an accurate control against loss.

At 850° a second stopping point in the composition of the sulphate appeared, corresponding to the basic salt, $(ErO)_2SO_4$; it did not, however, appear sharp enough for an equivalent weight determination.

	Oxide (grms.).	Sulphate (grms.).
I.	0·9048	1·4724
II.	0·4666	0·7594
III.	1·4181	2·3077
IV.	1·0789	1·7563

Hence, assuming that the metal is trivalent, the following atomic weights are obtained:—

I.	167·43
II.	167·37
III.	167·43
IV.	167·28

I. and II. correspond to the mother-liquor and the last crystals from the treatment with ethyl sulphate by Urbain's method; III. and IV. correspond to the limits of the ammonium oxalate fractionation, III. belonging to the easily soluble crystals, and IV. to those which dissolve with difficulty.

The most trustworthy numbers, because they were obtained with the purest material (*cf.* the spectra), are I. and III., which agree perfectly, viz., $R^{III} = 167{\cdot}43$ (O = 16, S = 32·06).

(Both in the crystallisation of the ethyl sulphates and of the ammonium double oxalates the impurities holmium and dysprosium, which are most difficult to remove, go into the first crystals).

In Abegg's new "Handbuch der Anorganischen Chemie" (1906, III., i., 318), B. Brauner states that with an erbium obtained from Cleve he found Er = 167·14, while Cleve himself gave Er = 166·25. The specific weight of the earth, obtained by igniting the sulphate at 1100°, was found to be 8·616 at 15°.

The absorption spectrum of the 10 per cent nitrate solution, after a two-minute exposure, using a layer 1·5 cm. thick, was taken on a panchromatic plate.

It must be stated that $\lambda = 653$ appears clear to the eye, and that, especially in concentrated solutions, $\lambda = 667$ and $\lambda = 541$ are also visible. In the ammonium carbonate solution two lines, $\lambda = 657$ and $\lambda = 653$, are situated in the red.

Comparison of Forsling's measurements (*Bih. Sv. Vet. Akad. Handl.*, xxiv., I., 7) with Cleve's neoerbium shows that in our preparation the lines 648, 549, and probably also 453 are missing; yet there is no decomposition in Krüss (*Ber.*, 1887, xx., 3067) and Nilson's sense of the word, because the lines ascribed by them to Er$\alpha = 653$ and Er$\beta = 523$ remain without perceptible alteration of intensity.

The oxide, prepared like an incandescent mantle, shows very interesting optical properties. In the heat of a Bunsen burner emission bands appear on continuous back-grounds; the position of these bands agrees fairly well with the absorption spectrum of the nitrate solution.

But if the concentrated crater light of an arc lamp is allowed to fall on the oxide through a quartz lamp, very many sharp absorption lines appear; in groups they cover the absorption region of a concentrated nitrate solution, and represent the reversal of the emission bands. In the red we counted between $\lambda = 669$ and $\lambda = 646$ nine lines, the strongest of which lay at 661, 653, and 651. Between $\lambda = 565$ and $\lambda = 518$ eleven lines were measured, of which the following were the most marked :—540, 525, 524, 521, 519, 518. The absorption lines between $\lambda = 495$ and $\lambda = 490$ were less numerous, viz., three; between $\lambda = 463$ and 445 two are easily seen.

The accurate measurements of this beautifully sharp spectrum, as well as experiments on changes in the magnetic field, will be reported elsewhere.

As Bauer (*Ber.*, 1901, xxxiv., 2460) and Marc showed, the pure earths do not emit a discontinuous light if they are exposed to cathode rays. Cathode luminescence appears if a solid solution of a coloured earth in a colourless earth is present. As the amount of coloured earth is increased the luminescence is gradually extinguished. Thus our oxide in comparison with the surrounding gas and with interspersed tungstate remained dark in the cathode tube.—*Berichte*, 1908, xli., 308.

DETERMINATION OF COCOANUT OIL IN BUTTER.

By G. R. THOMPSON, F.I.C., and ARNOLD R. TANKARD.

The results obtained by Mr. T. R. Hodgson with the oxidation process recently devised by him for the determination of cocoanut oil in butter, and published in the Chemical News (vol. xcvi., pp. 273, 288, 297) were so startling that, in view of the need for an accurate method for this purpose, we immediately submitted his process to a critical examination in this laboratory. The conclusions we then formed (in January last) are confirmatory in all respects of those given by Messrs. Ross and Race (Chemical News, vol. xcvii., p. 110), and prove the method to be valueless.

We first subjected one sample each of genuine butter, a vegetable butter substitute (largely cotton-seed oil) and cocoanut oil to the new method, and side by side with these samples ran a blank experiment with the alcoholic potash and other reagents employed. The following results were obtained, the procedure being strictly as detailed by Mr. Hodgson, using standard ferrous ammonium sulphate solution in the final titration :—

Sample.		N/10 $KMnO_4$ used. Cc.	= Oxygen equivalent.
Butter	*a.*	34·95	139·8
	b.	35·30	141·2
Butter-substitute	*a.*	35·75	143·0
	b.	36·70	146·8
Cocoanut oil	*a.*	37·70	150·8
	b.	38·00	152·0
Blank experiment on reagents		31·60	(126·4)

It will be seen that these figures fail to show that differentiation between the various samples, such as was obtained by Mr. Hodgson; further, the blank experiment itself showed a very considerable absorption of permanganate, and this caused us no surprise, for the destruction of the permanganate, even in the absence of fatty acids, is obvious during the operation. On heating quantities of standard potassium permanganate solution direct, at 100° C., with water and the sulphuric acid (50 per cent) as prescribed in the method, we obtained the following results amongst others :—

	N/10 $KMnO_4$ taken. Cc.	$KMnO_4$ left after heating. Cc.
1	50·0	14·2
2	25·0	7·0

It occurred to us that perhaps "50 per cent" (sulphuric acid) was an error for "5 per cent," and we therefore determined to what extent the weaker acid destroyed the permanganate solution. We found that even with 5 per cent sulphuric acid a decinormal solution of potassium permanganate is appreciably attacked. For example, in a typical instance 1·0 cc. N/10 $KMnO_4$, out of 50·0 cc. employed, disappeared after heating for thirty minutes at 100° C. with 50 cc. of 5 per cent sulphuric acid and 20 cc. of water.

There can be no doubt, therefore, that Mr. Hodgson's process is fundamentally unscientific and based upon error. We wish to add that, although we have written to Mr. Hodgson on two occasions (the first letter being despatched on January 18th last), pointing out the results of our experiments with his method, we have not received any reply from him up to the present time, hence this present communication.

County Analyst's Laboratory, Newport, Monmouthshire.

THE ATOMIC WEIGHT OF CHLORINE.*

By WILLIAM A. NOYES and H. C. P. WEBER.

(Continued from p. 137).

Method of Carrying out the Determinations. First Series.

There are three parts to the apparatus, which was prepared for a determination in the following way :—

The Palladium Tube.—This consisted of a cylindrical tube with a stopcock sealed on at each end. The tube at one end was bent downwards at right angles and drawn out to a tip at B. Connection with the hydrogen generator was made by sealing the tip into a corresponding socket with Khotinsky cement. The three-way stopcock at B was opened in the position so that the small amount of air in the limb of B was swept out. Communication was then established between the palladium and the hydrogen generator, and hydrogen was led in until no more was was absorbed. The stopcock at A was next opened, and the hydrogen allowed to sweep through the apparatus for a short while. The stopcocks were then closed, and after cleaning the apparatus it was ready for weighing. Before the apparatus was used the first time, it was repeatedly charged with hydrogen and the hydrogen driven out at 400°. After that the tube was ready for charging anew at the end of each experiment.

Chlorplatinate Tube.—This tube had the general form as shown in the diagram (Fig. 2). The potassium chlorplatinate was introduced through the curved neck which was open at D. For this purpose the hard glass tube in which the chlorplatinate had been heated to 400° was connected to it by a short piece of stout rubber tubing and the chlorplatinate was shaken into the apparatus. The end D was then sealed off without allowing vapours from the flame to enter the tube. After this was done the

* From *The Journal of the American Chemical Society*, xxx., No. 1.

apparatus was attached to the Sprengel pump and evacuated to a few thousandths of a millimetre at a temperature of 350°. This temperature was maintained for about four hours. After closing the stopcock, disconnecting and rinsing after it was cool, the apparatus was transferred to the desiccator before weighing.

Absorption Tube for the Hydrochloric Acid.—This consisted of a bulb having a volume of about 100 cc. It terminated in two tubes with stopcocks and sockets to fit the tips of the two tubes from the platinum apparatus at E. Fifty cc. of boiled distilled water were poured into this bulb. It was then evacuated by means of the Sprengel pump, which was protected by an extra phosphorus pentoxide tube in this case. The evacuation was continued as long as air could be removed from the apparatus or liquid. Usually it was found necessary to allow the partly evacuated apparatus to stand for a day before the discovered. After the three parts of the apparatus had thus been connected with each other and with the vacuum pump, the connections were evacuated. The gas in the two connecting limbs at E was removed by opening the stopcocks at F and pumping the gases out over the chlorplatinate, which had meanwhile been brought to a temperature of about 300°. When every part of the apparatus had been evacuated to a few thousandths of a millimetre, as shown by the McLeod gauge attached to the pump, connection with the pump was cut off. The stopcock of the hydrogen apparatus at B was then opened and gradual heating of the hydrogen tube commenced. Then the stopcock at C was opened very gradually and the hydrogen admitted to the chlorplatinate. Next, the four stopcocks communicating with the absorption tube were opened. This was done very gradually to prevent a sudden rush of gas into the absorption tube and consequent carrying over

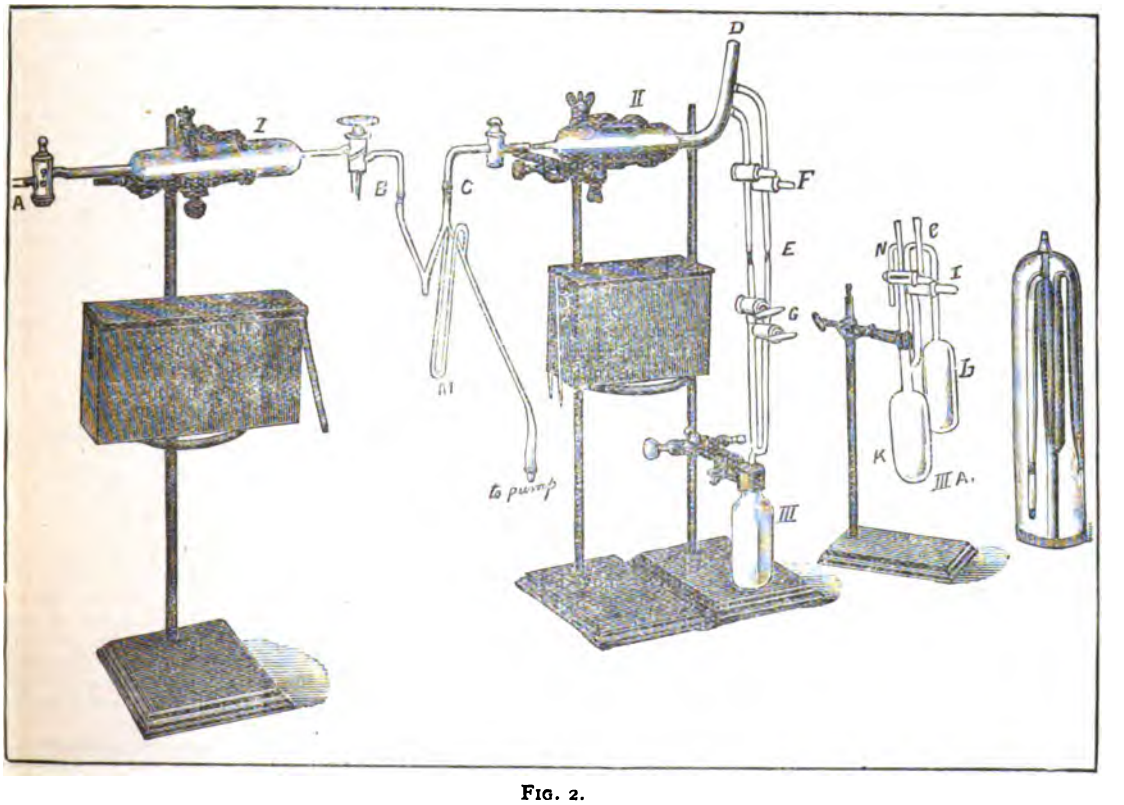


FIG. 2.

last traces of air could be removed from the water. After evacuation the apparatus was rinsed and set in the desiccator for weighing. Then, the different portions of the apparatus having been weighed, they were set up as shown in Fig. 2. The potassium chlorplatinate and the palladium charged with hydrogen were enclosed by electrically heated air-baths. These are lowered in the diagram to show the apparatus.

The tip B of the hydrogen tube and C of the chlorplatinate tube were connected with each other and with the Sprengel pump by means of a T-tube. The two tips from the chlorplatinate tube were connected to the two corresponding sockets of the absorption tube. These joints were made with Khotinsky cement. (P. G. Nutting, of this Bureau, has supplied us with a cement of the same character, which seems to answer the purpose as well as the Khotinsky. It is made by fusing together equal parts by volume of rosin and pure rubber).

The joints were perfectly tight and no leakage was ever of the finely divided potassium chlorplatinate. In doing this, the stopcocks were opened in such order that communication was first established through the tube entering the chlorplatinate apparatus at the lower level. Following this, communication was established by means of the adjoining tube. The purpose of the double connection between the chlorplatinate and the absorption tube was to prevent stagnation of the gas current between the two parts of the apparatus. A little hydrogen was always carried along with the hydrochloric acid toward the absorption apparatus. This would tend to accumulate and block the current. By making the level of the second tube somewhat higher than that of the first, the tendency of the hydrogen to rise would cause a direct and continuous flow. Actually, this arrangement proved entirely satisfactory.

The apparatus remainded in this condition for several hours. The temperature of the palladium tube generating the hydrogen was allowed to rise slowly at such a rate

that the pressure in the apparatus was kept at or below one atmosphere. This pressure was measured by means of a small mercury manometer M which formed a part of the connecting T-tube B C. The closed end of the manometer contained a little air. By this means it was possible to measure any pressure from zero to more than one atmosphere with a light manometer 8—10 cm. in length.

When it was deemed that a sufficient quantity of hydrogen had been evolved from the palladium tube the stopcock B of this part of the apparatus was closed and the palladium allowed to cool off. The temperature of the tube containing the chlorplatinate was allowed to rise to 350°. At the same time the absorption tube, which had been cooled by ice during the earlier part of the experiment was now cooled to −20° by a mixture of ice and dilute sulphuric acid. The hydrogen remaining in the apparatus upon cutting off the palladium tube was continuously converted into hydrochloric acid and removed as such by the water. This could be followed by means of the manometer M previously mentioned. After two or three hours the manometer had reached the lowest point which it would indicate. At this point the stopcocks G of the absorption tube were closed. The conditions prevailing at this moment were as follows:—

The chlorplatinate tube still contained an excess of potassium chlorplatinate and was at a temperature of 350°.

The absorption tube was at a temperature of −20°. The residual pressure throughout the apparatus was very low.

Under these conditions but a very minute quantity of hydrogen could have escaped conversion into hydrochloric acid. To determine this, connection with the Sprengel pump was again established, and that part of the apparatus between the stopcock B of palladium tube and the stopcocks G of the absorption tube was evacuated to the best vacuum obtainable by the pump, usually a few thousandths of a millimetre. The gas pumped out was collected in a eudiometer and analysed. In analysing the gases their volumes were read at a pressure of about one-sixth to one-seventh of an atmosphere, making accurate determination possible. Thus the volume of 1 cc. under these conditions represented less than 0·02 mgrm. of hydrogen.

The residual gas having been pumped out of the apparatus, all stopcocks were closed and the apparatus taken apart. All traces of the cement adhering to the glass where the various pieces had been joined were carefully removed. The pieces were then rinsed with distilled water, when sufficiently cool, wiped dry and transferred to the desiccator. The following day they were weighed. The determination itself required about eight hours, of which about two hours were used for the evolution of hydrogen and about three hours for the pressure to drop from atmospheric to practical zero.

Second Series.

Before giving the results obtained by the first series it may be just as well to turn to the manipulations giving the second set of values. They are essentially the same as in the first series with this difference: the hydrochloric acid generated was condensed as a solid by cooling with liquid air and connection with all other parts of the apparatus was cut off before it was absorbed by water. The point in view was this: During the period of absorption of the hydrochloric acid it might be possible that a transfer of water would take place from the absorption apparatus to the chlorplatinate apparatus and remain there in spite of the fact that there was not only a difference of 370° in temperature between the two parts but also a very high vacuum. This would cause the apparent amount of chlorine transferred to appear lower than the real. Or there was the possibility of the water vapour reacting with the material in the chlorplatinate tube. To eliminate these possibilities the reaction was so carried on that the chlorplatinate was at no part of the determination in contact with water vapour.

Further, this series differs from the first in that the hydrogen used was generated from a solution of barium hydroxide, the hydrogen in the first series being obtained from a sulphuric acid electrolyte. The absorption apparatus in the second series (which simply took the place of the water absorption tube) was constructed as follows:—

The bulb K was designed for the condensation of the hydrochloric acid and had a volume of 100 cc. It terminated in a neck from which led two exit tubes provided with the stopcocks H and I. The stopcock at I was provided with two perforations so that communication could be established either between the chlorplatinate tube and K or between the two bulbs K and L. The bulb L had a volume of 70 cc. and contained the water for the absorption of the hydrochloric acid. Below H a miniature mercury manometer was affixed. This was found absolutely necessary in order to follow the conditions of pressure during the transfer of the solid hydrochloric acid in K to the water in L. Indeed, previous to the attachment of this device to the apparatus every determination was lost either by the bursting of the apparatus or the blowing out of the stopcocks. By making the air space above the mercury of capillary tubing, while the remainder was about 1½ mm. in bore, satisfactory readings could be obtained both at normal and reduced pressures, and there was no danger of the mercury being sucked out of the manometer.

To prepare the apparatus for weighing, somewhat more than 50 grms. of water were filled into L through a small opening at P. The water was then boiled, and when all air had been expelled the opening at P was sealed off. The whole apparatus was then evacuated with the Sprengel pump, the last traces of air being removed from L by opening the stopcock I momentarily until the limit of the pump was reached. Rinsing, drying, and desiccation then completed the preparations for weighing as usual. The apparatus was then put together and prepared for the determination in precisely the same manner as in the first series, with the one difference that the absorption apparatus III A was now connected at E instead of the absorption tube III. Communication with the water bulb L was entirely cut off during the first part of the determination. The condensation bulb K was plunged in liquid air at the beginning and kept at the temperature of boiling air throughout the determination.

In opening the stopcocks to obtain communication between the various parts of the apparatus very great care had to be exercised, as the first rush of gases into the chilled condensation bulb often carried some of finely divided chlorplatinate with it. In a few cases it was not possible to avoid this. Since this chlorplatinate remained in the condensation bulb K, its amount could be found at the end of the determination and a suitable correction applied.

After communication had been established between the hydrogen tube, the chlorplatinate tube, and the condensation tube, the hydrogen tube was cautiously heated so as to obtain a constant and steady rise in temperature. Somewhat more care was necessary in this series, as there seemed to be a greater tendency for the pressure in the hydrogen apparatus to fall below that of the remaining parts. This would result in the finding of hydrochloric acid in the palladium tube at the end of the experiment. Suitable corrections were made for this and will be spoken of with the other corrections. When the hydrogen tube had reached a temperature of from 150° to 160°, it was judged that the requisite amount of hydrogen had been evolved. The stopcock from the hydrogen tube was then closed. Any temperature above 150° sufficed for the reduction of the chlorplatinate by the hydrogen, but at the end the temperature of the chlorplatinate tube was run up to 400°. The condensation bulb was kept fully submerged in liquid air. After the supply of hydrogen had been turned off, the pressure in the apparatus gradually sank until all hydrogen had been used up and all hydrochloric acid condensed. The conditions then were: excess of the chlorplatinate at 350° to 400°; the hydrochloric

acid at about − 180° and a small fraction of a millimetre residual pressure. The stopcocks of the condensation tube were then closed and the residual gases in the remaining parts of the apparatus pumped out.

The condensation tube was then separated from the remaining parts of the apparatus and the transfer of the hydrochloric acid to the water commenced. The water bulb L was plunged into ice water and the condensation bulb K removed from direct contact with the liquid air, but not entirely beyond the cold vapours. As soon as the pressure of the hydrochloric acid had risen to a small part of an atmosphere, communication was established with the cold water in L. After some hydrochloric acid had been absorbed by the water the bulb L was cooled by ice and dilute sulphuric acid instead of by ice alone. With the aid of occasional shaking of the absorption bulb the last of the condensed hydrochloric acid was finally absorbed by the water. With cautious manipulation the pressure in the apparatus did not rise above one-half atmosphere during the transfer and remained at a few millimetres at the close. The stopcock I between K and L was then closed, and the apparatus was cleaned, rinsed, wiped, and set aside to be weighed. The determinations of the second series required about ten hours from beginning to end. About two hours were consumed in transferring the solidified hydrochloric acid from the condensation to the absorption bulb. The solidified hydrochloric acid resembled snow in appearance and the greater part of it was absorbed by the water without passing into the liquid state. Towards the end of the transfer, when the absorption became less rapid, the remaining hydrochloric acid would liquefy attended by a sudden rise in pressure. Shaking of the absorption tube immediately reduced the pressure and caused the liquid hydrochloric acid to solidify to a glassy solid.

(To be continued).

THE USE OF TIN AS A CATHODE FOR THE RAPID QUANTITATIVE ELECTROLYTIC DEPOSITION OF ZINC, COPPER, SILVER, CADMIUM, AND NICKEL.*

By LAURENCE T. SHERWOOD and GELLERT ALLEMAN.

(Concluded from p. 139).

Silver.—When silver nitrate solution comes in contact with tin a black deposit forms on the tin. This action is, of course, objectionable; but if potassium cyanide were first added and the double cyanide formed, it did not take place. However, when potassium cyanide was used alone as an electrolyte the silver deposits were dark and loose. The addition of a suitable amount of oxalic acid afforded a reducing action, and this difficulty was also overcome, the deposit being the characteristic milk-white silver. Unless rather low currents were used the deposits had somewhat more tendency to sponginess than on platinum, but if a little clear gelatin solution were added, 1½ ampère could be used.

Potassium cyanide in the dish when no current is passing of course dissolves a small amount of tin (from 1 to 3 mgrms. if allowed to stand a minute), but when the tin surface is absolutely clean of oxide or any foreign material the dish does not lose appreciable weight in silver determinations if the circuit is closed before the addition of the cyanide. A number of experiments were made with the potassium cyanide alone in the dish, and also with the cyanide and oxalic acid together. Hot water was first put in the dish and the circuit closed, after which the respective amounts of cyanide or mixture of the two reagents that were used for the silver determinations were added. The remaining operations were the same as in the course of a regular analysis. (Table VI.).

From the *Journal of the American Chemical Society*, xxix., No. 7.

When silver is being deposited it is improbable that tin ever dissolves at all, for the determinations were fully as accurate as any made on the platinum dishes. To prevent possible solution of tin the following procedure was observed:—The cathode was placed upon its support and hot water added; the circuit was closed, having the rheostat adjusted so that about 1 ampère would flow when the electrolytes were introduced; oxalic acid, gelatin, and the cyanide solution of silver were added in the order named; the volume was diluted to 100 cc.; the electrodes were adjusted, the rotator started, and the current regulated. (The gelatin should be pure and the solution clear; "isinglass" was the material used). It was not thought that oxalic acid would dissolve tin appreciably when the current is not passing, except on standing. It is certain that it does not when the current is on.

There was no trouble in depositing one layer of silver upon another indefinitely if each time the loose metal were wiped out and the remaining coating well brushed, but it is probably safer not to deposit more than four or five layers without cleaning. When desirable the firm deposit may be cleaned off with potassium cyanide. The action may be hastened by passing a current of about 0·2 ampère through the cyanide, making the dish the anode. The deposit could also be scoured off without the aid of a solvent. (Table VII.).

Cadmium.—Exner's condition for cadmium applied to the tin cathode with little alteration (see *Journ. Am. Chem. Soc.*, xxv., 903). Sulphuric acid was the electrolyte, and this, of course, dissolved tin unless the dish was protected by the current. The circuit therefore had to be closed before adding the acid. Experiments showed also that only a small quantity could be used. With more than 1 cc. of acid, specific gravity 1·115 (concentrated acid diluted 1 to 10), the solvent action was more powerful than the tendency of the current to keep the metal at the cathode. But regardless of the solvent action, 1 cc. of the electrolyte gave the best deposits of cadmium. The experiments recorded in Table VIII. were made to show the solvent action of different amounts of acid of the specific gravity noted above. The dishes were filled with hot water, the circuit closed, the rotator started, and the acid added from a pipette. The regular procedure of a determination was then followed.

In the experiments of Table IX., made by Mr. Hill, all the reagents were put in the dish before the circuit was closed, except the acid, the addition of which was the final detail of the manipulation. The deposits were crystalline, closely resembling zinc. The adherent coating was cleaned out once in four or five determinations, only the loose material being removed after the other depositions. Sulphuric acid aided by a feeble current dissolved the coatings, or else they were scoured off without using any solvent.

Copper.—Copper, although usually most readily determined by electrolytic methods, presented considerable difficulty. When a solution of the neutral or slightly acid sulphate was put in a tin dish a black deposit came down. Also, with the common acid electrolytes, loose black deposits resulted in the attempt to separate the metal by a current. Additions of ammonium hydroxide to the sulphate solution prevented the immediate formation of the black coating until the current was introduced, but results from this electrolyte were not at all promising, the deposits being dark and loose.

An adaptation of E. Wagner's oxalate method gave fairly good results, although considerable manipulation was required (*Zeit. Electrochem.*, ii., 613). The dish, first of all, should be absolutely free from oxide of any sort, although a deposit may be made upon a surface of bright adherent copper. Then by observance of the following conditions good results may be obtained:—Mix in a beaker 55 cc. of saturated ammonium oxalate solution, 5 cc. of saturated oxalic acid solution, and 1 cc. clear solution of pure gelatin (1 grm. of gelatin = 1000 cc.). Place the dish on its support, introduce this mixture, start the rotator, and

TABLE VI.

Weight of dish.	KCN, in grms.	Saturated solution of oxalic acid, in cc.	Ampères.	Time, in minutes.	Loss of weight.
59·8008	2	10	0·6	20	—
65·1525	2	10	0·6	20	—
63·1403	2	10	0·6	20	0·0001
64·8920	2	10	0·6	20	0·0003
63·0190	2	10	1·0	20	—
64·8203	2	10	1·0	20	—

TABLE VII.

$AgNO_3$ = Ag, in grm.	KCN, in grms.	Oxalic acid in cc. of saturated solution.	Gelatin (1 grm. = 1000 cc.), in cc.	Volume when diluted.	Approximate temperature at start.	Current, N.D.$_{100}$ = A.	Volts.	Time, in minutes.	Ag deposited, in grms.	Error in per cent of Ag, in $AgNO_3$
0·2500	2	10	1	100	65°	1·0	6·0	25	0·2500	0·00
							6·0	25	0·2499	0·02
							6·0	25	0·2503	0·08
							6·0	25	0·2501	0·03
							6·0	25	0·2497	0·07
0·2500	2	10	1	100	65°	1·5	7·0	20	0·2502	0·05
							7·0	20	0·2504	0·10
							6·5	20	0·2497	0·07
							6·0	20	0·2499	0·02
							6·5	20	0·2495	0·12
							6·6	20	0·2498	0·05

NOTE.—Speed of rotator in first five determinations was 700 revolutions per minute; in the last six, run by Mr. Hill, the speed was 550 revolutions per minute.

TABLE VIII.

Weight of dish.	H_2SO_4 (sp. gr. 1·115), in cc.	Ampères.	Time, in minutes.	Loss of weight.
62·9874	3	5	10	0·0009
64·7832	2	5	10	0·0003
62·9865	1	5	10	0·00

TABLE IX.

$3CdSO_4.8H_2O$ = Cd, in grm.	Volume when diluted, in cc.	Approximate temperature at start.	Current N.D.$_{100}$ = A.	Volts.	Time, in minutes.	H_2SO_4 (sp. gr. 1·115), in cc.	Cd deposited, in grms.	Error in per cent Cd in $3CdSO_4.8H_2O$.
0·2500	100	65°	5	24—15	10	1·0	0·2502	0·04
						2·0	0·2495	0·09
						1·5	0·2504	0·07
						1·0	0·2503	0·05
						1·0	0·2499	0·02
						1·0	0·2501	0·02
						1·0	0·2503	0·05
						1·0	0·2500	0·00

NOTE.—Speed of the rotator was 550 revolutions per minute.

TABLE X.

$CuSO_4.5H_2O$ = Cu, in grm.	Saturated solution $(NH_4)_2C_2O_4$, in cc.	Saturated solution of $H_2C_2O_4$ at start, at 10, 15, and 18 minutes respectively.	Volume when diluted, in cc.	Approximate temperature at start.	Current, N.D.$_{100}$ = A.	Volts.	Time, in minutes.	Cu deposited, in grm.	Error in per cent of Cu in $CuSO_4.5H_2O$.
0·2500	55	5+10+5+5	100	20	5	19—10	24	0·2498	0·02
							21	0·2495	0·05
							20	0·2502	0·02
							20	0·2492	0·08
							20	0·2502	0·02
							22	0·2502	0·02
							21	0·2487	0·14
							22	0·2498	0·02
							20	0·2487	0·14
							21	0·2490	0·11
							20	0·2492	0·08

NOTE.—Speed of the rotator was 550 revolutions per minute.

TABLE XI.

$NiSO_4.7H_2O$ = Ni, in grm.	30 per cent acetic acid, in cc.	NH_4OH (sp. gr. 0·90), in cc.	Volume in cc. when diluted.	Approximate temperature at start.	Current N.D.$_{100}$ = A.	Volts.	Time, in minutes.	Ni deposited, in grm.	Error in per cent of Ni in $NiSO_4.7H_2O$.
0·2500	10	30	100	65°	5	9	13	0·2497	0·03
							14	0·2502	0·02
							13	0·2496	0·03
							13	0·2500	0·00
							13	0·2504	0·03
							13	0·2491	0·08
							13	0·2495	0·04
							13	0·2501	0·01

NOTE.—Speed of rotator was about 700 revolutions per minute.

TABLE XII.

	$(NH_4)_2SO_4$, in grms.								
0·2500	1·5	25	100	65°	5	18—10	15	0·2500	0·00
							15	0·2497	0·03
							16	0·2504	0·03
							15	0·2500	0·00

NOTE.—This series was run by Mr. Hill. Speed of the rotator was about 550 revolutions per minute.

add the copper sulphate solution. Without delay close the circuit and dilute to a suitable volume. At the end of ten minutes add from a pipette 10 cc. of oxalic acid solution, at fifteen minutes add 5 cc., and at eighteen minutes 5 cc. The deposition will then usually be complete after twenty minutes. The solution must be cold at the start, for otherwise the deposit will be black and loose. It is important too that the anode be rotating when the copper solution is added, since occasionally a very adherent blue material formed on it which could not be washed off. If the oxalic acid was not added at the stated times the results were invariably low, slight amounts of copper remaining in solution until the end of about thirty minutes. The deposits were dark red and crystalline, but adherent enough to wash and weigh. They were removed by a hot potassium cyanide solution. Series X. was run by Mr. Hill.

This method, while fairly accurate if the conditions are closely observed, requires more manipulation than the methods on platinum. It was observed, too late for an investigation to be undertaken, that from cyanide solutions copper, with a high current density, comes down on tin as a bright and extremely adherent deposit just as it does on platinum. Since the cyanide was a satisfactory electrolyte for the quantitative determination of silver on tin, it is quite probable that it may also be used for copper. A thesis written in 1906 by Miss Anna L. Flanigan at the University of Pennsylvania describes some recent cyanide methods for copper deposition on platinum, and it is intended to try and adapt them in this laboratory for use with tin cathodes.

Nickel.—Exner's conditions for nickel served very well for the determination of this metal (*Journ. Am. Chem. Soc.*, xxv., 899). There was no decided preference in the use of ammonium sulphate and ammonium hydroxide, or ammonium acetate and ammonium hydroxide as the electrolytes. The strong alkaline solutions should not stand longer than momentarily in the tin, unprotected by a current, but it is not necessary to have the circuit closed before putting in the reagents. The deposits were grey and very compact. A slight amount of loose material may be brushed out, and the dish used for another determination, but if too thick a coating of nickel is deposited it will be found very difficult to remove. The nickel was dissolved with potassium cyanide aided by the current or by nitric acid, specific gravity 1·52.

Faraday Society.—In consequence of the illness of Sir Oliver Lodge, the delivery of his Presidential Address arranged for Tuesday, March 24th, is postponed until further notice.

REVISIONS OF THE THEORY OF ELECTROLYSIS.*

By HENRY S. CARHART, LL.D.

(Continued from p. 142).

FROM the time of Grotthus there was a long pause of fifty years in the theory of electrolysis, for no important step was taken until Clausius, in 1857, published his profound modification of the Grotthus theory. Clausius's study of the kinetic theory of heat prepared him to apply similar principles to the interpretation of electrolytic phenomena. He leaves no doubt about his meaning; his conceptions are always clear and clearly expressed. I will let him speak for himself (*Ann. der Physik*, 1857, ci.):—

"Let there be a liquid, consisting wholly or in part of electrolytic molecules; and let it be assumed that these molecules are arranged in the natural condition of the liquid in any definite manner in which they persist, so long as no foreign force acts on them, while the individual molecules oscillate perhaps about their positions of equal librium, but are unable to get quite away from them. Further, let an attraction be assumed between two part-molecules, as there must be in every possible arrangement, and let two part-molecules be bound together into a whole molecule and, therefore, very near together; then the attraction binding them together is greater than the attraction between the positive part-molecule of one complete molecule and the negative of another. If now an electric force acts within this mass, and seeks to urge the positively electrified part-molecules in one direction and the negatively electrified ones in the other, then the question arises what influence this electric force must exert on the behaviour of the molecules.

"Inasmuch as the molecules are assumed to be capable of rotation, the first effect would plainly be to turn all of them in the same manner, so that the two oppositely electrified portions of each complete molecule would be turned in the direction in which they are urged by the acting force. Further, the force would seek to separate the part-molecules united in a whole or complete one and to move them in opposite directions; and if this motion ensues, then the positive part molecule of one whole one would meet the negative of the following and would combine with it. But now, in order that the once united part-molecules may be separated, the attraction which they

* Presidential Address delivered at the Seventh General Meeting of the American Electro-chemical Society. From the *Smithsonian Report* for 1906, p. 147.

exercise on each other must be overcome. Therefore a force of definite strength is necessary, and one is thus led to the conclusion that so long as the force acting on the conductor does not have this strength no decomposition whatever can take place, and that, on the contrary, if the force is increased to the requisite strength very many molecules must be decomposed at the same time, since they are all under the influence of the same force and have precisely the same relation to one another.

"With respect to the electric current, the conclusion can be expressed as follows if it is assumed that the conductor conducts only through electrolysis: So long as the force acting on the conductor is below a certain limit it will produce no current whatever, but if it has reached this limit, then suddenly a very strong current will flow. But this conclusion is flatly contradicted by experience. Even the smallest force causes a current, conducted by alternate decompositions and reunions, and the intensity of this current increases in accordance with Ohm's law in proportion to the electromotive force.

"It follows from these considerations that the above supposition to the effect that the part-molecules of an electrolyte are bound together in the fixed relation of whole molecules, and that these have a definite and regular arrangement, must be untrue.

. . . . .

"I believe, therefore, that the following hypothesis by which this contradiction is removed, and which, as it seems to me, is in harmony with other known facts, deserves some consideration.

"In my treatise 'On the Mode of Motion, which we call Heat,' I have expressed the view that in liquids the molecules have no definite positions of equilibrium, about which they only oscillate, but that their motions are so lively that they thereby constantly come into entirely changed and new relations to one another and move among one another in an irregular way.

"Let us now imagine in an electrolytic liquid a single part-molecule present, for example, an electro-positive one, the electrical condition of which we shall assume is exactly the same as at the moment when it was separated from a complete molecule. I believe now that while this part-molecule moves about among the whole molecules, under the many relations which it can assume, sometimes those will occur in which it will attract the negative part-molecule of an undissociated molecule with greater force than that with which the two parts belonging to an undissociated molecule, whose relation to each other is not entirely unchangeable, attract each other at this same instant. As soon as this condition occurs it will soon join itself to this negative part-molecule, and the positive part-molecule formerly bound to the same thereby becomes free. This one now in turn moves about free and after a time decomposes another whole molecule in the same manner, and so on. All these movements and decompositions occur in the same irregular manner as the heat motions by which they are set going.

. . . . .

"When now in a liquid, whose molecules already find themselves in such motion that they exchange their part-molecules in an irregular way, an electric force acts which tries to drive all the positive part-molecules in one direction and the negative ones in the opposite, then it is easy to understand what differences in the mode of the molecular movements must ensue.

"A free part-molecule will then no longer follow the irregularly changing directions which it is forced to pursue by the heat motions, but it will change the direction of its motion to correspond with the acting force; so that although the motions of the positive part-molecules are very irregular still a certain direction will prevail among them; and likewise the negative part molecules will move under compulsion in the opposite direction.

. . . . .

"If one considers within a liquid on which an electric force acts a small surface at right angles to the direction of the force, then through this area more positive part-molecules pass in unit time in the positive direction than in the negative, and more negative part-molecules in the negative than in the positive direction, . . . so that a certain excess number of positive part-molecules go in the positive direction and a certain excess number of negative part-molecules in the negative direction through the small area. The magnitude of these two numbers does not need to be the same, since it depends also, outside of the force urging them, which is the same for both, on the degree of their mobility, and this may for many reasons be different for different part-molecules.

"These opposite movements of the two kinds of part-molecules compose the voltaic current within a liquid.

. . . . .

"By this conception of the state of liquids the difficulty mentioned above vanishes. It is readily seen that the influence which the electric force exerts on the irregular molecular decompositions and motions already existing does not begin when the force has reached a certain value, but that even the smallest force must act on them, and that the amount of this action must increase with the magnitude of the force. The entire process then agrees well with Ohm's law.

. . . . .

"If we compare the older Grotthus theory with the one here developed, the difference lies chiefly in this: In the former it was assumed that the motion is first brought about by the electric force and takes place in two definite directions only, while the decompositions go on regularly from molecule to molecule, but in the latter the motions already present are only modified, not to the extent of making them entirely regular, but only so that among the great multitude of motions those in the two definite directions prevail."

These ideas of Clausius are so fundamental in the modern theory of electrolysis that I have thought it best to translate them freely rather than to paraphrase them. Clausius belongs to our own day. The grey hair and benign expression of this beautiful old man made a lasting impression on me as I saw him at the International Electrical Congress in Paris in 1881.

(To be continued).

Complete Analysis of Vegetable Matter.—J. M. Albahary.—The moisture and volatile matter in the fresh material are determined by drying at 110°. The ash is determined by carbonising the dry material, washing with boiling water, and igniting at a low temperature in a current of oxygen. The fresh material is triturated with alcohol and the residue gives the dry matter insoluble in alcohol. From the alcoholic liquid the volatile acids can be determined by titration with caustic soda. Colouring matter and fats are extracted with petroleum ether in a Soxhlet apparatus, using the dried extract of the plant. Reducing sugars, mineral acids, nitrogen, asparagine, and sulphur, &c., are estimated in the part which is insoluble in neutral alcohol.—*Comptes Rendus*, cxlvi., No. 7.

Simultaneous Production of 1.6 and 2.7-Dimethylanthracenes by the Action of CH_2Cl_2, $CHCl_3$, or of $C_2H_2Br_4$ on Toluene in Presence of $AlCl_3$.—James Lavaux.—When CH_2Cl_2 and $AlCl_3$ act on toluene the symmetrical ditolylmethanes para-para and meta-meta are first formed, $CH_3—C_6H_4—CH_2—C_6H_4—CH_3$. These under the action of CH_2Cl_2 yield dimethylanthracene dihydrides, which afterwards lose H_2, giving 2.7- and 1.6-dimethylanthracenes. $CHCl_3$ and $AlCl_3$ act similarly on toluene, the chief products of the reaction being the same dimethylanthracenes, and if it is assumed that dibromoditolylethanes are formed as intermediate products when $C_2H_2Br_4$ and $AlCl_3$ act on toluene, the formation of 1.6 and 2.7-dimethylanthracenes can readily be explained.—*Comptes Rendus*, cxlvi., No. 7.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 5th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

MESSRS. E. de B. Barnett, E. M. Eagles, R. C. Gale, J. M. Heron, C. W. Moore, A. R. Runeckles, H. E. Watson, and J. H. Williams were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Edward Coverdale, 68, Broad Street, Worcester; Frederick J. Maywald, 1028, 72nd Street, Brooklyn, N.Y., U.S.A.; Samuel Ernest Melling, The Cliff, Higher Broughton, Manchester; Edwin John Watkins, 10, Montpelier Road, Queen's Road, Peckham, S.E.

The PRESIDENT read the names of the Fellows recommended by the Council for election as Officers and as Ordinary Members of Council of the Society. It was also announced that the name of Prof. W. Jackson Pope, as Vice-President, and the names of Mr. John Allan and Prof. Adrian J. Brown, as Ordinary Members of Council, had been proposed by other Fellows.

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

*44. "*The Solubility of Iodine in Water.*" By HAROLD HARTLEY and NORMAN PHILLIPS CAMPBELL.

The solubility of iodine in water has been determined at 18°, 25°, 35°, 45°, and 55°, the value at 25° agreeing very closely with that found by Noyes and Seidensticker. The heat of solution has been calculated from the temperature coefficient of the solubility.

*45. "*Nitro-derivatives of o-Xylene.*" (Preliminary Note). By ARTHUR WILLIAM CROSSLEY and NORA RENOUF.

o-Xylene, when treated with a nitrating mixture, readily yields two trinitro-derivatives, which can be separated by means of their different solubilities in concentrated sulphuric acid. Both crystallise from alcohol, in which solvent they are fairly readily soluble, the one in faintly yellow glistening flattened needles, melting at 71°, and the other in long stout prismatic needles, melting at 115°.

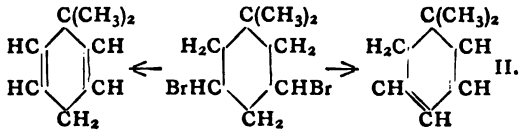
These facts are not in accord with the statement of Noelting and Thesmar (*Ber.*, 1902, xxxv., 634), that "*o*-xylene is incapable of yielding a trinitro-derivative even when submitted to the action of the strongest nitrating agents." The explanation of this statement is probably as follows :—Noelting and Thesmar further nitrated 4-nitro-*o*-xylene, melting at 29—30°, and obtained two dinitro-xylenes, melting respectively at 115—116° and 75—76°. The present authors arrived at the same results on repeating these experiments, except that they have not, so far, been able to raise the melting-point of the latter substance above 71°. There are therefore a dinitro- and a trinitro-*o*-xylene, melting at 71°, and also a dinitro- and a trinitro-*o*-xylene melting at 115°. When Noelting and Thesmar submitted 4-nitro-*o*-xylene to the action of a nitrating mixture above a temperature of 100°, they doubtless obtained the two trinitro-derivatives melting at the same temperatures as their dinitro-compounds. The mixed melting-point method, however, shows the substances to be quite distinct; the dinitro- and trinitro-derivatives, melting at 71°, when mixed in equal quantity, melt at 45—50°, becoming quite clear at 63°; and the dinitro- and trinitro-derivatives, melting at 115°, when mixed, melt at 82—83°, and become quite clear at 86°.

During the course of these experiments, a third dinitro-*o*-xylene, melting at 82°, has been isolated, and another substance, melting at 115°, which is not a nitroxylene, but a nitro-derivative of some condensed benzene ring derivative.

The authors are continuing the experiments, more particularly in the direction of the orientation of these hitherto unknown-*o*-xylenes.

*46. "*Substituted Dihydrobenzenes.* Part II. 1 : 1-*Dimethyl*-Δ^2 : 4-*dihydrobenzene and* 1 : 1-*Dimethyl*-Δ^2 : 5-*dihydrobenzene.*" By ARTHUR WILLIAM CROSSLEY and NORA RENOUF.

Dimethyldihydrobenzene has been prepared by the elimination of two molecules of hydrogen bromide from 3 : 5-dibromo-1 : 1-dimethylhexahydrobenzene, and the resulting hydrocarbon has been proved to consist of a mixture, in approximately equal parts, of 1 : 1-dimethyl-Δ^2 : 4-dihydrobenzene (II.) and 1 : 1-dimethyl-Δ^2 : 5-dihydrobenzene (I.). A detailed study of the properties of these substances leads to the conclusion that the 1 : 1-dimethyl-Δ^2 : 4-dihydrobenzene described by Crossley and Le Sueur (*Trans.*, 1902, lxxxi., 821) has the constitution ascribed to it, despite the adverse criticisms of Harries and Antoni (*Annalen*, 1903, cccxxviii., 88); but it contains traces of some oxygenated substance, probably a methoxy-derivative.



47. "*The Viscosity of Aqueous Pyridine Solutions.*" By ALBERT ERNEST DUNSTAN and FERDINAND BERNARD THEODORE THOLE.

In view of the criticism to which their former work (*Trans.*, 1907, xci., 1718) has been subjected (*Proc.*, 1908, xxiv., 22), the authors have repeated their experiments on the viscosity of aqueous pyridine solutions, and find that the same discontinuities occur in the curve as were previously observed.

DISCUSSION.

Mr. HARTLEY said that he understood Mr. Dunstan to use the word "discontinuity" to denote a point where two supposed sections of a curve pass imperceptibly into one another, but, as under these conditions the curve is continuous, he thought the use of the term "discontinuity" was very misleading. The only evidence for the existence of the secondary irregularities which Messrs. Dunstan and Thole had endeavoured to prove depended on discontinuities in lines drawn through series of experimental points without making any allowance for experimental error. Such a method of argument was only allowable if around each point a circle was described of radius equal to the probable experimental error. If this were done in the case of the physical properties of mixtures of pyridine and water, he thought that a smooth curve could be drawn through the series of circles so obtained, as had been found by Thomas, Appleby, and himself.

Mr. DUNSTAN agreed with Mr. Hartley as to the difficulty of expressing the change of curvature in a simple way, and thought that perhaps the term "discontinuity" was the simplest in the light of his explanation of the curves. With reference to Mr. Hartley's system of plotting, he was quite in agreement with it, having, as a matter of fact, taken similar precaution in allowing for experimental error.

*48. "*The Action of Thionyl Chloride on the Methylene Ethers of Catechol Derivatives.* II. *Piperonyloin, Piperil, and Hydropiperoin.*" By GEORGE BARGER and ARTHUR JAMES EWINS.

By heating the methylene ethers, mentioned in the title, with thionyl chloride to 180—200°, cyclic *dicarbonates* result, which in all cases contain chlorine. By elimination of chlorine from the substance derived from piperonyloin and from piperil, the *dicarbonate* of *tetrahydroxybenzil* and *tetrahydroxybenzil*, $(OH)_2C_6H_3{\cdot}CO{\cdot}CO{\cdot}C_6H_3(OH)_2$, m. p. 237°, was obtained.

A number of other derivatives were described.

49. "*Traces of a New Tin-group Element in Thorianite.*" By CLARE DE BRERETON EVANS.

In the course of an examination of some residues of 5 cwt. of thorianite belonging to Sir William Ramsay, traces of a supposed new element were discovered associated with the sulphides of the tin group.

The dark brown sulphide was separated with arsenious sulphide, which it resembles in being insoluble in hydrochloric acid, and readily soluble in ammonium carbonate solution, to which it gives a characteristic deep brown colour. In addition to these reactions, it dissolves readily in water, forming a deep brown solution; it is scarcely attacked by a mixture of hydrochloric acid and potassium chlorate, but dissolves in nitric acid, forming, on evaporation at 100°, a golden-red syrup, which leaves behind a hygroscopic brown oxide at 120—130°. A grey metal was obtained by reduction in hydrogen, but the quantity was too small to allow of its equivalent being determined.

Incidentally, proof was obtained of the presence in thorianite of arsenic, mercury, bismuth, molybdenum, and selenium, in addition to those elements already discovered in the mineral.

A new triple oxalate of thorium, uranium, and ammonium was described; it appears to have the composition $ThU_{25}(NH_4)_2(C_2O_4)_{10},14H_2O$.

50. "*The Sulphination of Phenolic Ethers and the Influence of Substituents.*" By SAMUEL SMILES and ROBERT LE ROSSIGNOL.

The authors have previously drawn the conclusion (*Proc.*, 1906, xxii., 158; *Trans.*, 1906, lxxxix., 696) that the sulphonium base derived from phenetole is produced in three stages at which the sulphinic acid, sulphoxide, and base are consecutively formed. The sulphinic acid, however, had not been observed in the products of the reaction, and thus the evidence was incomplete. The above view of the mechanism of the reaction has now been confirmed by the isolation of the sulphinic acid from substituted phenolic ethers. It is proposed to apply to the entire process the name "sulphination." The behaviour of benzene, toluene, and homologous phenolic ethers has been investigated, and it was shown that the products vary according to the position of the methoxyl and methyl groups. Generally speaking, the presence of a group in the ortho-position with respect to the entrant quadrivalent sulphur atom tends to prevent the formation of sulphonium base; on the other hand, this is favoured by groups of strong directing influence.

51. "*The Relation between Unsaturation and Optical Activity.* Part II. *Alkaloid Salts of corresponding Saturated or Unsaturated Acids.*" By THOMAS PERCY HILDITCH.

The study of the relative effects of saturated and unsaturated acids on an optically active base has been extended to alkaloid salts of β-phenylpropionic, cinnamic, phenylpropiolic, and succinic, maleic, fumaric, and acetylenedicarboxylic acids. Salts of brucine, coniine, codeine, and cinchonine have thus been examined polarimetrically in chloroform solution, and the results show very clearly that the change in optical rotatory power is influenced not only by the simple change of constitution associated with increasing unsaturation, but also by the structure of the base and the type of acid used. Thus, in general, the effect observed in the case of coniine salts differs from those observed with the derivatives of more complex bases, and appears to be of the same kind as that observed by Walden with the active amyl esters of the same series of acids. It is noticeable, however, that in all the instances now brought forward the change to an ethylenic linking is accompanied by an increase in optical effect.

52. "*The Wandering of Bromine in the Transformation of Nitroaminobromobenzenes.*" By KENNEDY JOSEPH PREVITÉ ORTON and CONSTANCE PEARSON.

2 : 6-Dibromo-1-nitroaminobenzene, when dissolved in aqueous, aqueous alcoholic, or acetic acid solutions of hydrochloric or sulphuric acids, yields not only 2 : 6-dibromo-4-nitroaniline, but also the isomeric 2 : 4-dibromo-6-nitroaniline, the nitro-group having partly migrated to the vacant para-position, and having partly displaced an atom of bromine from one of the ortho-positions.

The use of hydrobromic or nitric acid in the same solvents leads largely to the reduction of the nitroamine to the diazo-compound, but at the same time migration of the nitro-group and displacement of bromine occur.

In a comparison, the behaviour of other nitroamines when similarly treated was described.

53. "*A New Isomeride of Vanillin occurring in the Root of a Species of* Chlorocodon." (Preliminary Note). By ERNEST GOULDING and RUSSELL GEORGE PELLY.

A sample of the root of a species of *Chlorocodon* (probably *C. Whiteii*) was forwarded for examination to the Imperial Institute from Uganda, where the plant is known by the native name of "Murundo." This root has a pleasant odour, intermediate between those of vanillin and piperonal, and is said to be chewed by the natives for sweetening the breath.

The powdered root, on distillation with steam, yields 0·5 per cent of a crystalline *substance*, $C_7H_5O_2{\cdot}OMe$, which separates from the distillate in thin lustrous colourless plates, having the characteristic odour of the root. It melts at 41—42° and boils at 257—258°, a pale brown coloration being developed. The substance is readily soluble in most organic solvents, and fairly so in hot, but only sparingly so in cold, water. An aqueous solution gives a red or purplish brown coloration with ferric chloride, and, on warming a solution with ammoniacal silver nitrate, the latter undergoes reduction with the separation of silver. It dissolves freely in dilute alkali hydroxide, and is re-precipitated by acids. The aqueous solution does not give a precipitate with lead acetate.

The *oxime*, $OMe{\cdot}C_6H_3(OH){\cdot}CH{:}N{\cdot}OH$, crystallises in large, thin, lustrous, transparent plates melting at 138°; it is almost odourless, and readily soluble in hot water but sparingly so in cold.

The *phenylhydrazone*, $OMe{\cdot}C_6H_3(OH){\cdot}CH{:}N{\cdot}NHPh$, crystallises from hot alcohol in pale yellow lustrous plates, and melts at 137—138°.

The *sodium* derivative, $OMe{\cdot}C_6H_3(CHO){\cdot}ONa$, obtained by the addition of alcoholic sodium hydroxide to an alcoholic solution of the substance, separates in small, almost colourless, lustrous plates, and dissolves readily in water to form a pale yellow solution which is strongly alkaline.

These results, together with the analytical data obtained, show that the odorous constituent of *Chlorocodon* root is a monomethyl ether of a dihydroxybenzaldehyde, $OMe{\cdot}C_6H_3(OH){\cdot}CHO$, which is not identical with vanillin or any of its known isomerides.

Unfortunately, the amount of material available was so small that it has not been possible to carry out experiments with the object of ascertaining the relative positions of the hydroxy-, methoxy-, and aldehyde-groups, but the authors intend to continue the work in this direction as soon as a further supply of the root has been obtained.

54. "*The Volatile Oil of the Leaves of* Ocimum viride." (Preliminary Note). By ERNEST GOULDING and RUSSELL GEORGE PELLY.

A consignment of the leaves of *Ocimum viride*, forwarded for examination to the Imperial Institute from Sierra Leone, has been examined with the following results:—On distillation with steam, the leaves yielded about 0·35 per cent of an orange-yellow, volatile oil, which is very mobile, has an aromatic, thyme-like odour, a spicy pungent taste, D 15/15 0·9115, $[\alpha]_D$ +1° 30′ (approx.), and is soluble in all proportions in 90 per cent alcohol.

When distilled under the ordinary pressure 100 cc. of the oil yielded 25 cc. boiling at 165—180° with D 15/15 0·8614 and $[\alpha]_D$ + 0° 33′; 20 cc. at 180—200°, with D 15/15 0·8804 and $[\alpha]_D$ + 1° 40′; 20 cc. at 200—220°, with D 15/15 0·9164 and $[\alpha]_D$ +2° 38′; 20 cc. at 220—235°, with D 15/15

0·9548 and $[\alpha]_D$ +3° 38′; and 10 cc. at 235—250°, with D 15/15 0·9565 and $[\alpha]_D$ +5° 14′.

The composition of the oil is approximately as follows: Thymol, 32 per cent; alcohols (calculated as $C_{10}H_{18}O$), 40 per cent; esters (calculated as $C_{10}H_{17}\cdot OAc$), 2 per cent; the remainder consists chiefly of a terpene (or possibly a mixture of terpenes), $C_{10}H_{16}$, which is a mobile, highly refractive liquid of pleasant lemon-like odour, boiling at 160—166°, and having D 15/15 0·8456 and $[\alpha]_D$ +0° 10′.

The authors intend to make a more complete examination of the oil as soon as a larger supply of material has been received.

55. "*Experiments on the Synthesis of the Terpenes.* Part XII. *Synthesis of Terpins, Terpineols, and Terpenes derived from the Methylisopropylcyclopentanes*, $Me\cdot C_5H_8\cdot CHMe_2$." By WALTER NORMAN HAWORTH and WILLIAM HENRY PERKIN, jun.

An account was given of the synthesis of terpenes, such as $CH\lessgtr^{CH\cdot CH_2}_{CHMe}>CH\cdot CMe{:}CH_2$, which are analogously constituted to dipentene, but contain a *cyclo*pentene in the place of the *cyclo*hexene ring of the latter. The corresponding five-ring terpineols and terpins were also described.

56. "*The Initial Change of the Radium Emanation.*" By NEVIL VINCENT SIDGWICK and HENRY THOMAS TIZARD.

In their paper on this subject, Cameron and Ramsay (*Trans.*, 1907, xci., 1266) have shown that, after the removal of the hydrogen and oxygen, the radium emanation diminishes rapidly (in about an hour and a-half) to one-half of its initial volume. Hence it follows that the emanation (or a constituent) polymerises; the possibility of the simultaneous formation of helium or of a solid they consider they have disproved.

By measuring the rate of change, they show that the reaction is unimolecular; that is, the rate is proportional only to the amount of changing substance. They assume that two molecules of the original emanation Em_I polymerise to one molecule of Em_2, and they say (p. 1280) "this involves an exponential curve, and that has been realised." But their exponential curve implies a unimolecular reaction, and a polymerisation cannot in the nature of things be unimolecular, since it necessarily involves the combination of two or more molecules. The reaction—

$$2Em_I = Em_2$$

must be bimolecular, and, in general, any polymerisation must be a reaction of the n^{th} order, where n is the number of molecules that combine.

Hence the change they are measuring cannot be the polymerisation, and, as it is unimolecular, must be of the form—

$$Em_I = Em',$$

and the polymerisation which obviously occurs must follow this change, and must be rapid. We therefore have:—

1. $Em_I = Em'$ (Slow: unimolecular)
2. $nEm' = Em_2$ (Quick: n-molecular)

Cameron and Ramsay assume that $n=2$; that two molecules of Em_I give one of the final product. But this is not a necessary result of their equation, for, if the first reaction is unimolecular, we get—

$$-\frac{dV'_t}{dt} = kV't;$$

where V'_t is the amount of the changing substance Em_I (or its volume reduced to standard pressure) at the time t from the true beginning of the reaction, the observed volume of gas being V_t. Now if n molecules of the first product (Em′) polymerise to one molecule of Em_2, the amount of Em_2 present at time t is obviously—

$$(V_o - V_t)\frac{1}{n-1};$$

where V_o is the total volume of gas at the beginning.

Therefore—

$$V'_t = V_t - (V_o - V_t)\frac{1}{n-1}$$
$$= \frac{nV_t - V_o}{n-1}$$
$$= \frac{n(V_t - V_\infty)}{n-1},$$

since V_∞, the final volume, $= V_o/n$.

Hence—

$$-\frac{dV'_t}{dt} = \frac{n}{n-1}\cdot\frac{dV_t}{dt} = kV'$$
$$= \frac{n}{n-1}\cdot k\cdot(V_t - V_\infty).$$

Therefore—

$$-\frac{dV_t}{dt} = k\cdot(V_t - V_\infty).$$

Integrating this, under the condition that when $t=0$ $V_t = V_o$, we obtain—

$$\log\frac{V_o - V_\infty}{V_t - V_\infty} = kt,$$

which is the expression that Cameron and Ramsay have shown to agree with the experimental results. It is obvious that it is equally compatible with any value of n.

Their reason for assuming that $n=2$ is that during the time of observation the volume of the gas diminishes to about a half; and they suppose that the time when the first observation is made is the actual beginning of the change, and that the gas then wholly consists of Em_I. It is, however, difficult to see how the reaction cannot have begun earlier than this. The emanation gradually accumulates in and over the solution of the radium salt for several days; it is then transferred to the explosion-burette, exploded, the emanation and the residual hydrogen passed over phosphoric oxide and cooled with liquid air, the hydrogen pumped off, and the emanation allowed to evaporate and passed into the capillary. Mr. Cameron informs us that the time taken in the purification is less than an hour, and the time elapsing between the evaporation of the emanation and the first measurement is less than a quarter of an hour. It seems scarcely possible that the change of Em_I to Em′, which, as it is unimolecular, is not affected by the dilution, should not take place during these operations, and yet when they are finished should begin with a velocity which takes it to half completion in about nine minutes. A more probable hypothesis is that the change has already proceeded some way before the observations begin, and that the actual number of molecules of Em_I which go to form one molecule of Em_2 is greater than 2. Even if the reaction only begins when the liquid air has been removed, and the gas has assumed the temperature of the room, something like half the initial volume of Em_I must have changed before the first measurement is made. On the other hand, the change cannot have continued during the whole time that the emanation has been accumulating, for, if we reckon the time backwards, the volume must increase a thousand-fold every ninety minutes. It would therefore appear that for some reason the reaction does not begin until the liquid air is removed; before this point, the Em_I must have been in a different chemical state. But as soon as the emanation has evaporated, it must begin to change at once, and, as it is not measured for nearly ten minutes after this, the volume of Em_I at the first measurement cannot be much more than half the true initial volume, the period of half decay being about nine minutes. Hence the final volume is at most one-third of the initial, and n cannot be less than 3.

PHYSICAL SOCIETY.

Ordinary Meeting, March 13th, 1908.

Dr. CHARLES CHREE, F.R.S., President, in the Chair.

THE following candidates were elected Fellows of the Society:—Mr. A. E. Garratt, Mr. A. E. Hall, and Mr. W. Williams.

A paper on "*The Distribution in Electric Fields of the Active Deposits of Radium, Thorium, and Actinium*" was read by Mr. S. RUSS.

The first experiments were made with the active deposit produced from radium emanation. Whereas the amount of active deposit directed to a cathode decreases as the pressure in the containing vessel is reduced, after a certain pressure is reached, it was found that the amount going to an anode shows a corresponding increase under the same conditions. A comparison was made over a range of pressure extending from 0·01 mm. to 1·2 mm., between the amounts of active deposit obtained on a rod made positive or negative when exposed to the same quantity of radium emanation for equal periods of time. The main feature brought out by this comparison is that at the lowest pressure reached almost as much activity is obtained on the anode as on the cathode, while at atmospheric pressure the activity of the latter is about twenty times that of the former. Similar experiments conducted in hydrogen, air, and sulphur dioxide, three gases differing considerably in density, indicate that the collisions between the active deposit particles and the gaseous molecules play an important part in the ultimate distribution of the active deposit in electric fields. Experiments on similar lines with thorium and actinium show that while at atmospheric pressure nearly the whole of the active deposit particles of thorium are directed to the cathode, this is not necessarily the case with actinium, for it was found that under certain conditions the activity of the anode was fully one-half that of the cathode. Some observations made more recently than those cited above indicate that the sign of the electrical charge exhibited by the active deposit particles of actinium is a function of the distance that these particles have travelled through the containing gas before reaching the electrodes.

Dr. C. H. LEES expressed his interest in the paper, referring especially to the fact that the amount of active deposit which diffused on to a neutral rod varied with the pressure.

The CHAIRMAN referred to the radio-activity of the atmosphere, and remarked that the author's experiments might be of use to meteorologists in enabling them to settle the question of the source of the radio-activity. He expressed his interest in the results obtained with actinium.

Mr. RUSS, in reply to Dr. Lees, said that the fact that the quantity of active deposit on a neutral rod varied with the pressure was being investigated mathematically by Mr. Bateman. With regard to the Chairman's remarks he observed that the source of the radio-activity of the atmosphere was an interesting question. The radio-activity due to thorium presented more difficulties than that due to radium because of the long life of the radium emanation. He suggested that the results might be due to the active deposits themselves which had longer lives than the emanations.

A "*Note on certain Dynamical Analogues of Temperature Equilibrium*," by Prof. G. H. BRYAN, was read by the Secretary.

The note calls attention to the following results of a method described by the author in 1900 (*Archives Néerlandaises*) under the title of "Energy Accelerations":—1. In a system of uniformly distributed particles, a stationary state of statistical equilibrium cannot exist under the Newtonian law of force whether the forces between the particles be attractive or repulsive except when the particles are at rest in a state of unstable equilibrium. 2. For energy-equilibrium to exist the force between the particles, if repulsive, must vary according to a higher power of the inverse distance than the square (*e.g.*, the inverse fifth power); if attractive it must vary according to a lower inverse power than the square of the distance. 3. In a system in which the kinetic energy cannot be expressed as a quadratic function of the velocities with constant coefficients, the equations of energy-equilibrium no longer take the form of linear relations between the various components of kinetic energy, so that the commonly assumed analogue between temperature and kinetic energy becomes inapplicable.

Prof. CASSIE discussed the method and results of the paper, and remarked that the results of experiments appeared to indicate that the forces between particles varied with the distance according to some law more rapid than the inverse fifth power.

A paper on "*Experiments on Artificial Fulgurites*" was postponed.

NOTICES OF BOOKS.

Immune Sera. By Dr. CHARLES FREDERICK BOLDUAN. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

THIS small book contains a good introduction to the study of immunity and immune sera. It is based upon a monograph by Prof. Wassermann, which was translated into English by the author, who has added in this edition chapters on snake venoms and their antisera, agglutinins, opsonins, &c., and has also discussed some aspects of the subject rather more fully than was possible in Prof. Wassermann's small book. The development of our knowledge of each group of immune sera is traced in short historical accounts, which are distinguished by unbiassed judgment and clearness of expression. A chapter on serum sickness gives a brief description of the clinical manifestations which sometimes follow the injection of diphtheria antitoxic serum, and of the means which may be taken to allay them.

MEETINGS FOR THE WEEK.

MONDAY, 30th.—Royal Society of Arts, 8. (Cantor Lecture). "Fuel and its Future," by Prof. V. B. Lewes.

TUESDAY, 31st.—Royal Institution, 3. "The Egyptian Sudan—its History, Monuments, and Peoples, Past and Present," by E. A. Wallis Budge, M.A., &c.

—— Royal Society of Arts, 8. "Enamel Portraits," by Cyril Davenport.

WEDNESDAY, April 1st.—Royal Society of Arts, 8. "Dr. Schlick's Gyroscopic Apparatus for Preventing Ships from Rolling," by M. Wurl.

—— Society of Public Analysts, 8. "Lead in Tartaric Acid, Cream of Tartar, and Baking Powders," by The President. "The Nitrogen Factor for Casein" and "The Recovery of Amyl Alcohol from Waste Gerber Liquors," by H. D. Richmond. "Carapa Oil," by J. Lewkowitsch. "Rapid Method for the Estimation of Mercuric Salts in Aqueous Solution," by S. G. Liversedge.

THURSDAY, 2nd.—Royal Society of Arts, 8. (Howard Lecture). "The Navigation of the Air," by H. S. Hele-Shaw, F.R.S., &c.

—— Royal Institution, 3. "The Animals of Africa," by R. Lydekker, F.R.S.

—— Chemical, 8.30. "Condensation of Epichlorhydrine with Phenols," by D. R. Boyd and E. R. Marle. "Rate of Hydrolysis of Chloroacetates and Bromoacetates and of α-Chlorhydrine by Water and by Alkali, and the Influence of Neutral Salts on the Reaction Velocities," by G. Senter. "New General Method of Preparing Diazonium Bromides," by F. D. Chattaway. "Probable Nature of the Impurity found in the Triphenylmethane Spectrum," by W. N. Hartley. "Absorption Spectrum of Triphenylmethane," by A. G. G. Leonard. "Constituents of Cyprus Origanum Oil—Isolation of a New Terpene (Origanene)," by S. S. Pickles.

FRIDAY, 3rd.—Royal Institution, 9. "The Modern Motor Car," by the Right Hon. Lord Montagu of Beaulieu.

SATURDAY, 4th.—Royal Institution, 3. "Electric Discharges through Gases," by Prof. J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

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LUTECIUM AND NEO-YTTERBIUM.

By G. URBAIN.

IN a note which I presented to the Académie on November 4th, 1907, I showed that Marignac's ytterbium was a mixture of two elements, which I defined by their spectral properties and the approximate values of their atomic weights. The element with atomic weight about 174 I called lutecium, and I gave the name neo-ytterbium to the element with lower atomic weight. By keeping the term ytterbium in this last name I left the honour of his original discovery to Marignac.

In this note I propose to give some details, which, although important, could not be included in the first summary of my experiments.

These researches on ytterbium extend back to 1904 when I began to examine the earths from xenotime, from which I had first extracted the ytterbia. The first experiments eliminated the earths of the cerium group, gadolinium, terbium, dysprosium, and holmium. This was effected by the fractional crystallisation of the ethyl sulphates. The last mother-liquors contain only yttrium, erbium, thulium, and the ytterbiums. The greater part of the yttrium was eliminated by the fractional ignition of the nitrates. The nitrates of the earths of high atomic weight are more easily decomposed than yttrium nitrate in nitric acid of density 1·3. These earths were then fractionated by the crystallisation of the nitrates with five molecules of water. By this method in some months the greater part of the raw ytterbium which is concentrated in the mother-liquor could be separated. The raw ytterbia was then fractionated by the same method, and divided into 22 consecutive fractions. No fewer than 15,000 successive crystallisations were necessary to get these results. This extremely tedious work was completed by a series of spectral measurements and of atomic weight determinations, of which only the most important results can be given.

The following are the numbers obtained for the atomic weight by transforming the octohydrated sulphates into oxides by heat. The international atomic weights were adopted, O = 16.

No. of fraction.	Weight of octo-hydrated sulphate.	Weight of oxide.	Atomic weight.
17.	1·3650	0·6859	170·66
18.	1·6545	0·8352	171·89
19.	1·7255	0·8722	172·42
20.	2·1674	1·0970	172·94
21.	2·8650	1·4500	172·91
22.	2·2545	1·1412	172·98
23.	2·4411	1·2363	173·18
24.	3·2193	1·6315	173·45
25.	3·2743	1·6597	173·53
28.	3·1227	1·5842	173·89
29.	3·1565	1·6015	173·91
30.	2·4756	1·2565	174·04
30.	3·1267	1·5868	174·02

By the fractional precipitation with dilute soda of a solution of ytterbium sulphate of mean atomic weight 173·5, I obtained the following numbers for the extreme fractions :—

	Octohydrated sulphate.	Oxide.	Atomic weight.
First fractions (weakest bases)..	3·6358	1·8443	173·82
Last fractions (strongest bases) .	3·2868	1·6584	171·70

The fractionation extended to 16 consecutive fractions; the total number of precipitations was 240. From this it is seen that lutecium is a weaker base than neo-ytterbium. I observed the same spectral differences between the extreme members of this fractionation as between the extreme members of the fractionation of the nitrates.

G. Jantsch and I, when we determined the magnetic susceptibility of these oxides, found considerable differences. The two earths appear paramagnetic; neo-ytterbium is much more magnetic than lutecium. The susceptibility of my best earths is in the ratio 53 : 13.

At the meeting on December 19, 1907, *i.e.*, forty-four days after my report to the Paris Académic des Sciences, Auer von Welsbach, without alluding to my researches, communicated a short note to the Vienna Académie des Sciences, in which he agreed with me in regarding ytterbium as a mixture of two elements. He characterised them only by the atomic weights 174·5 and 172·9, and merely stated that there are differences in their spectra, without further defining them.

He called the first aldebaranium and the second cassiopeïum. Aldebaranium is evidently identical with lutecium and cassiopeïum with neo-ytterbium.

It is true that Auer von Welsbach and I, independently of one another, have studied the same question for some years, as I have already stated in my first note: it is not less true that I was the first to give numerical results, both of atomic weight determinations and of spectral measurements, to characterise the new elements. As Auer von Welsbach's communication only confirms researches previously published there can be no question of new names for lutecium and neo-ytterbium, which have already been named.—*Comptes Rendus*, vol. cxlvi., No. 8, p. 406.

THE FLUORIDES OF GADOLINIUM, NEODYMIUM, AND PRASEODYMIUM.

By J. POPOVICI.

THE salts of gadolinium have been investigated and described by C. Benedicks (*Zeit. f. Anorg. Chem.*, 1900, xxii., 393). Gadolinium fluoride, which has not yet been described, I have obtained by precipitating a concentrated gadolinium sulphate solution with hydrofluoric acid. The nitrate, which was used as the initial material, was first converted into the difficultly soluble sulphate, which crystallises very readily. A concentrated aqueous solution of the sulphate gives a colourless gelatinous precipitate with hydrofluoric acid. When this precipitate is warmed on a water-bath a white granular powder settles. This is filtered off and washed with cold water; the fluoride is rather soluble in hot hydrofluoric acid, insoluble in water.

The substance was analysed by evaporating it with concentrated sulphuric acid, and thus converting it into the corresponding sulphate, which yields the oxide (Gd_2O_3) when it is strongly heated with small quantities of ammonium nitrate. Its orange-yellow colour is probably caused by traces of terbium oxide, as Benedicks has shown (*Ibid.*). Acids have hardly any effect on the oxide in the cold, but dissolve it completely on warming.

0·1659 grm. substance : 0·1396 grm. oxide. GdF_3 : Calculated, Gd 73·23; found, Gd 72·94

The fluorides of neodymium and praseodymium have been mentioned by H. Moissan (*Comptes Rendus*, 1900, cxxxi., 595) as the products of the ignition of the corresponding carbides in fluorine gas. When hydrofluoric acid is added to solutions of the nitrates the fluorides result as gelatinous precipitates.

The neodymium precipitate is deposited on warming as a pale lilac-coloured crystalline powder. The praseodymium precipitate, when filtered off, dried in the air and in a desiccator, gives yellowish glittering crystals which appear green by reflection. Both fluorides were converted into sulphates and oxides. Neodymium fluoride, on ignition with small quantities of ammonium nitrate, gave the white higher oxide corresponding to the formula Nd_4O_5. According to Bohuslav Brauner's statements (*Chem. Soc. Proc.*, 1897—8, 70; *Chem. Zentralbl.*, 1898, I., 919) the oxide obtained by him contained rather more

oxygen than corresponds to the formula Nd_2O_5. He suggested that the element could probably be further split up, and would yield the oxide, Nd_2O_6.

Praseodymium contains traces of samarium, and thus rather high values have been obtained. But since the halogen compounds of neodymium and praseodymium have the same composition, praseodymium fluoride has probably the same formula as neodymium fluoride, NdF_3. Calculated, Nd 71·58; found, Nd 71·34.—*Berichte*, 1908, xli., 634.

NOTE ON THE PURIFICATION OF MERCURY.

By WILLIAM BETTEL.

SOME twelve years ago, while engaged upon the examination of a "refractory" gold ore, I used weighed quantities of mercury (containing about 16 mgrms. gold per kilo., this being the purest mercury purchasable in Johannesburg at that time) together with a weak solution of cyanide, for combined amalgamation and cyanide treatment (in imitation of crushing with weak cyanide solution and amalgamation). My first experiment not yielding very encouraging results, the duplicate experiment was set aside for about a week. At the end of that period I collected the mercury, and found that it was free from gold, the whole of the "free" gold in the ore, together with that originally present in the mercury, having been dissolved by the cyanide solution. Cyanide, as is well known, has been in use for many years in amalgamation for keeping the "plates" in good condition, but its use in this connection has been deprecated owing to the likelihood of loss of gold through the solvent action of the cyanide on the fine ("float") gold; but, to me, it was a novelty to know that gold (amalgam) in solution in mercury could be so readily removed.

Until recently I regarded this reaction as merely an interesting chemical novelty, but having to purify about 7 kilos. of impure mercury (containing zinc, tin, lead, copper, iron, and gold, 150 mgrms. per kilo.) I decided, before resorting to distillation, to subject the mercury to a treatment with cyanide, using sodium peroxide to shorten the operation by facilitating oxidation of the "base" metals.

The metal was placed in a shallow enamelled iron pan with flat bottom, the mercury thus exposing its maximum area to the cyanide solution. The latter consisted of 1500 cc. of a 2·0 per cent solution of "98" per cent cyanide, together with 20 grms. of Na_2O_2 added at intervals. This solution was allowed to act upon the mercury, the whole being gently agitated at intervals.

For the first four days of treatment, during which the "base" metals were being dissolved, only traces of gold were dissolved, but on the fifth day the gold contents dropped from 150 to 90 mgrms. per kilo. The bulk of the base metals being removed, the gold now dissolved rapidly, as will be seen from the following record:—

Gold Contents.

Sixth day of treatment	..	12	mgrms. per kilo. of Hg.
Seventh "	.. ..	6	" " "
Eighth "	.. ..	5	" " "

The solution was now removed, and replaced by one of one-tenth its strength. On the fourteenth day of treatment the gold contents of the mercury were too minute to be estimated, being under 1/50 mgrm. fine gold per kilo.

The mercury after this treatment is purer than that usually obtained by distillation *in vacuo*. The mercury dissolved by the cyanide solution is quite negligible in amount, so that the cost of purification is practically that of the cyanide used.

This process of mercury refining may therefore be made use of in chemical laboratories, &c., in preference to the distillation method.

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THE ACTION OF THIONYL AND SULPHURYL CHLORIDES ON SELENIUM AND SELENIUM DIOXIDE.

By VICTOR LENHER and H. B. NORTH.

WHEN selenium dioxide and thionyl chloride are brought together the two begin to react immediately, considerable heat is liberated, and the needle-like crystals of the dioxide are quickly changed to a white and finely divided crystalline powder. When the reaction is carried out in a sealed tube and heat applied, larger crystals can be obtained. Examination of these crystals showed them to be selenium tetrachloride, the reaction being as follows:— $2SOCl_2 + SeO_2 = SeCl_4 + 2SO_2$.

When the tubes are opened the sulphur dioxide escapes, and the excess of thionyl chloride can be removed from the crystals of the selenium tetrachloride by extraction with carbon bisulphide.

A more satisfactory method of carrying out this reaction consists in placing the selenium dioxide in a porcelain boat in a glass tube and heating in the vapour of thionyl chloride.

Selenium tetrachloride prepared in this manner gave on analysis—

	I.	II.	Calculated for $SeCl_4$.
Se.. ..	35·76	36·05	35·83
Cl.. ..	64·01	64·10	64·17

Selenium and Thionyl Chloride.—When selenium is brought in contact with thionyl chloride at the ordinary temperature only very slight action takes place, but when the two are sealed together in a tube and heated they react on each other more readily as the temperature is raised. In two weeks' time, by continuous heating at 200°, a few grms. of selenium tetrachloride can be produced, while at 300° the same quantity of substance can be formed in a few hours. In carrying out this experiment it is more convenient, both for readiness in carrying out the reaction and for obtaining a purer product, to heat the elementary selenium in a porcelain boat in a glass tube in the vapour of thionyl chloride. The reaction takes place as follows:— $2SOCl_2 + Se = SeCl_4 + SO_2 + S$.

Analysis of the product formed gave—

	I.	II.	Calculated for $SeCl_4$.
Se.. ..	35·63	35·66	35·83
Cl.. ..	64·51	64·31	64·17

Selenium and Sulphuryl Chloride.—When these two substances are brought together, reaction immediately ensues, a large amount of heat is liberated, and on cooling selenium tetrachloride deposits in crystals. This reaction, like the previously described ones, can be advantageously carried out by heating the selenium in the vapour of sulphuryl chloride. The reaction takes place as follows:— $2SO_2Cl_2 + Se = SeCl_4 + 2SO_2$.

Analysis of the tetrachloride showed—

	I.	II.	Calculated for $SeCl_4$.
Se.. ..	35·95	35·79	35·83
Cl.. ..	64·51	—	64·17

Selenium Dioxide and Sulphuryl Chloride.—When these two substances are brought together, no reaction takes place even at elevated temperatures or under strong pressure. Several tubes containing these substances were allowed to stand for a year, but at the end of this time no reaction had taken place. The two when heated together in tubes of very heavy glass, which had been obtained for work of this character, would not react, all of the tubes exploding when the temperature was sufficiently raised, but without previously showing any signs of change in the contents. After numerous attempts to bring the two to react the dioxide of selenium was vaporised from a porcelain boat in a glass tube in the vapour of sulphuryl

chloride, and was condensed in a cooler portion of the tube. Analysis of the sublimed dioxide showed it to be chlorine-free, thus showing that it is possible to sublime selenium dioxide in the vapour of sulphuryl chloride without any reaction taking place.—*Journal of the American Chemical Society*, xxix., No. 1.

THE ATOMIC WEIGHT OF CHLORINE.*

By WILLIAM A. NOYES and H. C. P. WEBER.

(Concluded from p. 149).

Errors and Corrections.

Hydrogen.—If there were any errors due to a contamination of the hydrogen they are not apparent. The hydrogen was prepared and purified with all possible precaution. It was repeatedly tested for impurities in the work on hydrogen and oxygen, and none or only negligible quantities found (Noyes, *Journ. Am. Chem. Soc.*, xxix., 1724).

Two corrections on the weight of hydrogen were found necessary. The first of these was the amount of hydrogen remaining in the chlorplatinate tube at the end of the determination, and pumped out with the residual gases to be analysed. In eight cases out of the twelve this correction was applied, the maximum being 0·11 mgrm., the minimum 0·01 mgrm., and the average 0·047 mgrm. The determinations affected are 1, 2, 4, 5, 6, 7, 11, and 12. The second correction was due to hydrochloric acid in the palladium tube. Under certain conditions, when the current of hydrogen from the palladium tube was not sufficiently rapid, hydrochloric acid found its way back into the palladium tube, either by diffusion or by being drawn back. Correction for this was readily applied. After having been weighed, the hydrogen apparatus was charged for the succeeding determination. The tube was fitted with a stopcock at both ends, as may be seen in the photograph. After the palladium had been saturated with hydrogen the stopcock farthest from the hydrogen generator was connected to a Liebig flask containing water coloured by a drop of methyl-orange. The stopcock at A was opened while the hydrogen generator was kept going, and the hydrogen bubbled through this water before escaping. If the presence of hydrochloric acid made itself known, the palladium was heated to 160° to expel the larger part of the hydrogen it had absorbed, and with it any hydrochloric acid present. It was then allowed to cool with a current of hydrogen passing through it, and finally filled again at normal temperatures. The hydrochloric acid absorbed by the water was then titrated by N/10 sodium or barium hydroxide. The real weight of the hydrogen was greater than the apparent loss of the tube by the weight of hydrochloric acid found. This correction was applied in determinations 1, 3, 4, 10, and 11, varying between 0·35 and 9·26 mgrms. and averaging 4·8 mgrms.

Chlorine from the Loss of the Platinum Tube.—The purity of the chlorine entering into the composition of the chlorplatinate has been spoken of. The maximum amount of bromine in the ingredients used seems to have been 1 in 50,000. The resultant error in the weight would be half of this, since 35·5 grms. are replaced by 80, or 1 : 100,000. There seems to be ample justification for considering this point beyond question.

The only other impurities which could possibly affect the results were volatile products in the platinum or elements capable of producing volatile products, such as ammonia, water, hydroxyl, or oxygen. The method of preparation seems to preclude the possibility of the presence of ammonium salts. The potassium chloride was especially treated to free it from these. Following this there was repeated treatment with chlorine in hot solution. The final heating of the chlorplatinate to 400° over an extended period of time must have caused the destruction and removal of any ammonium compounds which had escaped previous treatment.

The three following impurities, water, hydroxyl, or oxygen in the platinum salt, were somewhat more difficult of treatment. It is known that potassium chlorplatinate hydrolyses in aqueous solution. With this point in view the precipitation of potassium chlorplatinate was carried out in concentrated solutions with both an excess of potassium chloride and hydrochloric acid, and the mother-liquor was removed as soon as practicable. It was shown that by heating sufficiently long at 400°, all occluded hydrochloric acid could be removed, the chlorplatinate being perfectly neutral after this treatment. This served as indirect evidence that the water was also removed. The agreement between Series 1 and 2 may be considered as additional evidence on this point. In the first series the chlorplatinate had opportunity to become saturated with water vapour at the temperature of 350° during the course of the experiment. In the second series it was in equilibrium with solid hydrochloric acid at −180°. Now hydrochloric acid with its well-known affinity for water vapour may be considered as a very perfect drying agent. Yet the difference between the two series is 1 in 10,000. 120 grms. of potassium chlorplatinate were used. The presence of 0·05 per cent moisture in this salt would have raised the atomic weight of chlorine found from 35·184 to 35·244.

Further, in the second series it was noticed that if the condensation tube for the hydrochloric acid was allowed to contain a trace of moisture before the determination was begun this would remain as a trace of aqueous hydrochloric acid after the gas had been transferred from this part of the apparatus to the absorption bulb, the temperature during this transfer remaining, of course, below zero. If, however, the condensation tube was perfectly dry to start with, no such trace of aqueous hydrochloric acid remained; that is, no water had been carried over from the chlorplatinate.

A final test of the chlorplatinate was made for water, hydroxyl, or oxygen. 100 grms. of potassium chlorplatinate were treated exactly as for a determination. The chlorplatinate was heated to 400° in a current of dry air, transferred to the apparatus used in the determinations, and then evacuated at 350°. Next, pure hydrogen was led over the chlorplatinate until it was completely reduced. The hydrochloric acid formed was led through a narrow U-tube surrounded by a mixture of solid carbon dioxide and alcohol (−78°). Finally, the whole apparatus, including the U-tube, was evacuated, the final conditions being, 350° in the chlorplatinate tube, −78° in the U-tube, and several thousandths mm. pressure. Upon weighing, the U tube had shown an increase in weight of 0·9 mgrm. or 1 in 30,000 on the hydrochloric acid formed.

A number of corrections on the weight of the chlorplatinate tube were necessary. The first of these was necessary on account of the traces of air or nitrogen found in the chlorplatinate tube at the end of the determination. These corrections were found necessary in Experiments 4, 5, 6, and 7, their magnitude being 0·35, 0·76, 0·25, and 2 mgrm. This air may have been occluded by the chlorplatinate, or it may have come from the water of the absorption tube. It was immaterial how this correction was applied as it lay within the limits of the experimental errors, the maximum correction being 1 : 10,000.

In the second series it sometimes happened that with the most cautious manipulation, chlorplatinate was blown over into the condensation bulb at the beginning of the experiment. After the hydrochloric acid had been absorbed by the water and the apparatus weighed, this chlorplatinate was removed by dissolving in water, and weighing, first as potassium chlorplatinate and then again as potassium chloride + platinum, after reduction. This correction was applied in Experiments 8, 9, and 11, the amounts being 2·03, 15·0, and 36·5 mgrms. The apparent loss of the chlorplatinate tube was, of course, diminished by these quantities.

Hydrochloric Acid.—From the agreement of Series I. and II. it seems reasonable to assume that no errors were

* From *The Journal of the American Chemical Society*, xxx., No. 1.

introduced by using water as the absorbing agent for the hydrochloric acid.

The corrections on the apparent gain of the absorption tube were of the following nature:—First, the apparent gain was increased by the hydrochloric acid found in the palladium tube, and by the hydrochloric acid pumped out from the chlorplatinate tube. The former has been spoken of under hydrogen. In Experiments 1, 6, and 7 there were found 1·27, 0·8, and 0·15 mgrm. of hydrochloric acid, respectively, in the gases pumped out.

In Experiments, 8, 9, and 11 the gain of the absorption tube was diminished by the amount of the chlorplatinate blown over. The corrections were 2·03, 15·0, and 36·5 mgrms.

The final check on correctness of manipulation, freedom from leaks and other losses, was found in the checking of the sum of the weights of the hydrogen and chlorine with the weight of the hydrochloric acid. In the preliminary experiments of both series, discrepancies were found until the details of the determination had been mastered. On this account and on account of other known errors the preliminary determinations were rejected entirely.

Results.

The values obtained are given in the following tables. The weights represent those found after all correction had been applied. The second part of Experiment 5 was lost.

The value as found for the atomic weight of chlorine is 35·184 with a probable error of ±0·0013. The value obtained for the molecular weight of hydrochloric acid is 36·184 with a probable error of ±0·0012. The combined average of both sections of the two series is 35·184 with a probable error of ±0·0008. This is, of course, on the basis of hydrogen = 1.

	Hydrogen.	Chlorine.	Hydrochloric acid.	At. wt. Cl.	Mol. wt. HCl.
1.	0·25394	8·93293	9·18695	35·177	36·178
2.	0·28004	9·85590	10·13259	35·195	36·183
3.	0·51821	18·23468	18·75359	35·188	36·189
4.	0·67631	23·79587	24·47123	35·186	36·185
5.	0·58225	20·48158	—	35·177	—
6.	0·47989	16·88423	17·36310	35·184	36·182
7.	0·64132	22·55816	23·20054	35·175	36·176
	Average of Series I. ..			35·183 and	36·181
8.	0·81608	28·71691	29·53167	35·188	36·187
9.	0·83194	29·28055	30·11207	35·195	36·195
10.	0·39074	13·74926	14·14078	35·187	36·188
11.	0·75560	26·58427	27·33926	35·183	36·182
12.	0·77518	27·26746	28·04110	35·177	36·175
	Average of Series II. ..			35·186 and	36·185
	Total average			35·184(3)	36·183(7)

On the oxygen basis this value becomes 35·452 if H = 1·00762 (Morley's value) and 35·461 if H = 1·00787 (Noyes' recent value). The values for silver calculated from Richards's ratio and these two values are, respectively, 107·87 and 107·89.

Note.—The values calculated from the results of Dixon and Edgar in the same manner are 35·463 or 35·472 for chlorine and 107·90 or 107·93 for silver. The mean values 35·467 and 107·91 must be considered, for the present, as the most probable which can be calculated from their work. The values for silver are calculated from the results of Richards and Wells (*Journ. Am. Chem. Soc.*, xxvii., 525), who found that 100 parts of silver gave 132·867 parts of silver chloride.

The mean values must be considered as most probable at the present time. These are 35·457 for chlorine and 107·88 for silver.

In eleven experiments 6·41925 grms. of hydrogen were united with 225·86017 grms. of chlorine, and yielded 232·27288 grms. of hydrochloric acid. The values obtained from these figures are 35·1846 and 36·1838.

	H+Cl.	HCl.	Difference.
1.	9·18687	9·18695	+0·00008
2.	10·13594	10·13259	−0·00335
3.	18·75289	18·75359	+0·00070
4.	24·47218	24·47123	−0·00095
6.	17·36412	17·36310	−0·00102
7.	23·19948	23·20054	+0·00106
8.	29·53299	29·53167	−0·00132
9.	30·11249	30·11207	−0·00042
10.	14·14000	14·14078	+0·00078
11.	27·33982	27·33926	−0·00056
12.	28·04264	28·04110	−0·00154
	232·27942	232·27288	−0·00654

It may be interesting to note the discrepancies between the weights of hydrogen and chlorine and the hydrochloric acid formed in the individual experiments.

In these eleven experiments there are seven with an apparent loss of weight, and four with an apparent gain, the total loss being 1 in 35,000.

REVISIONS OF THE THEORY OF ELECTROLYSIS.*

By HENRY S. CARHART, LL.D.

(Concluded from p. 152).

Grotthus conceived of the motion of the part-molecules as taking place under electric force only by the progressive exchange of partners in a polarised chain of molecules. Clausius rejected the fixed equilibrium in the normal condition of an electrolyte, and assumed some free part-molecules or, as Faraday named them, ions; and the dissociation imagined by Clausius may be described as temporary, or a continuous exchange of partners in chemical association. Williamson as early as 1851 declared "that in an aggregate of the molecules of every compound a constant interchange between the elements contained in them is taking place." This view Clausius rejected. The assumption that only a few of the molecules in a solution are dissociated into ions appeared to him to satisfy the facts of electrolysis.

The first attempt to answer the question as to the manner in which the facts of electrical conductivity are reconciled with those of general chemistry was contained in the theory of Grotthus; the second attempt was made by Clausius in 1857, and thirty years later a further answer was made in the work of Arrhenius.

Another question relates to the intimate relation between the passage of electricity through an electrolyte and the simultaneous motion of the ions, the ponderable attendant of the electrical transfer. The law of Faraday paved the way for an answer to this question; the reply of the present is largely the work of Hittorf and Kohlrausch.

The simplest statement of Faraday's discovery in electrolysis is that the passage of a fixed quantity of electricity is always associated with the transfer of a grm. equivalent of the ion. The passage through an electrolyte of 96,550 coulombs of electricity always releases or deposits a grm. equivalent of an ion; that is, a grm. molecule of an ion whose valence is one, or half a grm. molecule of an ion whose valence is two. This law demonstrates that there is a fixed minimum, called by Helmholtz *the atomic charge*, conveyed by univalent ions, others conveying only integral multiples of this charge.

The researches of Hittorf on the migration of ions demonstrated that the observed change in concentration at the electrodes during electrolysis makes it necessary to assign to the positive and negative ions different velocities.

* Presidential Address delivered at the Seventh General Meeting of the American Electro-chemical Society. From the *Smithsonian Report* for 1906, p. 147.

Hittorf's work, though of fundamental importance, commanded but little attention at the time of its publication. In fact, it was opposed by the leaders of physical science and was not accepted till thirty years later.

Let me now recount several steps in the revision of electrolytic theory.

Grotthus supposed "that at the moment of the segregated appearance of the hydrogen and oxygen there takes place a division of their natural electricity, either by their contact or by mutual friction, so that the former assumes the positive, the latter the negative condition," and that the links of his chain exchanged partners in such a way as to leave only the end links free.

Clausius assumed "that the ions are not permanently united with each other; that part of them exist in the liquid in an uncombined state, wandering about seeking partners." The electric force imposes on all free ions a uniform drift. To Clausius, therefore, should be assigned the introduction of the theory of dissociation to explain electrolysis. But the dissociation of Clausius was only slight and was conceived to be the accompaniment of a shifting and unstable equilibrium.

Scientific judgment respecting the assumption of Clausius remained in abeyance for thirty years, when Arrhenius published his celebrated memoir on "The Dissociation of Substances Dissolved in Water." An intermediate step, not originally devoted to the theory of dissociation, was van 't Hoff's paper on "The Rôle of Osmotic Pressure in the Analogy between Solutions and Gases." The significant feature of this paper is the generalisation of Avogadro's law to the effect that—

"The pressure which a gas exerts at a given temperature if a definite number of molecules is contained in a definite volume is equal to the osmotic pressure which is produced by *most substances* under the same conditions if they are dissolved in any given liquid."

The major part of van 't Hoff's paper deals with non-electrolytes or organic compounds, such as a solution of sugar, which show little or no deviation from Avogadro's law as applied to osmotic pressure. When he alludes to those substances which exhibit abnormally large osmotic pressure, he acknowledges his indebtedness to the personal suggestion of Arrhenius to the effect that the solutions obeying the law of Avogadro are non-conductors of electricity, a fact indicating that they are not broken down into ions, while solutions which give higher values of the osmotic pressure than accord with the laws of gases are all electrolytes. But if these suffer partial dissociation in solution, then the number of particles is increased, each ion contributing to the pressure as much as a complete molecule. The excessive osmotic pressure is thus accounted for.

Arrhenius divided the molecules in a conducting solution into active and inactive portions. The former are those whose ions are independent of one another in their movements; the latter are the remaining molecules whose ions are firmly bound to each other, and the ratio between the two he called "the activity coefficient."

The significant conclusions of Arrhenius are:—

1. "That van 't Hoff's law holds not only for *most*, but for *all substances*, even for those which have hitherto been regarded as exceptions (electrolytes in aqueous solution)."

2. "That every electrolyte (in aqueous solution) consists partly of active (in electrical and chemical relation) and partly of inactive molecules, the latter passing into active molecules on increasing the dilution, so that in infinitely dilute solutions only active molecules exist."

The ratio of the active to the inactive molecules, or the activity coefficient, is intimately connected with the electrical conductivity of solutions. Molecules dissociated into ions are alone capable of conducting or conveying electricity through a solution. The inactive molecules are at best only inert and take no part in the electrical transport. The activity coefficient increases with the dilution—that is, the molecular conductivity, which expresses essentially the conductance of a given number of molecules in solution, is greatest when the dilution is such that all molecules of the solute are dissociated. This is the essential significance of the researches on electrolytic conductivity, so far as they bear on the theory of electrolysis.

The transition from the incidental and almost infinitesimal dissociation assumed by Clausius to the ideal infinite dilution and complete dissociation taught by the "Leipzig School" marks the essential revision of the theory of electrolysis made in recent years.

The theory of ionisation has now passed beyond the bounds of electrolytic solutions. As van 't Hoff imported the gas law into solutions to explain osmotic pressure, so others, like J. J. Thomson, have seized on electric convection by ions to explain electrical discharges through gases. It is now conceded that the only tenable explanation of electric currents through gases is that of convection by ions. The ionisation of gases is brought about by ultra-violet light, by Röntgen rays, and by the radiations from radio-active substances. The electric charge conveyed by ions in gases appears to be identical with the charge conveyed by ions in an electrolyte in aqueous solution, but the masses conveying negative charges are only about the one-thousandth part of the hydrogen ion.

The passage of electricity through a gas, as well as through an electrolyte, is accompanied by chemical changes; and chemical decomposition, says J. J. Thomson, is not to be considered an accidental attendant on the electrical discharge, but an essential feature without which it could not occur.

In reviewing the changes that have occurred in the theory of electrolysis I would not be understood to imply that we now have the ultimate truth. Many cogent objections have been urged against the theory of dissociation in its present form. Theories should be regarded as helps or scaffolds only; they are necessary for the construction of the edifice of truth, and they finally disappear like the staging. We should use them as temporary expedients, not retaining them till the whole edifice is completed, but only until a grand arch is finished, some minaret or tower emerges against a clear sky or light streams through some noble window.

The physicist or chemist who is more intent to ascertain the truth than to preserve inconsistency, holds to a theory no longer than he finds it able to furnish support. Faraday, the prince of research, said that experimental work is a great disturber of preconceived theories.

Just now the dissociation theory is in a state of siege, with many valiant defenders. The objection is urged that there are many cases of electrolytes in solution in which the osmotic pressure does not exceed that required by the gas law. Hence, there can be no dissociation. Also that the simplest cases of electrolysis are those of a molten salt, such as silver electrodes in molten silver chloride. In these cases there is no complication with a solvent and no dissociation by solution. In what way, then, is that migratory freedom of the electrically charged part-molecules, which is assumed in the theory of dissociation, secured in a molten salt? Doctor Kahlenberg has shown that "a normal solution of trichloracetic acid in allyl mustard oil is a poorer conductor of electricity than the purest water which Kohlrausch ever prepared in contact with air, and yet this solution attacks dry magnesium rapidly, and decomposes dry carbonates of sodium and potassium." But chemical reactions are assumed to depend on dissociation into ions, as does electrical conductivity.

This much is generally accepted: "The ions must be free to move; but this migratory freedom may be secured either by ionic interchanges between the molecules, as Clausius imagined, or by a prolonged separation in accordance with the dissociation hypothesis of Arrhenius and Planck. The essential point in the general ionic theory is the migratory freedom."

The solution of obscure problems, like those of electrolysis, in which event the chief agent itself is an elusive

enigma, is necessarily one of prolonged effort, with many a flamboyant processional and the not infrequent refrain of the later recessional. But there is no occasion for discouragement, for we are destined to struggle for ever with the unsolved problems of the here and the hereafter.

It is often darkest just before the dawn. Sometimes, too, we emerge into the light with a suddenness that blinds before the eye adjusts itself to the new illumination. One dreary day in April I took the train in Switzerland over the St. Gothard route. We entered the north end of the tunnel at Goeschenen with a clouded sky and snowflakes swirling through the air. Ten minutes passed in the darkness a thousand feet beneath the village of Andermatt —fifteen, seventeen, and then the train ran out on the Italian side of the great divide at Airola into a burst of sunshine and clear sky and white-capped Alpine peaks and tempered winds and the pale green of olive groves. So sudden was the transformation that an involuntary exclamation of surprise and delight ran through the train. The experiences of the last twenty years warn us that we must be prepared for similar surprises in the illumination that physical science is shedding on the world of nature. We need not prophesy; we need only work and wait.

AN EXPERIMENTAL INVESTIGATION OF THE NATURE OF THE γ-RAYS.*

By W. H. BRAGG, M.A., F.R.S.,
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and
J. P. V. MADSEN, DSc., Lecturer on Electrical Engineering.

In papers recently published in the *Proceedings of the Royal Society of South Australia* (May and June, 1907) and in the *Philosophical Magazine* (October, 1907) an attempt was made to show that the ether-pulse theory of γ- and X-rays might prove to be incorrect after all, and that most of the known properties of these rays could be explained more simply and directly on the supposition that they were material and consisted of neutral pairs. The arguments were based on comparison of known phenomena with deductions from each of the two opposing hypotheses. At that time there did not seem to be any opportunity of appeal to a decisive experiment.

The object of this paper is to give a preliminary account of an investigation which appears to us to give a final answer as regards the γ-rays, and to show that they are material in nature.

Secondary radiation, which is excited in an atom by a passing wave or pulse, must be distributed symmetrically with regard to a plane passing through the atom perpendicular to the direction of motion of the pulse. If we speak of the primary pulse as going forwards, the secondary radiation is just as likely to go backwards as forwards. This is a well-recognised principle. For example, J. J. Thomson divides the secondary radiation, due to γ-rays, into two equal parts, which he supposes to move away symmetrically in opposite directions, and, for convenience of calculation, parallel to the direction of the primary rays ("Conduction of Electricity through Gases," p. 406). Supposing, therefore, a pencil of γ-rays to pass normally through a plate so thin that its absorption may be neglected, the secondary radiation should be exactly the same on the two sides of the plate—in amount, in quality, and in distribution; and it ought not to be possible to discover, by any comparison of the secondary radiations on the two sides, which is the face of entry and which of emergence.

Consider now the ionisation-chamber represented in Fig. 1. The two ends are closed by plates, of which A and A′ are alike; so also are B and B′. The substance of A and A′ is different to that of B and B′. The nature of the side walls is immaterial. A pencil of γ-rays passes along the axis of the chamber, which is represented by a dotted line. The ionisation current within the chamber is measured as usual by inserting a high potential electrode connected to an electroscope.

When the plates A and B are inverted, there is a change in the amount of the current; so also when A′ and B′ are inverted. By an extension of the principle already stated, it ought not to be possible, on the ether-pulse theory, to

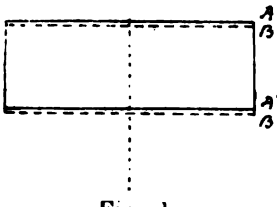


Fig 1.

discover which way the rays are going, up or down, in the figure, by comparing the consequence of inverting A and B with that of inverting A′ and B′.

As a matter of fact, the direction can be discovered with ease; the more easily the greater the difference between the atomic weights of A and B.

For example, in one experiment of ours the chamber was of cylindrical form, 3 inches high and 10 inches diameter. The plates used were of aluminium and lead. The thickness of each plate was a little less than 2 mm. Inversion of the top plates A and B made a difference in favour of Al of less than 1 per cent, *i.e*, the current was slightly larger when Al was next the chamber. On the

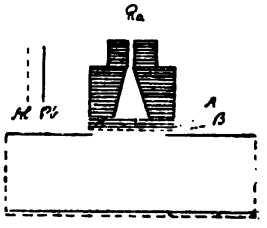


Fig. 2

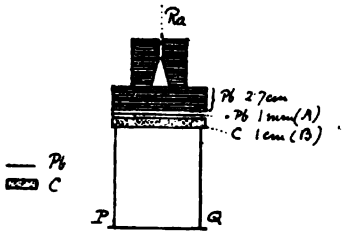
other hand, inversion of the bottom plates made a difference of 44 per cent in favour of Pb, *i.e.*, the current was 44 per cent larger when the Pb was on top. The details are shown in the figure. Allowance was made for all radiation other than that which proceeded down the conical opening in the lead block.

It may be well to point out that this effect cannot be ascribed to any complication due to secondary or tertiary rays. No doubt the radiation in the chamber is very complex; but the fact is immaterial. Provided that the chamber is symmetrical in the first place, then the secondaries must be symmetrical also if the ether-pulse theory is correct, and therefore the tertiaries and so on. Nor is it necessary to consider whether the secondary radiations are β-rays or scattered γ-rays. Also, it must be remembered that the secondary radiations which enter the chamber have their origin almost entirely in a very few millimetres of material bordering on the chamber. Therefore, the γ-rays are in almost exactly the same condition, both as to quality and as to quantity, when they excite secondary radiations from the top plate as they enter the chamber, and secondary radiations from the bottom plate as they leave.

The details of the experiment may be varied greatly; but in all the cases we have tried the want of symmetry is obvious. In Fig. 3 are shown the details of one other case, in which carbon and lead were the materials used, and the form of the chamber was different. It seems

* From the *Transactions of the Royal Society of South Australia*, 1908, xxxii.

unnecessary to give more, because, in the first place, the experiments are easy to repeat; and in the second place, the complete quantitative analysis of the figures depends on several factors, the influence of which is imperfectly understood, such as the previous screening of the rays, the form of the chamber, and the respective parts played by the



(1) Current with plates arranged as above = 59·8
(2) " A and B inverted ..... = 54·4
(3) As in (1), but base PQ changed to carbon = 50·5

Fig. 3.

original γ-rays, cathode rays, and secondary γ-rays, if any such exist. The experiments, as they stand, show how far away is that symmetry which the ether-pulse theory demands. It seems to us that there is no escape from the conclusion that the γ-rays are not ether-pulses.

Let us, therefore, proceed to consider the hypothesis that the γ-rays are material. In the paper already mentioned, it was argued that they might well consist of neutral pairs, liable to be broken up on encountering atoms or parts of atoms; and that the secondary cathode radiations might be the negative particles thus set free. Let us suppose, provisionally, that the particles, when set free, move at first in the direction of the γ stream, but are subsequently scattered in the usual manner of β-rays. (It is here that the absence of symmetry arises. On the pulse theory the particles should go equally backwards and forwards; indeed, if they were ejected by atomic explosions, the result of energy accumulated from passing pulses, as suggested by J. J. Thomson in the case of X-rays, they would move equally in all directions).

Wigger gives a table (*Jahrbuch der Radioaktivität*, Bd. ii., p. 431) showing that the γ-rays are absorbed according to a density law pretty strictly, except for small thicknesses of substances of large atomic weight.

Assume this law to hold good, and also assume for the present that the absorption of β-rays follows the density law. The latter is only roughly true, of course; but we may deal with quantities in a broad fashion first, and

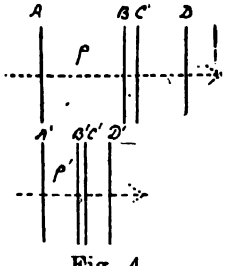


Fig. 4.

make the proper amendments afterwards. We can now compare the quantities of cathode radiation which should emerge from the far sides of two plates of different densities ρ and ρ'. Let these be represented by AD and A'D' in the figure, and let BC and B'C' be corresponding strata of equal weight; in fact, let $AB/A'B' = BC/B'C' = CD/C'D' = \rho'/\rho$. Let the plates be crossed by equal pencils of γ-rays, as shown in Fig. 4. A certain quantity of γ radiation is absorbed in crossing BC. In the language of our present hypothesis we should say that a certain number of γ particles are stripped of their positives, and the negative remainders go on. An equal number of negatives are set free in B'C' because the two strata are of equal weight. Of those set free in BC only a certain number emerge from the face D, because of the absorption of the plate CD. Since CD and C'D' are of equal weight, a similar absorption occurs in the case of the particles set free in B'C'. Thus the same number emerge from each plate. Integrating for all effective strata, the whole cathode radiations emerging from the two plates are equal.

We thus find that if the absorption of β- and γ-rays both followed the density law, the secondary cathode radiation on the far side of a plate—we may call it the "emergence" radiation—would be the same for all materials. There should be no such relation between the amount of the radiation and the atomic weight of the plate, as various observers have shown to be true for the secondary cathode radiation of "incidence," a relation which is closely parallel to that found in the case of β-rays.

Experiment is in agreement with this theory, for it shows that no such relation exists in respect to the emergence radiations; in marked contrast to what happens in the case of the radiations from the front sides of plates of various materials, the incidence radiations.

It is true that the emergence radiations are not all equal, but this is to be expected, because (1) the amount of secondary cathode radiation depends, as Kleeman has shown, on the previous screening of the γ-rays; (2) the β-rays are not absorbed strictly according to a density law; (3) the γ-rays also depart from this law. We have made no serious attempt as yet to disentangle the effects of these various disturbing factors. In fact, the task promises to be long and intricate, for it will be necessary to find out how much of the ionisation in the chamber is due to each class of rays; to discover the law of distribution of the radiations in space, so that the form of the chamber may be allowed for, if necessary; to find out the nature of the departures from the density law of those β- and γ-rays which are in question; and so on. Nevertheless, the results are satisfactory, so far as we have gone. The amount of emergence radiation is found to depend on the previous screening of the rays. In one case the inversion of a C—Pb pair of plates from C—Pb to Pb—C, altered the current in the ratio 1 : 1·11 when the rays had been previously screened by Pb; but in the ratio 1 : 0·96 when the screen was changed to C. Again, when the rays had previously passed through an iron screen, the inversion Pb—Fe to Fe—Pb changed the current in the proportion 1 : 1·12, but when a lead screen was substituted for an iron one the change was 1 : 1·04. In illustration of the effect of the second disturbing factor mentioned above, we have found that, other things being equal, the substances of small atomic weight give the most secondary radiation, in a general way; and it may be no coincidence that in some cases we have found Sn and Fe to give surprisingly small amounts. This is in agreement with what is to be expected, for it is clear, on consideration of the argument already given, that the greater the β-ray absorption of a substance in proportion to its density, the less "emergence" radiation should issue from it. Some observers have found Sn and Fe to possess exceptional absorbing powers. We do not wish, however, to lay any stress upon these last observations, some of which we may not have interpreted correctly; but we mention them in order to show that the inequalities that are found to exist between the emergence radiations of various substances promise to be reducible to order as soon as the difficulties of interpretation have been surmounted.

Let us now consider the cathode radiations on the front sides of the plates. Of the cathode particles set free in BC and moving at first in the direction of the γ-rays, a certain proportion, say p, is returned by what is beyond.

These move towards the face A, and a certain number of them succeed in reaching it and emerging therefrom. In the case of the other plate the proportion returned is p'. The absorption in B′A′ is the same as in BA, because the weights are the same. Comparing the two plates, stratum by stratum, we find that the "incidence" radiation of one plate is to the incidence radiation of the other plate as p to p'. Now p and p' are the well-known constants of the β-rays.

When a stream of γ-rays is allowed to fall upon a plate the cathode radiation which issues from the place of incidence must be divisible into two parts. One consists of scattered β particles derived from the stream of such particles which was travelling with the γ-rays before incidence, and which was formed during the previous transit of the screens employed, solid, liquid, or gaseous. This part is scattered to an extent which depends on the atomic weight of the plate, according to the usual law of β-particles. The other part is originated in the plate itself in the manner just described, and the amount of it is also regulated according to the β-ray law. When, therefore, observers have measured the secondary radiation, due to γ-rays, and have found a law corresponding to that for β-rays, the reason of the correspondence has been that they really were measuring the secondary radiation due to β-rays. Properly speaking, the secondary radiation, produced by γ-rays, or, rather, *from* γ-rays, is proportional to the density of the substance traversed (*cf.*, Wigger's table), and this is only another form of the law of absorption of γ-rays.

The relative importance of the two parts of the incidence radiation just mentioned must depend on the circumstances of the experiment. (In a recent letter addressed by one of us to *Nature*, too great a preponderance was assigned to the first part under all circumstances). The researches of Kleeman (*Phil. Mag.*, Nov., 1907) show very well how the second part, which is influenced by previous screening, modifies the effect of the first part, which is not so influenced, but which follows the law of β-rays strictly.

It is easy to show, by comparing corresponding strata at the front and back of one plate, that the incidence radiation should be somewhat less than p times the transmitted radiation. Somewhat less, because the cathode radiation, which is turned back, is scattered and softened in the process.

To sum up:—On the ether-pulse theory we ought to find perfect symmetry in the secondary radiations from the two sides of a plate. But experiment shows nothing of the kind.

On the material or neutral-pair theory, the "incidence" radiations should follow the β-ray law. This is known to be the case. The emergence radiations should not follow the β-ray law, and experiment shows that they do not. If the density law held for both β- and γ-rays, and if the γ-rays were homogeneous, the emergence radiations should all be equal. As already explained, experiment shows that the observed inequalities give promise of ready explanation, on the ground that no one of these suppositions is quite true.

It is, perhaps, better not to extend the preliminary account of these experiments by any lengthy discussion of the issues arising from them. Many points that invite consideration have been discussed already in the papers first referred to. Moreover our own further experiments are incomplete, and their full interpretation is not yet certain. We will, therefore, confine ourselves to one or two questions which seem of special interest. The X-rays resemble the γ-rays so closely that it is practically inconceivable that the two radiations should be essentially different. The secondary cathode radiations, which are set free when X-rays impinge on any material, must therefore have been part of the X-ray stream, and must start their independent existence by moving on in the line of the X-ray motion. Their velocity is much smaller than that of the secondary cathode rays due to γ-rays, and they are much more readily scattered. It may still remain an open question whether or no the X-ray stream contains ether pulses. Perhaps their existence must be supposed in order to explain the velocity experiment of Marx, and the diffraction experiment of Haga and Windt. Possibly they are also required in order to explain Barkla's polarisation experiments; but we do not think that the experiment described by Barkla in *Nature* (October 31, 1907) is in any way decisive.

It seems proper to consider a possibility that the negative particle, when it moves on in the original line of motion of the pair from which it came, retains also its original velocity. It is a striking fact that the cathode particle, due to the γ-rays, has the same speed, very nearly, as the β particle issuing from the original radioactive material. And it looks quite unlike a coincidence that similar comparisons can be made in the case of the X-rays. The secondary cathode radiations due to these rays have velocities which, at the least, are of the same order as the velocities of the cathode particles in the X-ray bulb. If we examine the table given by Innes (*Proc. Royal Soc.*, Aug. 2, 1907, p. 461), and if we may be allowed to adopt an interpretation differing somewhat from the author's, but more natural, it seems to us, in view of the conclusions of this paper, we find that the velocities of the electrons emitted by all the metals are practically the same, zinc being an exception, because it is unable to break up the hardest rays. We find that the velocities range from about 6×10^9 to $7{\cdot}5 \times 10^9$ for soft rays, and 6×10^9 to 8×10^9 for hard rays. Remembering that bundles of X-rays are very heterogeneous, the natural conclusion seems to be that the softest rays give the slowest speeds, and that the velocity of the secondary rays increases with the hardness of the X-rays from which they are derived. (By independent experiment, Bestelmeyer, *Ann. der Phys.*, 1907, xxii., p. 429; and Cooksey, *Am. Journ. Sci.*, Oct., 1907, arrive at the same conclusion). Now the hardness of the rays grows with the speed of the cathode particles in the bulb. Is it then possible that the cathode particle is first set in motion by the electromotive force in the bulb, strikes the anticathode, and picks up a positive there, becomes neutral, and is now called an X-ray, is subsequently stripped of the positive, and becomes a secondary cathode particle, the identity of the negative remaining the same throughout, and its speed invariable, or nearly so? The difficulty comes in when we try to consider the part played by the mass of the positive. Probably it becomes necessary to consider it as small compared to the mass of the negative. In many ways such a supposition would fit in very well. We should then understand why the positive is so hard to isolate: also a radio-active atom, in ejecting a γ-particle would not lose appreciably in weight. Lilienfeld believes he has found the positive electron to be less massive than the negative (*Deutsch. Phys. Gesell. Verh.*, 9, 7, April 15, 1907).

And, again, may not the β and γ forms be interchangeable at times? A γ-particle, which had been stripped of its positive, and become a secondary cathode, or β-ray, would be lost to measurement as a γ-ray; and we should thus have an explanation of how the γ-rays are "absorbed," and why the absorption follows an exponential law. And in the same way, if a β-particle picked up a positive, it would disappear from view as a β-particle, it would be "absorbed."

Although we have made a few experiments with magnetic fields, we have not yet come to any conclusions as to whether or no there are γ pairs which have become loosened in the attachment of positive to negative, forming a softer and more ionising radiation. Their existence might be suspected since there is an analogous effect in the case of X-rays; and probably they would be found more at the back of the penetrated plate than in front of it.

A few further experimental illustrations are shown diagrammatically in Figs. 5, 6, and 7.

The upper part of Fig. 5 shows the general arrangement,

The lower figures are diagrammatic, and show the currents for different arrangements of the Pb and Al at the bottom of the chamber, and at the top, with the exception of the plate through which the γ-rays enter. Inverting the top plates makes little difference where the upper of the two

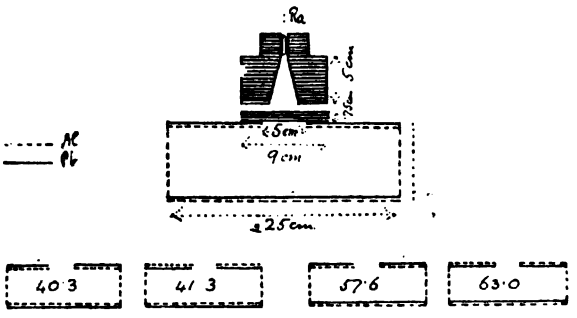


Fig. 5.

plates at the bottom is Al, but an appreciable difference when it is Pb, because in the latter case a good deal of secondary radiation is thrown upwards by the Pb, and there is a tertiary from the top plate.

The same, when the conical opening is completely filled by a Pb stopper:—

12·6 12·6 17·7 18·3

The differences show the effects of those rays only which which do not pass through the Pb stopper:—

27·7 28·7 39·9 44·7

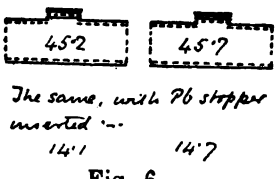


Fig. 6.

Fig. 6 shows the effect of inverting that portion only of the top plate where the γ-rays enter. Three Pb plates = 0·55 cm., Al plate = 0·16 cm.

The upper part of Fig. 7 shows the general arrangement. The wall of the cylindrical vessel was of brass; a Pb or an Al lining could be inserted as shown. The lower

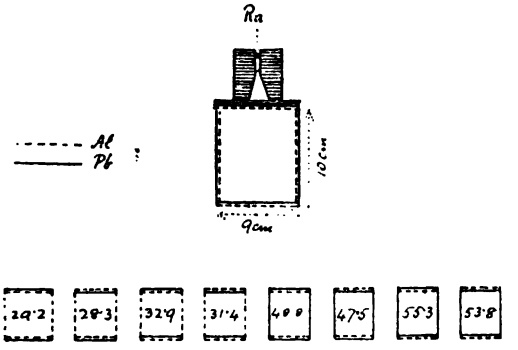


Fig. 7.

figures are diagrammatic, and show the currents for different arrangements of Pb and Al at top, bottom, and sides. Inversion of the plates, *through* which the γ-rays pass into the chamber, makes little difference; but there is a great alteration if the material is changed on which the γ-rays fall, or the emergence radiation from the top plate. The base is of less importance than in Fig. 5; but the sides of more importance. This should clearly be so, for geometrical reasons.

When the conical opening was filled by a Pb stopper, the currents were all reduced considerably, but retained the same proportions pretty nearly.

On the other hand, when a small pencil of β-rays was admitted through a hole in the centre of the top plate, a change of the material of the bottom became more effective, and of the sides less effective than before; but this difference became smaller when thin Al sheets were so placed as to scatter the β-rays on their entry into the chamber.

In conclusion, we should like to add that Wigger was the first, so far as we know, to show clearly that the secondary radiation of Al, on the far side of the plate, might be greater than that of Pb. A comparison of the emergence radiations of different metals was made by Dawes (*Phys. Rev.*, xx., p. 182), who showed that they did not follow the law of the incidence radiations. The same effect was indicated in the experiments of Eve (*Phil. Mag.*, December, 1904). We have little doubt that the interesting experiment of Mackenzie (*Phil. Mag.*, July, 1907) is to be explained on the lines indicated in this paper. In fact, it is clear that this is the case in a broad sense; but it is difficult to give a complete explanation until the laws are so completely worked out that they can be applied to the interpretation of experiments, which are really very complicated, although at first sight they may seem to be simple.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 19th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President in the Chair.

MESSRS. W. R. Bousfield, M. J. A. Braun, J. A. Carpenter, T. P. Hilditch, O. Oberländer, A. W. Oke, and T. M. Tyson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Leonard Clifford Green, B.E., Wienholt Street, Torwood, Brisbane; William Hall, B.Sc., Inglewhite, Manchester Road, Bolton; Hugo Stefan Kohn, Ph.D., 3A, Hythe Road, Willesden Junction; Gerald Roche Lynch, 160, Holland Park Avenue, W.

The PRESIDENT announced that Prof. W. Jackson Pope had expressed himself unwilling to accept nomination for Vice-Presidency.

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

*57. "*A New Form of Pyknometer.*" By WILLIAM ROBERT BOUSFIELD.

The author described a new form of pyknometer, intended for very accurate density determinations.

*58. "*The Action of Heat on α-Hydroxycarboxylic Acids.* Part IV. *Racemic αα'-Dihydroxyadipic Acid and Meso-αα'-dihydroxyadipic Acid.*" By HENRY RONDEL LE SUEUR.

When αα'-dihydroxyadipic acid melting at 146° (compare *Proc.*, 1907, xxiii., 196) is heated above its melting-point, it loses water, and its dilactone (m. p. 134°) is formed as a crystalline sublimate. The acid has been resolved into its optical antipodes by fractional crystallisation of its cinchonidine salt. The *d*-acid melts at 157°, and has $[\alpha]_D$ 16 +3·8°; its *ammonium salt* is lævorotatory, and has $[\alpha]_D$ 11 −21·4°.

When the αα'-dihydroxyadipic acid melting at 174° is heated at 180—190° it loses water, forming a lactone-lactide. All attempts to resolve this acid have failed, and

it must therefore be regarded as the meso- or internally compensated variety.

That the acid which admits of resolution into its optically active components readily forms a dilactone, whereas the meso-variety does not, is in complete agreement with the spacial formulæ of these substances. Characteristic derivatives of both acids have been prepared.

*59. "*The Spontaneous Crystallisation of Sodium Sulphate Solutions.*" By HAROLD HARTLEY, BERNARD MOUAT JONES, and GEORGE ADRIAN HUTCHINSON.

The authors have examined the spontaneous crystallisation of sodium sulphate solutions, and have found that if the solutions are subjected to mechanical friction three of the four possible solid phases, namely, ice, $Na_2SO_4,7H_2O$, and Na_2SO_4, are produced spontaneously at definite temperatures. Supersolubility curves have been traced for these three phases which, in conjunction with the solubility curve, define the labile and metastable regions for the system. The spontaneous crystallisation of the fourth solid phase, $Na_2SO_4,10H_2O$, is of rare occurrence compared with that of $Na_2SO_4,7H_2O$, and seems to take place irregularly without any definite relation to the temperature and concentration of the solution.

*60. "*Constitution of Hydroxyazo-compounds. Action of Diazomethane and of Mercuric Acetate.*" By CLARENCE SMITH and, in part, ALEC DUNCAN MITCHELL.

Diazomethane reacts with *p*-hydroxyazo-compounds to form the methyl ethers obtained by the ordinary methods of alkylation. Benzeneazo-*p*-cresol, *p*-chlorobenzeneazo-*p*-cresol, and β-benzeneazo-α-naphthol do not react with diazomethane.

The action of mercuric acetate in boiling aqueous-alcoholic solution on benzeneazophenol, 2 : 4 : 6-tribromobenzeneazophenol, benzeneazo-*o*-nitrophenol, benzeneazo-*oo'*-dibromophenol, benzeneazo-*p*-cresol, and benzeneazo-*o*-bromo-*p*-cresol has been examined, with the result that the number of mercuriacetate groups entering the molecule of the hydroxyazo-compound is equal to the number of unsubstituted positions in the ortho-position with respect to the oxygen atom. The substances obtained are yellow, red, or reddish brown compounds, readily soluble only in acetic acid, and not melting below 300°, with the exception of benzeneazo-*p*-cresol mercuriacetate, $C_6H_5{\cdot}N_2{\cdot}C_7H_5(OH){\cdot}Hg{\cdot}CO_2{\cdot}CH_3$, which melts at 269—270° with decomposition, and is identical with the compound obtained by Dimroth (*Ber.*, 1902, xxxv., 2864). The corresponding mercurichlorides and mercuribromides have been obtained from the mercuriacetates by means of sodium chloride or potassium bromide in alkaline or acetic acid solution.

DISCUSSION.

Mr. BALY wished to put in a plea for the spectroscopic evidence which so decidedly pointed to the fact that, of the hydroxyazo-compounds, the ortho were quinonehydrazones, whilst the para had the true hydroxyazo-structure. He emphasised the fact that where a possibility of tautomerism existed as in the case under discussion, chemical means failed to determine which of the two possible desmotropic forms a substance possessed. Mr. Tuck had shown that the quinonehydrazone form on the one hand, and the hydroxyazo-form on the other, each represented by compounds, the structure of which was beyond cavil, exhibited two types of spectra which differed very greatly in the relative dilution at which the absorption bands appeared, and also in the shape of the bands themselves. Inasmuch as the parent hydroxyazo-compounds conformed to one or other of these types, so was their constitution in alcoholic solution established, notwithstanding any chemical evidence to the contrary.

It appeared further from Dr. Smith's paper that a slightly different interpretation might be put upon his results. Dr. Smith had pointed out that, in the case of the para-hydroxyazo-compounds, both methyl sulphate and diazomethane introduce a methyl group into the hydroxyl group, thus proving the hydroxyazo-configuration. In the case of the ortho-compound, diazomethane had no action and methyl sulphate only acted at 100°, and then the compounds behaved as if they possessed the hydroxyazo-structure. Again, Dr. Smith had pointed out that his experiments with mercuric acetate were carried out at 85°, but he (the speaker) thought these results rather led one to believe that the para-hydroxyazo-compounds were true hydroxyazo-bodies, but that the ortho-isomerides were quinonehydrazones at the ordinary temperature, and at 100° they tended to favour the hydroxyazo-form. In other words, as the temperature rose the equilibrium between quinonehydrazone and hydroxyazo-forms was shifted towards the hydroxyazo-side, so that at 100° the compounds could react in this form.

Dr. MORGAN said that, in 1889, Prof. Meldola and he had found that benzeneazo-β-naphthol could be benzoylated and ethylated only with some difficulty, and that the products, when mildly reduced in the presence of acids, underwent the benzidine transformation to 4 : 4'-diaminophenylnaphthyl bases which still contained the benzoyl and ethyl groups attached to the phenolic oxygen. They drew from these results the conclusion that the acyl and alkyl derivatives of benzeneazo-β-naphthol were true azo-compounds and not β-naphthaquinonehydrazones. It was interesting to find that the authors held the view that the ortho-hydroxyazo-compounds were really azo- and not hydrazino-derivatives.

The presence of many other constituents, besides the azo-group, in the contiguous α-position greatly modified the properties of β-naphthol or β-naphthylamine, but it was scarcely possible in every instance to ascribe this effect to the existence of a quinonoid configuration.

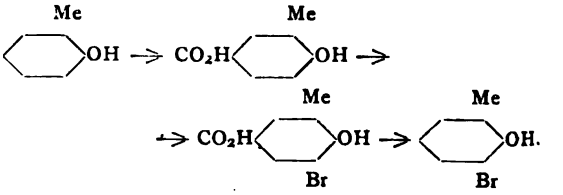
Dr. HEWITT drew attention to the fact that benzeneazo-*p*-cresol behaved as a phenol towards substituting agents even at the ordinary temperature. A cold solution of the substance in glacial acetic acid, containing excess of fused sodium acetate, brominated exclusively in the phenolic nucleus.

It should be remembered that spectrographic evidence, valuable though it was, ultimately depended on the determination of the constitution of typical substances by chemical methods.

Dr. SMITH, in reply, expressed the opinion that the spectrometric evidence by no means conclusively proved the quinonehydrazone structure of *o*-hydroxyazo-compounds and of their acyl derivatives. Benzoquinone-benzoylphenylhydrazone, which was undoubtedly a quinonehydrazone, gave a totally different absorption spectrum from that of the isomeric benzoylbenzeneazophenol, which had the azo-structure, whilst benzoylbenzeneazo-*p*-cresol gave an absorption curve closely resembling that of benzeneazophenol. With regard to the point raised by Mr. Tuck, the reduction of β-benzeneazo-α-naphthyl acetate resulted first in the formation of the hydrazo-compound, then wandering of the acyl group from the oxygen to either of the nitrogen atoms took place, and, finally, fission occurred, yielding the four products, aniline and N-acetyl-2-amino-1-naphthol, acetanilide and 2-amino-1-naphthol.

*61. "*Orthobromophenols and some Bromonitrophenols.*" By PHILIP WILFRED ROBERTSON.

The method of direct bromination cannot be employed for the preparation of *o*-bromo-*o*-cresol or the corresponding *o*-bromoguaiacol. Accordingly, these compounds were obtained by an indirect method, as is indicated in the following scheme illustrating the changes in the case of *o*-cresol :—



The constitution of the *o*-bromo-derivatives was confirmed by the fact that, on nitration, they yielded the same *o*-bromo-*p*-nitrophenols as are obtained from the *p*-nitrophenols by bromination.

*o-Bromo-*p*-nitro-o-cresol*, *p-bromo-o-nitro-o-cresol*, and *o-bromo-*p*-nitroguaiacol* form a red and a yellow series of *potassium* salts, being a confirmation of the recent work of Hantzsch (*Ber.*, 1907, xl., 330).

Bromonitrothymol is anomalous, as only one isomeride (m. p. 109°) is obtained by the reactions: (1) nitration of *p*-bromothymol, (2) bromination of *o*-nitrothymol, (3) nitration of *o*-bromothymol, (4) bromination of *p*-nitrothymol; this isomeride must be *o-bromo-*p*-nitrothymol*, as it forms bromo-*p*-thymoquinone on oxidation.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 7, February 17, 1908.

Lithium in Radio-active Minerals. — Mdlle. Gleditsch. — The author has determined the amount of lithium in certain radio-active minerals spectroscopically by comparing the intensity of lithium lines in the residue, after dissolving the mineral and separating the other constituents, with the intensity of the corresponding lines in artificial mixtures containing lithium. The results obtained were as follows:—

	Copper, per cent.	Lithium, per cent.	Activity referred to uranium.
Joachimstal pitchblende	1·2	0·00017	1·5
Colorado pitchblende	0·15	0·00034	1·75
Carnotite	0·15	0·030	0·52
Cornwall chalcolite	6·54	0·00011	2·0
Autunite	—	0·00083	1·48
Thorite	Trace	0·0033	0·59

The relatively large amount of lithium in carnotite is interesting, especially as the mineral contains but little copper. The results obtained do not contradict Ramsay's theory of the transformation of copper into lithium, though they do not support it; they show, however, that there is no simple ratio between the copper and lithium in radio-active minerals.

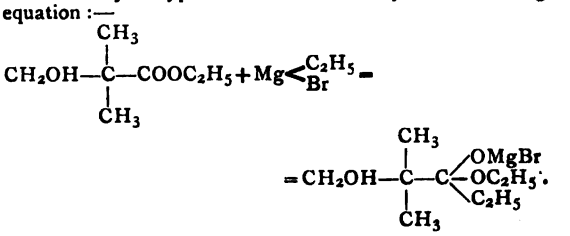
New Method of Determining Sulphur in Organic Matter.—Isidore Bay.—The organic matter is ignited in a combustion tube in presence of sodium carbonate and bromide and calcined magnesia. The contents of the tube are washed out into a dish, dissolved in dilute hydrochloric acid, boiled to drive off the bromine, and filtered. The sulphur in the filtrate is determined as sulphate by adding barium chloride. This method is as accurate as Carius's, and much quicker.

Separation of Silver Chloride and Iodide.—H. Baubigny.—To separate a mixture of silver iodide and chloride the precipitate of the two salts is washed and treated with a solution of commercial ammonium sesquicarbonate at 70—80°. After a few minutes the liquid is allowed to cool and decanted off, and the same treatment is repeated. Finally, the residual iodide is washed on a filter with dilute ammonia. The chloride is separated from its solution by the addition of nitric acid, and is determined in the usual way. This method is more accurate than Hager's process of approximate separation.

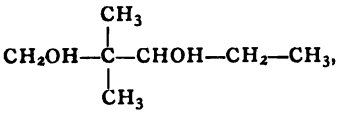
Complete Analysis of Vegetable Matter.—J. M. Albahary.—Already noticed.

Reciprocal Displacement of Hydrocarbon Groups in Friedel and Craft's Reaction.—H. Duval,—When diphenylmethane in cold carbon disulphide solution is subjected to the action of acetyl chloride in presence of aluminium chloride, *p-p*-diacetyldiphenylmethane, *p*-monoacetyldiphenylmethane, and a considerable quantity of acetophenone are formed. The latter can result only by the replacement of a $C_6H_5—CH_2$ group by the group $CH_3—CO$, under the influence of aluminium chloride.

Reducing Properties of Organo-metallic Compounds. — M. Letellier. — Ethyl magnesium bromide reduces ethyl oxypivalate, as shown by the following equation:—



The product is then further reduced to the glycol,—



with disengagement of ethylene.

Simultaneous Production of 1.6 and 2.7-Dimethylanthracenes by the Action of CH_2Cl_2, $CHCl_3$, or of $C_2H_2Br_4$ on Toluene in presence of $AlCl_3$.—James Lavaux.—Already noticed.

Essence of Tetranthera Polyantha, var. Citrate Nees.—Eug. Charabot and G. Laloue.—The analysis of the essence extracted from the leaves of this tree shows that it contains 6 per cent of citral, 21·2 per cent of cineol, and 31·3 of alcoholic principal (geraniol?). The essence of the bark contains 8 per cent of citral, 20 per cent of citronellal, 56·5 per cent of geraniol, and 2·4 per cent of ethers, while the essence of the fruit consists of 64 per cent of citral, 19·4 per cent of geraniol, and 2 per cent of ether.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xli., No. 3, 1908.

Formation of Oxides of Nitrogen in Ozoniser.—W. Manchot.—Ozone prepared from oxygen mixed with nitrogen always contains oxides of nitrogen, but when only small percentages of nitrogen are present the amounts of oxide formed are so small that they cannot be detected unless large volumes of the gas are passed through an absorption agent. The acid properties of ozone are to be ascribed to the presence of oxides of nitrogen, and when the latter are removed the acid reaction also disappears. Thus ozone is not an acid anhydride; its reaction with bases may simply be an addition reaction.

Three Lecture Experiments.—Edmund Knecht.—*Synthesis of Calcium Carbide and Acetylene.*—A piece of calcium as large as a pea is placed upon a hollowed-out piece of coal, and gently heated before the blowpipe. In a few seconds the metal catches fire, and burns with an intense orange-coloured flame, meanwhile sinking into the coal. When the latter is broken, a lump of calcium carbide is found embedded in it. If this is placed in a test-tube and water is added, acetylene is generated. *A Visible Autoxidation.*—A solution of potassium permanganate acidified with sulphuric acid is divided into two parts. One is kept for comparison, and to the other small quantities of titanium sesquisulphate solution are added. The colour of the permanganate solution changes gradually from blue-red to scarlet, and finally the pure orange of titanium superoxide appears. Excess of the reagent decolorises the solution. Titanium sulphate gives

no reaction with permanganate. *Precipitation of Copper as Metal by Titanium Sesquisulphate.* — Commercial titanium sesquisulphate solution is added to a 10 per cent copper sulphate solution, and the whole is well stirred. After a few minutes the metal begins to separate; it appears blue in transmitted light, but the characteristic colour of the metal is seen in incident light. The precipitate is so finely divided that most of it runs through filter-paper. The test is sensitive enough to show the presence of one part of copper in 1,000,000 parts of solution.

Preparation of Bromine Cyanide and Cyanamide Derivatives.—Fritz Baum.—Scholl has shown that when a cold concentrated solution of potassium cyanide is added to some bromine in water, the whole being well cooled, and the crystalline mass obtained is distilled on the water-bath, bromine cyanide distils over. Since, however, the isolation of the cyanide by distillation is a very unpleasant process the author finds that it is preferable to add ether to the crystalline mass, dry the ethereal solution with calcium chloride, and use the bromine cyanide in this form. Such a solution can be directly converted into the corresponding cyanamides by means of methylamine and aniline.

Heat of Formation of Antimony Hydride.—Alfred Stock and Franz Wrede.—The heat of formation of antimony hydride can very easily be determined by measuring the heat evolved when the gas is decomposed by an electric spark. The gas is purified by repeated fractional distillation, and introduced into an exhausted glass tube, which is then fused up. The vessel is placed in a water calorimeter, and a spark is passed by means of platinum wires fused through the glass. The mean of three experiments gave for the heat evolved 34·27 cals. per. grm.-molecule at constant volume, and 33·98 cals. per grm.-molecule at constant pressure, the error being less than 1 per cent. Thus the equation for the formation of antimony hydride at the ordinary temperature is $Sb\,(metal) + 3H = SbH_3 - 33{\cdot}98$ cals. This value does not fit in well with those found for NH_3 (+12·2 cals.), PH_3 (+11·6 cals.), and AsH_3 (−36·7 cals.). Antimony hydride is undoubtedly a more endothermic compound than AsH_3, and probably a fresh determination of the heat of formation of AsH_3 will give a lower value.

Phosphorus Pentasulphide.—Alfred Stock.—The author describes an improved form of apparatus for preparing large quantities of phosphorus pentasulphide, and gives the results of vapour density determinations carried out at different temperatures. These experiments show that the pentasulphide when distilled or sublimed undergoes decomposition, to a slight extent only at atmospheric pressure; in a vacuum or in a current of carbon dioxide the decomposition is more pronounced. Evidently the sulphide with lower melting-point, prepared by Stock and Thiel, consisted of a mixture produced by heating the pentasulphide.

MISCELLANEOUS.

Preparation of Triphenylmethyl.—Julius Schmidlin.—The author describes a convenient apparatus for preparing triphenylmethyl by the decomposition of the magnesium compound of triphenylchlormethane with excess of triphenylchlormethane. A distilling flask is connected with an upright condenser, its side-tube being corked, and in it triphenylchlormethane and iodine are dissolved in absolute ether by gently heating. Then dry magnesium powder is added, and the flask is heated on a water-bath to a temperature just below the boiling-point of ether. After about forty minutes the warming is stopped, and the side-tube of the distilling flask is connected by means of a glass cylinder with the neck of another distilling flask. The glass cylinder is fitted with a filter. The liquid is hen filtered in a current of hydrogen, by inclining the whole apparatus in a vertical plane until the filter is vertical, the second flask being filled meanwhile with coal-gas. When the whole of the liquid has been filtered into the second flask the latter is connected with the condenser and heated on a water-bath until the ether solution begins to boil and triphenylmethyl separates out in colourless crystals. By the use of this apparatus the β-magnesium compound of triphenylchlormethane can be isolated.—*Berichte*, xli., No. 2.

MEETINGS FOR THE WEEK.

Monday, 6th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Considerations affecting the 'Strength' of Wheat Flours," by J. L. Baker and H. F. E. Hulton. "Note on Murexide as a quondam Dyestuff and Printing Colour," by Watson Smith.
Tuesday, 7th.—Royal Institution, 3. "The Egyptian Sudan—its History, Monuments, and Peoples, Past and Present," by E. A. Wallis Budge, M.A., &c.
—— Royal Society of Arts, 4.30. "The Imperial Problem of Asiatic Immigration," by Richard Jebb.
Wednesday, 8th.—Royal Society of Arts, 8. "Technical Education in America," by Sir William H. Preece, K.C.B., F.R.S.
Thursday, 9th.—Royal Institution, 3. "The Animals of South America," by R. Lydekker, F.R.S.
Friday, 10th.—Royal Institution, 9. "The Carriers of Positive Electricity," by Prof. J. J. Thomson, F.R.S.
—— Physical, 8. "Experimental Investigation of the Nature of the γ-Rays," by W. H. Bragg and J. P. V. Madsen. "Experiments on Artificial Fulgurites," by Miss D. D. Butcher. "Short Spark Phenomena," by W. Duddell.
Saturday, 11th.—Royal Institution, 3. "Electric Discharges through Gases," by Prof. J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

Vol. XCVII., No. 2524.

"TELLURIUM."

Is it a Mixture of Two Elements?

By WILLIAM BETTEL.

The following record of a curious experience in the examination of a "telluride" silver ore is now published in order to enlist the interest of chemists, metallurgists, mining engineers, and others engaged in silver mining, with whom the writer has not come into contact (during the past quarter of a century), with a view to the possible discovery of a "telluride" silver ore giving reactions similar to, if not identical with, those obtained in his experiments.

In 1883 the attention of the writer was called to a curious behaviour of silver obtained from assays of a silver "telluride" ore (some three tons of which were under

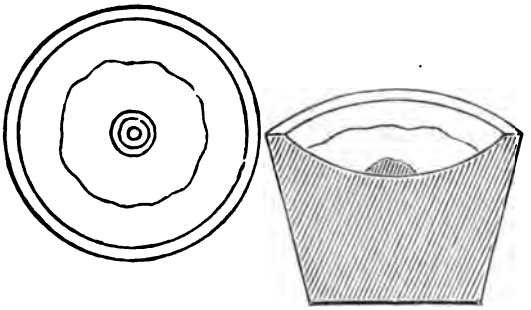


Fig. 1.

offer for sale) at the apparent completion of cupellation. The beads of silver "brightened" and cleared, but, instead of solidifying to buttons in the usual manner, they suddenly lost their surface tension, wetted the cupels as a drop of mercury would wet clean surfaces of zinc, copper, or tin, and spread out in irregular films, leaving a protuberance in the centre of each cupel more or less marked as the bead was exposed for a longer or shorter period to a temperature above that of melting silver, after brightening.

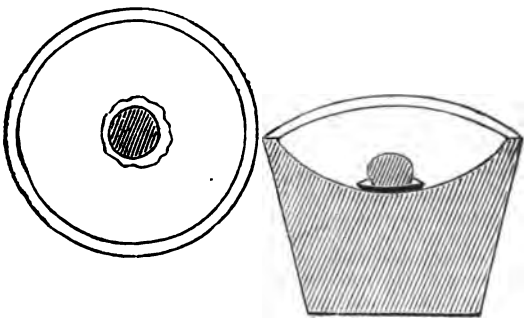


Fig. 2.

In some instances the silver films were over an inch in diameter, the pimple or protuberance being from 2 to 3 mm. diameter by about 1·5 by 2 mm. high, to a "refined" bead, a bead having at its base a ring of silver about 2 mm. width of section, the bead being about 12 to 13 grains in weight (see Figs. 1 and 2).

It was not found possible by the existing methods of potting or scorification, followed by cupellation, to arrive at a satisfactory estimate of the silver contents of the ore, so preliminary treatments were given, having as their object the removal of the tellurium or other constituents which caused the trouble.

Analysis of the ore showed "tellurium" to the extent of 5 to 6 per cent, and the only difference between so-called "chemically pure" tellurium as purchased, and that extracted from the ore, was that the chemically pure element when alloyed with lead and silver left after scorification and cupellation a rim of an average width not exceeding 2 mm., generally 0·5 to 1 mm.

About five pounds of the powdered ore was secured and set aside for further examination as the work in a smelting works and refinery would permit, but stocktaking intervening, a too zealous laboratory attendant consigned this sample to the ore heap, and it was therefore lost. Endeavours were made by the firm, through the sellers, to ascertain the name of the mine, or its locality, without result, as the shippers were merely agents who kept no record of the transaction, and since that period, although the writer has made personal enquiries of a great many English-speaking chemists and metallurgists with whom he has come into contact, not one has had under his observation similar results to those recorded.

Some four years subsequent to these experiences another firm (to which the writer at the time was metallurgist and chemist) purchased the contents of a refinery and smelting establishment which had, it appears, purchased the refractory telluride silver ore, but only small quantities of the element, which the writer ventures to call (provisionally) "β-tellurium" were observed. It was present (in traces) in the otherwise fine silver, also in larger amounts in slags, skimmings, flue dust, stained surfaces of firebrick ("cobbing"), argentiferous copper-matte, and litharge (all of which were purchased). The maximum width of ribbon or fringe round the silver beads did not measure in any case more than 2 mm., generally from 0·5 to 1 mm., about the same as is noticed in cupelling ordinary silver-lead to which has been added so-called pure tellurium.

The element present in the originally examined ore possessed the following properties (in combination with silver):—

1. It formed a true chemical compound with silver less easily oxidisable than lead, bismuth, tellurium, selenium, antimony, &c.

2. It prevented the absorption of oxygen by silver at the close of the cupellation.

3. It was not finally removed by repeated cupellation with lead or bismuth, even after allowing the silver bead in which it was contained to remain fluid long after "finishing" as ordinarily understood.

4. It was soluble in sulphuric acid, and imparted the same tint to that acid as is produced by ordinary tellurium.

5. Its other chemical reactions called for no specia notice, the substance being estimated as "tellurium."

6. Distinct amounts of this substance have been found in all "tellurium" samples examined (by testing its action on silver in cupellation) by the writer.

7. The present accepted atomic weight of tellurium (127·6) places it in an anomalous position in regard to other elements in the periodic system. In "Select Methods in Chemical Analysis," 1905, p. 420, is the following:—

"On account of the fact that the most trustworthy determinations of tellurium have given results which place it in the eighth group of the periodic system of the elements, notwithstanding its striking similarity to sulphur and selenium, the hypothesis has been put forward that tellurium is a mixture of true tellurium with an atomic weight of about 125 and another element with a higher atomic weight.

"Brauner (*Journ. Chem. Soc.*, lxv., 382, and lxvii., 549), who spent a number of years studying tellurium, has expressed this as his opinion."

8. No known substance produces the effects in cupellation of silver as were witnessed in the experiments with

the "telluride" ore in 1883, nor has any substance other than the "tellurium" of commerce yielded results which approximate in any degree to those of the experiments in 1887.

9. The silver film and protuberance previously referred to in the description of the 1883 experiments, when freed from litharge and cupel matter, dissolved completely in nitric acid, and also in sulphuric acid, in both of which the "β-tellurium" was presumably oxidised.

As desultory enquiries during twenty-five years have yielded no results, it is now time to apply to a wider circle, and by the kind consent of the Editor, to whom the writer (in Johannesburg in 1896) detailed his experiences in this direction, an appeal is made to all interested in deposits of "telluride" silver ores to submit samples to the writer for examination. Should any be found giving the same reaction as has been here described, and presumably containing the long-looked-for new element, they will be forwarded to Sir William Crookes for his opinion.

Chemical and Metallurgical Laboratories,
379, Commissioner Street,
Johannesburg, Transvaal, South Africa.

[We wish to draw the attention of our readers to the request made by Mr. Bettel in the above paper. It has long been surmised that tellurium is accompanied by another element of a different atomic weight, but this is, we believe, the first hint given by chemistry that such an element may really exist. Mr. Bettel writes saying he will be very pleased to receive and examine specimens of silver telluride ores which have been found difficult to assay by the usual process, and if full particulars regarding locality of the ore deposit, name of mine and sender, with address of the latter, be attached, he will forward to the Editor of this journal any sample which he considers may contain the sought-for element.

We shall be glad if editors of mining, metallurgical, and technical papers will copy Mr. Bettel's article and this Editorial Note in order to secure greater publicity by circulating the information among mining men, and others who are not chemists but are interested in silver mining and reduction works, in Mexico and elsewhere.—*Ed.* C. N.]

THE CONVERSION OF DIAMOND INTO COKE IN HIGH VACUUM BY CATHODE RAYS.*

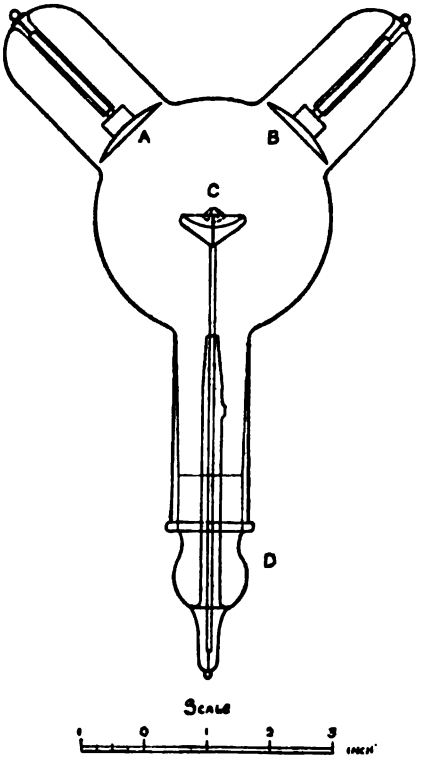
By the Hon. CHARLES A. PARSONS, C.B., F.R.S.,
and
ALAN A. CAMPBELL SWINTON.

THE objects of the experiment were three-fold: firstly, to ascertain whether a diamond could be entirely converted into coke or graphite by heating in a vacuum by cathode rays; secondly, in the event of this being found practicable, to make a determination by Féry's optical pyrometer of the temperature at which the conversion takes place; thirdly, to endeavour to ascertain if, during the conversion, any gas was emitted or absorbed by the carbon.

The vacuum tube employed is shown in the illustration, where A and B are the two aluminium electrodes, C the diamond, and D an air-tight ground-glass stopper joint, through which the diamonds were introduced. Alternating current was employed, each of A and B acting as cathode and anode in turn, while their concave curvature was such as to accurately focus the cathode rays on to the diamond. The latter was supported on a plate of iridium, which, in turn, rested in a platinum cup, this arrangement being designed to prevent any stray cathode rays which might miss the diamond from striking the glass walls of the tube and melting the latter. During the experiment the tube was connected to two mercury pumps of the Toepler type, and in connection with the tube there were also attached two spectrum analysis discharge tubes for the purpose of collecting and examining some of the residual gas in the tube, both before and after the conversion of the diamond into coke.

The alternating current from the mains, which was of 85 periods per second, was passed through the primary of a 10-inch Rhumkorff coil, with the contact-breaker and condenser disconnected, with an adjustable choking coil in series in the primary circuit, so that the secondary voltage could be varied from about 5000 to 12,000 volts. A reflecting milliampère-meter was employed to read the current through the tube, while the volts across the tube's terminals were measured by an electrostatic voltmeter.

The two diamonds, each about 0·2 inch in diameter, were experimented with. The first was entirely converted into coke without difficulty, while in the case of the second



the process was stopped when most of it had been so converted, the residue being black throughout its mass. As the proper degree of vacuum was reached by working the mercury pumps, and as the volts were raised, the diamond in each case became red, and then intensely white-hot, till, with about 8000 volts and 44 milliampères (352 watts) passing through the tube, the diamond began to throw off small sparks. On the volts being increased to 9600, and the current rising to 45·5 milliampères (436 watts), the sparks thrown off became more numerous and the diamond commenced to become black. Finally, with 11,200 volts and 48 milliampères (537 watts), a rapid disintegration of the diamond took place, with considerable increase in volume, the residue having much the appearance and consistency of coke.

The temperature of the diamond, as given by the pyrometer during disintegration, was 1890° C.

During the heating up of the diamond and of the tube, large amounts of gas were driven off, and had to be pumped out, but there was nothing to indicate that any

* A Paper read before the Royal Society, January 16, 1908. From the *Proceedings of the Royal Society*, A, vol. lxxx., p. 184.

of this gas originated from the diamond rather than from the metal parts and glass walls of the tube. Two experiments were made, and in the latter there was distinct indication of a rise in vacuum just about the time of the conversion. These rises in vacuum are, however, not unusual in tubes in which there is highly heated metal, and it was impossible to decide whether any of the absorption of gas took place in the diamond.

In the experiment in question, one of the spectrum discharge tubes was sealed off just before the conversion, when the diamond was commencing to blacken on the surface, while the other was sealed off after the diamond had been converted into coke. These two tubes, therefore, respectively contained samples of the residual gas before and after the conversion. Their spectra have been photographed alongside of one another, but though they are not altogether the same, the differences do not appear sufficiently marked to determine with exactitude any variation in the nature of the gases present.

The experiments were arranged and carried out by Mr. Swinton at his laboratory in London.

THE HISTORY OF VALENCY.

By J. NEWTON FRIEND, Ph.D., M.Sc.

The Origin of the Theory.

It seems at first sight rather remarkable that the enunciation of Dalton's law of multiple proportions did not at once lead chemists to a conception of valency. Although it was now known that compounds were formed by the union of atoms of different elements, the idea that the individual atoms possessed a definite attractive force was not for many years entertained. In fact, forty-four years elapsed between the publication of Dalton's famous book in 1808, entitled "A New System of Chemical Philosophy," and Frankland's discovery of that atomic force, known to-day as valency, which was announced in 1852 in the *Philosophical Transactions*. In 1858 two papers appeared simultaneously, one by Couper (*Ann. Chim. Phys.*, [3], liii., 469; *Comptes Rendus*, xlvi., 1157), the other by Kekulé (*Ann.*, cvi., 129) in which Frankland's views were enlarged.

Couper rejected the type theory entirely, and constructed formulæ for various compounds by applying his knowledge of the valencies of the constituent atoms. Had he employed the same atomic weights as we to-day his formulæ would in many cases have been identical with those still in vogue.

Kekulé, on the other hand, was impregnated with the type theory, and endeavoured to harmonise the new views with the old.

Variability of Valency.

The early development of the theory of valency was beset with difficulty. It is true that hydrogen forms an excellent standard, in that its atom is never known to combine with more than one atom of any other element. The numerical value of its valency may therefore be taken as unity, and by analysing its hydrides the valency of any other element could be determined. But not only was this method soon found to be unsatisfactory on account of the paucity and instability of the metallic hydrides known, but the method yielded contradictory results.

Thus, writing the formula for hydrochloric acid as H.Cl, it is clear that the valency of chlorine can only be unity. But two chlorides of phosphorus are known, namely, the trichloride, PCl_3, and pentachloride, PCl_5, in which the valency of phosphorus is 3 and 5 respectively.

It is obvious, therefore, that if the above reasoning is valid, valency cannot be regarded as a constant quantity.

Both Frankland and Kolbe were of this opinion. Kekulé, on the other hand, preferred to regard valency as a fundamental property of the atom, and as unchangeable and invariable as the atomic weight—a view which he retained to the last (*Zeit. Chem.*, vii., 689).

In order to explain the formation of phosphorus pentachloride, Kekulé argued that it was a molecular compound, and that its formula would be more correctly written as $PCl_3.Cl_2$.

The fact that this substance dissociates on vaporisation was taken as supporting this view.

A similar explanation was applied in the case of ammonium chloride, $H_3N.HCl$.

During the past few years, however, a large number of facts has been been accumulated which cannot be reconciled with Kekulé's doctrine of constant valency. The discovery of phosphorus pentafluoride, PF_5, which can exist in the gaseous state without dissociation, definitely proves the pentavalence of phosphorus (Thorpe, *Ann.*, 1876, clxxxii., 201).

The remarkable researches of Baker have further established the pentavalence of nitrogen, by showing that perfectly dry ammonium chloride may be vaporised without dissociation (*Trans. Chem. Soc.*, 1894, lxv., 612).

In nitric oxide, NO, nitrogen is apparently divalent, for the molecules of this gas have been proved to be single, even at $-100°$ C.

Kolbe ("Lehrb. d. Anorg. Chem.," 1856, i.) believed that each element possessed a definite maximum valency, and when this was saturated, further combination became impossible. Erlenmeyer, some years later, adopted a similar view (*Zeit. Chem.*, 1863, pp. 65, 97, 609; 1864, pp. 1, 72, 628).

Mendeleeff assumed that the highest oxygen compounds, omitting peroxides, give the maximum valency of the elements (Ostwald's "Klassiker," lxviii., 48), and Abegg has adopted the same suggestion (*Zeit. Anorg. Chem.*, 1904, xxxix., 340).

Not only is this method uncertain, owing to the divalent nature of oxygen, but it is inconsistent. The valency of manganese, for example, is decided by a much higher and more unstable oxide (Mn_2O_7) than the peroxide (MnO_2) (compare Friend, *Trans. Chem. Soc.*, 1908, xciii., 262).

Abegg further suggests that the maximum valency of every element is 8, and apparently Morozoff is of the same opinion (*Journ. Russ. Phys. Chem. Soc.*, 1906, xxxviii., [2], 481).

Although this is true for the majority of the amphoteric elements, it can scarcely be so in the case of the inert gases, hydrogen, and the alkali metals.

Up to the present no satisfactory theory has been advanced to account for the variability of valency. Abegg assumes that all the valencies of an atom are of the same strength before actual combination, but saturation of one weakens the rest. The extent of that weakening determines the numerical value of the valency in the circumstances (see Abegg and Bodländer, *Zeit. Anorg. Chem.*, 1899, xx., 453).

Nef, on the other hand, believes that the unused valencies do not lie latent in the ordinary sense of the term. They saturate one another. He therefore writes Cl≡Cl for the molecule of chlorine, R—Cl⊐ for alkyl chlorides, and $H_3N\sqsupset$ for ammonia (*Ann.*, 1897, ccxcviii., 202). This theory offers no explanation for the existence of *one* unsaturated valence such as occurs, for example, in cuprous chloride, CuCl. This difficulty was overcome by doubling the formula, a procedure which was apparently justified by the results of vapour density determinations effected by Biltz and V. Meyer (*Ber.*, 1889, xxii., 725), and V. Meyer and C. Meyer (*Ber.*, 1879, xii., 609, 1112, 1185, and 1292).

In 1897, however, Werner (*Zeit. Anorg. Chem.*, xv., 565) showed that in solutions of pyridine, cuprous chloride consists of single molecules. Rügheimer and Rudolphi (*Ann.*, 1905, cccxxxix., 311) have shown that the same is true for solutions in fused bismuth chloride, and E. Beckmann and Gabel have obtained similar results in a series of experiments carried out with quinoline as solvent (*Zeit. Anorg. Chem.*, 1906, li., 236). Copper must there-

fore be regarded as truly monovalent in cuprous salts, one valence remaining inactive. Other metals have been found to offer similar difficulties, and no explanation is as yet forthcoming.

The Valency of Carbon.

The determination of the numerical value of the valency of carbon was an important advance in the theory of valency, and one destined to exert an enormous influence on the study and progress of organic chemistry.

In 1854, Williamson and Kay prepared tri-ethyl ortho-formate—

$$C\begin{cases}H\\(OC_2H_5)_3\end{cases}$$

by the action of chloroform on sodium ethoxide,—

$$CHCl_3+3NaOC_2H_5=3NaCl+CH(OC_2H_5)_3.$$

They described it as "a body in which the hydrogen of three atoms of alcohol is replaced by the tri-basic radical of chloroform" (*Proc. Roy. Soc.*, vii., 135). In the light of our present knowledge it seems most remarkable that these investigators did not at once realise the tetravalency of carbon. This, however, was seemingly reserved for Kekulé.

In a paper on the constitution of fulminic acid (*Ann.*, 1857, ci., 200) Kekulé drew up a table of the compounds belonging to the marsh-gas type. Thus :—

C_2 H H H H	Marsh-gas.
C_2 H Cl Cl Cl	Chloroform.
$C_2(NO_4)Hg$ $Hg(C_2N)$	Mercuric fulminate.

It is clear from this table that Kekulé regarded C_2 as tetravalent, where by C_2 he understood G, the symbol used by the Gerhardt-Williamson school to denote the atom C = 12.

In a paper published later in the same year (*Ann.*, 1857, civ., 129), he distinctly states in a foot-note (p. 133) that he regards one atom of C = 12 as equivalent to four atoms of hydrogen.

The valency of carbon has proved to be remarkably constant, and it is largely due to this property that the application of the theory of valency to the study of organic chemistry has met with such success. Until quite recently carbon was believed to be divalent in carbon monoxide, C = O. The discovery of Collie and Tickle (*Trans. Chem. Soc.*, 1899, lxxv., 90), that oxygen can function as a tetravalent atom, renders this assumption doubtful. Nevertheless, Nef (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1549) prefers to write divalent carbon in carbon monoxide, hydrocyanic acid, H—N = C, &c.

In triphenyl methyl, $C(C_6H_5)_3$, carbon appears at the first blush to function as a trivalent element (Gomberg, *Ber.*, 1900, xxxiii., 3150), but the question is by no means settled, several other formulæ having been suggested. It may therefore be safely asserted that up to the present no compound has been prepared in which carbon functions other than as a tetravalent atom.

Thiele's Theory.

Thiele studied compounds of the type—

$$\begin{matrix}R_1\\R_2\end{matrix}\!\!>\!C=CH-CH=C\!<\!\!\begin{matrix}R_3\\R_4\end{matrix},$$

and concluded that the double bonds do not represent a complete saturation of the atoms, but that each atom possesses a "partial" valency in addition. In this way he finds an explanation for the fact that bromination of such a group gives a double bond in the middle. Thus,—

$$\begin{matrix}R\\R\end{matrix}\!\!>\!CBr-CH=CH-CBr\!<\!\!\begin{matrix}R\\R\end{matrix}.$$

In order to represent this partial valency, Thiele proposes the use of dotted lines. Thus, for carbon monoxide he writes $\overset{\vdots\ \vdots}{C=O}$, $\overset{\vdots\ \vdots}{N=N}$ for nitrogen, &c. Thiele has further extended his theory to the study of the benzene nucleus and aromatic compounds generally (*Ann.*, 1899, cccvi., 87; cccviii., 213).

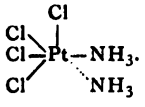
Following along somewhat similar lines, Baeyer was led to advance his theory of "complex valency" (*Ber.*, 1901, xxxiv., 2685), and Bulow a theory of "crypto valency" (*Ber.*, 1901, xxxiv., 3920).

Werner's Theory.

After a careful study of the complex ammino compounds, Werner was led to suggest a new theory of valency, by means of which he was able to group these substances in well defined classes.

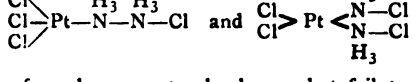
It is impossible to do full justice to his ingenious theory in the limited space at our command, but the student will find a very clear exposition of the same in Werner's book, entitled "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 1905. Werner distinguishes two kinds of valency, known as Principal and Auxiliary. The former correspond to the generally accepted valencies of the elements. The latter, however, possess a smaller energy content, and groups attached by them are not dissociable. It is regarded as possible, however, for several auxiliary valencies to unite to form a principal valence.

An example will make this clear. Two compounds are known having the empirical formula $PtCl_4(NH_3)_2$. Neither isomer shows any appreciable dissociation in aqueous solution. It is therefore assumed that the six elements or groups are attached directly to the platinum, the four chlorine atoms by principal valencies, and the two NH_3 groups by auxiliary. Thus—



It is clear that if the groups are arranged spatially around the platinum atom two different schemes are possible, namely, one in which the two NH_3 groups are adjacent, and one in which they are opposite to one another. These represent the two isomers known.

The formulæ which must be employed according to Cleve and Jörgensen, who have adhered to the usually accepted views on valency, are—



These formulæ are not only clumsy, but fail to explain the undissociable nature of the complexes.

Electro-chemical Theories.

The theories which, up to the present, have engaged our attention, have assumed that valency is merely an attractive force. The most casual observer, however, cannot fail to be struck by the fact that the most stable compounds are formed by the union of elements of opposite electrical character. It is not remarkable, therefore, that numerous attempts should have been made from time to time to account for chemical combination on electro-chemical grounds.

The Dualistic Theory of Berzelius was essentially electro-chemical, and even in 1869 Blomstrand made the interesting observation that an element which is decidedly electropositive or negative has the lowest saturation capacity. Thus, if the halogens act decidedly negatively their valency is always unity (*Chemie der Jetztzeit*, 1869, 217, 243).

In 1899, Abegg and Bodländer (*Zeit. Anorg. Chem.*, xx., 453; see also Abegg, *Ibid*, 1904, xxxix., 331) discussed an electrochemical theory of valency in full, but it presented several difficulties and has not been generally accepted.

In 1902, Spiegel suggested that certain elements possess what he calls *neutral affinity*, that is, valencies which can

be called out in pairs of equal opposite sign, and which when not externally saturated, neutralise one another. They exert, therefore, no action on the electrochemical character of the element (*Zeit. Anorg. Chem.*, 1902, xxix., 365).

Arrhenius ("Theorien der Chemie," 1906) has given expression to somewhat similar views. Neither author has, however, worked out the subject with any degree of fulness.

Friend (*Trans. Chem. Soc.*, 1908, xciii., 260) distinguishes three kinds of valency, namely :—

1. *Free Positive Valency*, such as that possessed by hydrogen and the metals. Its numerical value for any particular element is determined by analysis of the fluorides.

2. *Free Negative Valency*, such as that possessed by fluorine and chlorine. Its numerical value in any particular case is determined by analysis of the hydrides. All the non-metals, with the exception of the two already mentioned, possess free positive valency in addition to negative. They are therefore termed *amphoteric* elements.

3. *Latent* or *Residual Valencies*.—These are possessed by every element, not excepting the inert gases. They are called out in pairs of equal and opposite sign, and in this respect resemble those of Spiegel and Arrhenius. It is assumed that in all cases latent and free valencies possess the same chemical nature, and in support of this the work of Victor Meyer on the alkyl ammonium iodides is cited.

No theory may be regarded as final. But let not the investigator be discouraged. Each new thought, even if it be wide from the mark, serves to stimulate us to further research, and to promote the interests of science and truth.

DETERMINATION OF THE ATOMIC WEIGHT OF EUROPIUM.

By G. JANTSCH.

DETERMINATIONS of the atomic weight of europium have been published in three articles. E. Demarçay (*Comptes Rendus*, 1900, cxxx., 1469) gave the value Eu = 151. This is certainly too low, and it is probable that his earth contained samarium, or that his measurements were incorrect. G. Urbain and H. Lacombe (*Comptes Rendus*, 1904, cxxxviii., 627) published a series of determinations of the successive members of a fractionation by which they obtained spectroscopically pure europium. These determinations were performed chiefly in order that there might be no doubt about the constancy of the atomic weights and the homogeneity of the europium. The method consisted in transforming the octohydrated sulphate into anhydrous sulphate, and the numbers thus obtained were verified by converting the anhydrous sulphate into oxide. The mean of the values obtained (adopting the international atomic weights, O = 16) was Eu = 151·99. More recently. W. Feit and Przibylla (*Zeit. Anorg. Chem.*, 1906, l., 248) have performed fresh determinations with a europium prepared by Urbain. Their method consisted in dissolving the ignited oxide in a known volume of titrated sulphuric acid, and determining volumetrically the excess of acid. Thus they found Eu = 152·57.

A new determination was necessary owing to the differences between these results. I am indebted to M. Urbain for some europium which he kindly gave me for this purpose.

In order to convince myself that this earth was pure, I photographed on the same plate, one above the other, the spectra of gadolinium, europium, and samarium in the order specified. The spectrum of iron was used as a reference spectrum. These spectra were obtained by the electric arc, following the directions recently published by Griner and Urbain (*Bull. Soc. Chim.*, 1907 [4], i., 1158). It was shown that none of the gadolinium lines, nor those of samarium, were prolonged into the europium spectrum. The only lines common to the three spectra were the parasitic lines of the arc, appearing owing to the presence of a small amount of iron, silicon, and magnesium in the carbon electrodes.

As there was no doubt about the purity of the material, my attention was concentrated on perfecting the experimental details of the determination. For this purpose I studied specially the method which has been devised by Urbain and Lacombe.

I proceeded as follows :—

About 1·2 grms. of oxide were converted into neutral nitrate. To the solution of this nitrate (amounting to about 10 cc.) a slight excess of pure sulphuric acid was added, and the whole was poured into a large volume (about 1 litre) of alcohol at 95°. Under these conditions the transformation of the europium nitrate into octohydrated sulphate has been found to be complete. The sulphate appears as a precipitate formed of fine crystalline silver-white needles. This precipitate was then washed with alcohol until all the sulphuric and nitric acids were eliminated, and dried in an air-oven at 300° to transform it into anhydrous sulphate. The sulphate was dissolved in the least possible quantity of water, and the perfectly neutral solution was evaporated very slowly in an air-oven, kept nearly closed, at a constant temperature of 105°. The crystals were deposited on the walls of the vessel. Those which formed on the sides, and which had thus not been constantly washed with the mother-liquor, were rejected. Only those crystals which were deposited on the bottom of the vessel were used for the determinations. These crystals were powdered and dried over sulphuric acid. The drying took two or three days.

Under these conditions the octohydrated sulphate loses all water of interposition, but no water of crystallisation. The salt was weighed in a tared platinum dish. I had found that when this dish was heated to 1600° it suffered absolutely no loss of weight. The weighed sulphate was first dried in an air-oven in a double platinum crucible. The temperature was slowly raised to 325°. The drying was completed by maintaining this temperature for an hour. Then the crucible, without being cooled, was introduced into a little gas furnace, inside another platinum dish. The temperature of the furnace was raised to a white heat, and maintained for one hour. Then the crucible was allowed to cool in a phosphoric anhydride desiccator for ten minutes only, in order to avoid absorption of dry gases by leaving it too long. This absorption is very slight, but it falsifies any correction of weight for the pressure of the air.

The crucible was then weighed and heated a second time. There was generally no change in the second weighing.

In order to prove that the oxide retained no trace of sulphur, one part of the oxides was fused with a mixture of pure sodium carbonate and sodium nitrate. When the fused mass was taken up with water no sulphuric acid was ever detected in the filtered liquid.

The weighings were performed with a Curie's aperiodic balance, sensitive to one-tenth of a mgrm.

The initial and final states of the transformation being perfectly definite, and the method being affected by no causes of loss, the results can be affected only by accidental errors. The exiguity of these can be seen from the following table :—

O = 16, H = 1·008, S = 32·06.

Weight of sulphate, $Eu_2SO_4\,8H_2O$.	Weight of oxide, Eu_2O_3.	Atomic weight.
1·3501	0·6455	152·032
1·5054	0·7197	152·009
1·5213	0·7274	152·054
1·2881	0·6159	152·056

The mean value is 152·03, with an error ± 0·02

These numbers agree with those obtained by Urbain and Lacombe.—*Comptes Rendus.*, 1908, cxlvi., 473.

SELENIUM NITRIDE.

By VICTOR LENHER and E. WOLESENSKY.

WHEN ammonia gas is brought in contact with selenyl chloride in the cold, the reaction, according to Michaelis (*Jeanische Zeit.*, vi., 91), proceeds as follows: $6SeOCl_2 + 16NH_3 = 3SeO_2 + 3Se + 4N + 12NH_4Cl$. Michaelis in studying this reaction, brought ammonia gas directly in contact with selenyl chloride. At low temperatures only slight action was noted, while at higher temperatures, the reaction proceeds with evolution of heat.

In studying the behaviour of ammonia gas when conducted into a solution of selenyl chloride in either benzene or oluene, the reaction under these conditions was found to be of a different character than that indicated by the equation of Michaelis, one of the principal products being the nitride of selenium.

When dry ammonia gas is conducted into a strong solution of selenyl chloride in benzene or toluene, considerable heat is evolved and a brick-red precipitate forms, which, when treated with cold water, leaves a bright red residue. This residue when dissolved in nitric acid shows complete absence of chlorine, but a large percentage of selenium.

Quantitative data obtained on the precipitate obtained before treatment with water seem to indicate that it consists of ammonium chloride, selenium, selenium dioxide, and a small amount of selenium nitride.

By using a more dilute solution of selenyl chloride (2 to 4 per cent) in benzene, the reaction is materially moderated, and a buff-coloured precipitate appears, which on drying becomes orange-red. This material, when washed with cold water to remove the ammonium salts, and then extracted with potassium cyanide to remove the free selenium, left a brick-red nitride, which proved to be a highly explosive body. Analyses showed:—

	I.	II.	Calculated for SeN.
Se	84·7	84·7	84·8
N	15·5	16·3	15·2

Espenscheid (*Ann. Chem.*, cxiv., 101) obtained this compound by conducting dry ammonia gas diluted with hydrogen over selenium tetrachloride cooled by a freezing mixture, and obtained a brown mass which, when treated with water and extracted with carbon bisulphide or potassium cyanide, left an orange red powder of SeN, which exploded violently when struck or when brought in contact with chlorine or hydrochloric acid either in the gaseous form or in concentrated solution. When heated to 150° it began to darken, and exploded at 200°. On the other hand, the nitride obtained by the action of ammonia on selenyl chloride dissolved in benzene begins to darken at a comparatively low temperature, and explodes at 130°. When the substance has been carefully purified and is thoroughly dry a slight shock will cause it to detonate violently.

Verneuil, in a manner differing but slightly from that of Espenscheid, obtained a similar substance, but to which he ascribed the formula Se_3N.

The result of the interaction between ammonia and selenyl chloride in benzene solution evidently depends on the temperature and the concentration of the reacting substances. When the temperature is not too high and the solution is dilute, a highly explosive compound of selenium and nitrogen is formed which has the composition SeN. If, however, a solution of considerable strength be employed, the temperature of the reaction causes the separation of a large quantity of free selenium.—*Journal of the American Chemical Society*, xxix., No. 1.

Phosphorus Oxybromide.—E. Berger.—Phosphorus oxybromide can be prepared by mixing the pentabromide and phosphoric anhydride, and heating the mixture until bromine begins to be evolved. The mass then gradually liquefies, and at the end of the reaction it is distilled. The yield is 85 per cent, the equation being $3PBr_5 + P_2O_5 = 5POBr_3$. The oxybromide fuses at 55—56°, and boils at 189·5° under 774 mm. pressure. Its vapour density is normal.—*Comptes Rendus*, cxlvi., No. 8.

THE IODOMETRIC DETERMINATION OF COPPER.*

By F. A. GOOCH and F. H. HEATH.

WHEN potassium iodide is added to a suitable solution of a cupric salt, cuprous iodide is precipitated while iodine equivalent to the amount of iodine fixed in the cuprous iodide is liberated. This reaction has been made the basis of an iodometric method for the determination of copper. The first suggestion of such a method appears to have been made by De Haen in 1854. In this process cupric sulphate was treated in solution with potassium iodide and the free iodine determined by sulphurous acid according to Bunsen. From the amount of iodine thus found the copper was calculated, according to the equation $2CuSO_4 + 4KI \rightarrow 2K_2SO_4 + Cu_2I_2 + I_2$.

This method was mentioned in the following year by Mohr ("Titrirmethode," p. 387), with the modification suggested by Schwarz that the free iodine be determined by sodium thiosulphate instead of by sulphurous acid. E. O. Brown (*Journ. Chem. Soc.*, x., 65), apparently without knowledge of De Haen's previous work, proposed, in 1857, similar procedure, and in 1868 the method with slight modification was presented again by Rümpler (*Journ. Prakt. Chem.*, cv., 193). Concerning the utility of the method opinions have varied. Mohr never favoured it. So late as 1877 Mohr ("Titrirmethode," 5 Aufl., 288), after quoting Meidinger to the effect that cuprous iodide freshly precipitated and washed is capable of taking up iodine, and Carl Mohr's criticism that potassium iodide acts upon cuprous iodide according to the concentration, states that the method is not exact and has nowhere found practical application. On the other hand, Fresenius ("Quant. Anal," 1875, 6te Aufl., 335) recommended the method for the determination of small amounts of copper, noting that ferric salts and other substances capable of setting free iodine from an acidified solution of potassium iodide must not be present, and indicated the most favourable procedure. The copper salt treated, he says, should be the sulphate, preferably in neutral solution, though a moderate amount of sulphuric acid is not objectionable. Much free sulphuric acid and any free nitric acid should be neutralised by sodium carbonate, and the precipitate dissolved in acetic acid, an excess of which does no harm in the iodometric process.

Of recent writers some have favoured the method while others have commented upon it unfavourably. Low (*Journ. Am. Chem. Soc.*, xviii., 468; xxiv., 1083) has been outspoken in praise, to the extent of declaring a preference for this method in the most accurate technical work over all other methods, even the electrolytic method.

According to Low's earlier modification, metallic copper is dissolved in nitric acid, the solution is freed from nitrogen oxides by boiling, a considerable amount of zinc acetate is added, and in the solution having a volume of 50 cc. an excess of solid potassium iodide is dissolved. Zinc acetate is preferred to sodium acetate to take up the free nitric acid. It is said that an excess of potassium iodide is necessary to insure rapidity of action and is harmless. According to the later modification of this method Low prepares the cupric salt by dissolving the metal in nitric acid (sp. gr. about 1·20), boils the solution, adds bromine water to destroy the nitrogen oxides, boils to expel the bromine, treats with ammonium hydroxide in excess, adds acetic acid, and boils again if necessary to get a clear solution. The advantage of using an excess of potassium iodide is emphasised, and the statement is made that unless an excess of this reagent is present the reaction does not proceed to completion until the titration of the free iodine takes place. Low recommends the use of 1 grm. of potassium iodide, an excess of 0·6 grm., for every 0·075 grm. of copper.

Various criticisms have also been made of the reaction

* From the *American Journal of Science*, [4], xxiv., p. 65.

when employed in gravimetric estimations of the cuprous iodide precipitated. Pisani (*Comptes Rendus*, xlvii., 294) notes that potassium iodide can be used to effect the precipitation of cuprous iodide, and that satisfactory separations may thus be brought about.

Flajolot (*Journ. Prakt. Chem.*, xi., 105) states that potassium iodide cannot be used as the precipitant since it dissolves cuprous iodide, and recommends the precipitation of cuprous iodide from the solution of copper sulphate slightly acidified with sulphuric acid, by treatment with sulphurous acid and hydriodic acid. Kohner (*Zeit. Anal. Chem.*, xxvii., 213) affirms that cuprous iodide is soluble both in hydriodic acid and in potassium iodide.

Browning (*Am. Journ. Sci.*, 1893, [4], xlvi., 280) has shown that cuprous iodide may be satisfactorily precipitated and separated from a cadmium salt by adding to a solution of cupric sulphate a moderate excess of potassium iodide (1 grm. to 4 grms. in all), expelling iodine and hydriodic acid by evaporating the solution to dryness, and treating the residue with water, filtering off the precipitate, and weighing upon asbestos in the perforated crucible.

As a result of elaborate study Moser (*Zeit. Anal. Chem.*, 1904, xliii., 597) has reached the conclusion that the reaction by which cuprous iodide is formed from potassium iodide and cupric sulphate in neutral solution is complete at very high concentration of the solution; that the completeness of the reaction is greatly affected by the volume of liquid; that the amount of potassium iodide employed is almost without influence either in neutral solution or in acid solution; and that the presence of free sulphuric acid even in large amounts or of hydrochloric acid present in amount equivalent to the cupric sulphate is advantageous. Moser recommends, therefore, the addition of sulphuric acid for the purpose of bringing the reaction to completion. To the cupric sulphate (about 0·6 grm.) dissolved in 50 cc. of water contained in a 300 cc. stoppered flask are added 5 cc. of 10N/1 H_2SO_4, and 2 grms. of solid potassium iodide; the mixture is shaken frequently for two minutes, and the free iodine is titrated by sodium thiosulphate, with stirring, to the end-reaction of the starch indicator.

According to Fernekes and Koch (*Journ. Am. Chem. Soc.*,, xxvii., 1229), an excess of acetic acid does not influence titrations, while a certain amount of potassium iodide—1·5 to 2 grms. for 0·0038 grm. of copper, and 2·5 grms. for 0·0939 grm. of copper—must be added to bring about complete action in a volume of 100 cc.

Quite recently Cantoni and Rosenstein have tested the reaction between potassium iodide and a cupric salt under various conditions (*Bull. Soc. Chim.*, 1906, [3], xxxv., 1067); but these investigators do not give the absolute values of the amounts of copper taken and found, merely recording the relative effects of varying conditions. From the record of their results it would appear that a fivefold increase of the minimum amount of potassium iodide added to portions of 100 cc. of solution containing the same amount of copper salt is without influence upon the result; that increase of volume from 100 cc. to 350 cc., other conditions being the same, may affect the results by as much as 5 per cent of their value. The authors conclude that the method gives good results under properly controlled conditions.

So evidence and opinions as to the effects of various conditions in the process are contradictory.

The chief matters of difference concern the influence of an excess of potassium iodide used as the precipitant, the dilution at which the precipitation should take place, and the effects of acids upon the formation of the cuprous iodide. We have thought it desirable, therefore, to again study these points experimentally.

In the experiments detailed in Table I., small amounts of a solution of pure copper sulphate, standardised by the electrolytic method and containing 0·0020 grm. to 1 cc., were drawn from a burette and treated with potassium iodide in solution. In some of the experiments the iodine set free was titrated without previous dilution, while in others the mixture was diluted previous to the titration. The volumes at precipitation and at the end of the titration are noted. In Series A is shown the effect of twice the amount of potassium iodide theoretically required, at volumes varying from 30 cc. to 80 cc. at precipitation and from 36 cc. to 86 cc. at the end of the titration.

In the experiments of Series B the effect of increasing the amount of potassium iodide under conditions otherwise similar is studied. In Series C is shown the effect of large dilution of the solution containing the amount of potassium iodide used in the experiments of Series A.

TABLE I.—*Effects of Volume of Solution and Concentration of Potassium Iodide.*

Copper taken as $CuSO_4$.	Volume at precipitation.	Volume at end of titration.	KI used.	Copper equivalent to 1 found by $Na_2S_2O_3$.	Error in terms of copper.
Grm.	Cc.	Cc.	Grms.	Grm.	Grm.
			A.		
0·0400	30	36	0·4	0·0391	−0·0009
0·0400	40	46	0·4	0·0387	−0·0013
0·0400	50	56	0·4	0·0388	−0·0012
0·0400	60	66	0·4	0·0391	−0·0009
0·0400	80	86	0·4	0·0391	−0·0009 (*a*)
			B.		
0·0400	40	46	0·8	0·0400	—
0·0400	30	36	8·0	0·0399	−0·0001 (*b*)
0·0400	45	54	13·0	0·0599	−0·0001 (*b*)
			C.		
0·0400	30	200	0·4	0·0033	−0·0367 (*c*)
0·0400	30	300	0·4	0·0004	−0·0396 (*c*)
0·0400	30	500	0·4	0·0004	−0·0395 (*c*)
0·0400	30	1000	0·4	0·0005	−0·0395 (*c*)

(*a*) End-point slow in coming.
(*b*) The Cu_2I_2 was completely dissolved in KI before titrating.
(*c*) Visible precipitation of Cu_3I_2 took place on titrating the free iodine.

From the results recorded in A it appears that, though the excess of potassium iodide is about 0·2 grm., the amount used being approximately twice that required by the theory, the reaction resulting in the formation of cuprous iodide and liberation of iodine is not quite complete. On the other hand, the results recorded in B show plainly that at similar dilution the reaction yields excellent indications of the amount of copper handled when the amount of potassium iodide is considerably more than the theoretical amount, varying from four to sixty times the amount required by theory, the absolute excess varying from 0·6 to 12·7 grm.; and this is true even though the amount of potassium iodide is sufficient to dissolve completely the cuprous iodide formed.

So it is plain that the amount of potassium iodide used has within limits an influence upon the result. In a volume of about 50 cc. an excess of 0·2 grm. of potassium iodide is not enough, while an excess of 0·6 grm. appears to be sufficient. Beyond this limit the addition of potassium iodide has no appreciable effect. It is natural to suppose that at high dilutions a larger excess of potassium iodide would be needed to complete the reaction than is required at lower dilutions. Table II. contains the results of experiments made to test the efficiency of potassium iodide in precipitating 0·0010 grm. of copper, taken as sulphate, in a volume of 100 cc.

TABLE II.—*Effect of Potassium Iodide in Neutral Solutions at a Fixed Volume of* 100 cc.

Copper taken as $CuSO_4$.	KI used.	Acid added.	Volume.	Copper found.	Error.
Grm.	Grms.	Cc.	Cc.	Grm.	Grm.
0·0010	1	—	100	0·0003	−0·0007
0·0010	2	—	100	0·0006	−0·0004
0·0010	3	—	100	0·0009	−0·0001
0·0010	4	—	100	0·0009	−0·0001
0·0010	3	—	100	0·0013	+0·0003

From the results of these experiments it appears that while the action upon a milligrm. of copper, taken as the sulphate in 100 cc. of solution containing no free acid, is not completed by 1 grm. or 2 grms. of potassium iodide, it is practically complete when an excess of 3 to 5 grms. of potassium iodide is present. The fact is again emphasised that up to a certain proportion, increasing with the dilution, the amount of potassium iodide influences the completeness of the reaction in neutral solution. An excess of potassium iodide amounting to 0·6 to 1 grm. in a volume of 50 cc., and to from 3 to 5 grms. in a volume of 100 cc., will precipitate completely 0·0020 grm. of copper. In the practical application of these facts it must be borne in mind that it is the excess of potassium iodide and not the full amount added which is important.

So we may very properly fix upon 2 grms. as the uniform amount of potassium iodide suitable for the precipitation of cuprous iodide in a volume of 50 cc. of a neutral solution containing 0·2 grm. of copper; and upon 5 grms. as the amount of potassium iodide suitable in neutral solutions having a volume of 100 cc.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 19th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President in the Chair.

(Concluded from p. 167).

62. "*The Constitution of Thiocyanates containing an Electronegative Group.*" By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

Examination of a number of acylthiocarbimides shows the contained ·NCS group to have the same refraction value as in hydrocarbon thiocarbimides; since this holds also for acetyl "thiocyanate" (Hawthorne, *Trans.*, 1906, lxxxix., 556), it seems probable that the ·NCS group is contained equally in acyl "thiocyanates" and acylthiocarbimides, true acyl thiocyanates being still unknown.

Moreover, the partial decomposition with formation of thiocyanic acid characteristic of "acyl thiocyanates" also takes place in the case of acylthiocarbimides, the latter undergoing this change with caustic alkalis or alkaline bases, but not with arylamines. The chemical differences between acyl thiocyanates and acylthiocarbimides are due, not to diversity of constitution, but to the variable resistance offered by the acyl radicle to its separation from the combined ·NCS group; when this is high, thiocarbimidic function preponderates, and when low, thiocyanic decomposition. Hence external circumstances, in so far as they affect that separation, may predominate in determining the direction of change.

Diphenylamine unites with acetyl, benzoyl, carboxymethyl- or carboxyethyl-thiocarbimide, forming an *a*-acyl-*bb*-diphenylthiocarbamide. a-*Acetyl*-bb-*diphenylthiocarbamide*, m. p. 141° (corr.), gives with alcoholic potash aa-*diphenylthiocarbamide*, m. p. 212°, and by distillation yields acetylthiocarbimide, identical with the compound produced from acetyl chloride and metallic thiocyanates; with acetic anhydride, *aa*-diphenylthiocarbamide regenerates *a*-acetyl-*bb*-diphenylthiocarbamide.

a-*Benzoyl*-bb-*diphenylthiocarbamide*, a-*carboxymethyl*-bb-*diphenylthiocarbamide*, *and* a-*carboxyethyl*-bb-*diphenylthiocarbamide* melt at 135°, 128°, and 125° respectively; by lead or silver salts these trisubstitution compounds are desulphurised with difficulty, or not at all.

a-*Carboxymethyl*-ab-*diphenylthiocarbamide*, isomeric with the *bb*-diphenyl derivative, is obtained from methyl chlorocarbonate and thiocarbanilide; it melts at 106°, and, like *a*-carboxyethyl-*ab*-diphenylthiocarbamide, is desulphurised readily by alkaline salts of silver or lead.

63. "*The Quantitative Conversion of Aromatic Hydrazines into Diazonium Salts.*" By FREDERICK DANIEL CHATTAWAY.

All primary aromatic hydrazines can be quantitatively converted into the corresponding diazonium salts either by chlorine or by bromine.

If either halogen be allowed to act at a low temperature on the hydrazine dissolved in alcohol, the diazonium salt separates out in a pure state.

Unless, however, the solid salt is required, the operation can be most easily carried out by dissolving the hydrazine in glacial acetic acid, cooling the solution to about −15° by the addition of crushed ice, and either passing in a rapid stream of chlorine or adding the calculated quantity of bromine dissolved in acetic acid and similarly cooled by ice.

The formation of the diazonium salt is without doubt effected by a substitution of two atoms of hydrogen in the hydrazino-group by halogen, followed by the elimination of halogen acid, thus:—

$$C_6H_5\cdot N\cdot H \;\rightarrow\; C_6H_5\cdot N\cdot Cl \;\rightarrow\; C_6H_5\cdot N\cdot Cl$$
$$\quad\;\; |\qquad\qquad\quad |\qquad\qquad\quad \|$$
$$\quad H\cdot N\cdot H\qquad\quad H\cdot N\cdot Cl\qquad\quad N$$

As in other cases where hydrogen attached to nitrogen is replaced by halogen, an additive product is probably first formed, in this instance by the addition of four halogen atoms, each nitrogen atom becoming quinquivalent, the elimination of halogen acid then gives rise to the diazonium salt, which being stable under the conditions of the experiment can be isolated.

64. "*Quantitative Separation of Thallium from Silver.*" By JAMES FREDERICK SPENCER and MARGARET LE PLA.

A quantitative separation of the salts of silver and thallium is effected by treating the mixture with a stream of chlorine, whereby the thallium is oxidised to the very soluble thallic chloride and the silver is precipitated as silver chloride. After removing the latter, the solution is concentrated, and reduced by means of sulphur dioxide (either liquid or gaseous). The excess of sulphur dioxide is removed by boiling, and the thallium precipitated as thallous iodide, filtered, washed, and dried at 140°. The results are quantitative, and are obtained very quickly.

Thallous chloride was found to be more soluble in potassium carbonate than in water, for whereas water dissolves 3·86 grms. per litre at 25°, a 5N-solution of potassium carbonate dissolves 21·84 grms. per litre at the same temperature.

65. "*Molecular Volumes of the Nitrites of Silver, Mercury, and the Alkali Metals.*" By PRAFULLA CHANDRA RAY.

The author finds that the molecular volumes of the nitrites of lithium, sodium, potassium, silver, and mercury are 63·44, 63·98, 88·88, 69·16, and 83·04 respectively.

66. "*Lithium Nitrite and its Decomposition by Heat.*" By PRAFULLA CHANDRA RAY.

Lithium nitrite is a mono-hydrated salt, and does not crystallise with half a molecule of water as stated by Lang.

In its general properties it resembles the nitrites of the other alkali metals.

67. "*The Existence in Aqueous Solutions of a Univalent Cadmium Ion, a Subvalent Thallium Ion, and a Bivalent Bismuth Ion.*" By HENRY GEORGE DENHAM.

The method of continuous circulation used by Denham and Allmand (*Trans.*, 1908, xciii., 424) to prove the existence of a univalent lead ion in aqueous solution has been applied to investigate the existence of similar ions of other metals.

A hot solution of cadmium sulphate was kept circulating over a column of granulated cadmium, and in thirty-six hours well-marked crystals began to appear, proving that the ionic reaction $Cd^{\cdot\cdot} + Cd \rightarrow 2Cd^{\cdot}$ had taken place with absorption of heat, and had been reversed in the cold part of the apparatus.

Granulated thallium, in contact with a solution of

thallous sulphate, gave a similar crystalline deposit in three days, demonstrating the reaction $Tl^{\cdot} + Tl \rightarrow Tl_2^{\cdot}$, and in the light of this experiment it is considered probable that the darkening of thallous haloid salts on exposure to sunlight is due to the formation of coloured sub-haloid salts, analogous to the case of silver.

Bismuth, heated in contact with a solution of the oxychloride in hydrochloric acid, soon gave unmistakable evidence of the production of the ion $Bi^{\cdot\cdot}$, but it is of interest that no evidence for such an ion was obtained in the case of arsenic or antimony. Nickel and nickel sulphate solution showed no signs of crystals, although in this case a suboxide Ni_2O has been described.

68. "*Note on the Oxidation of Phenylhydrazine by Caro's Acid.*" By JOHN CANNELL CAIN.

In explaining the mechanism of the oxidation of aromatic hydrazines by free oxygen and other oxidising agents, Chattaway (*Trans.*, 1907, xci., 1323; 1908, xciii., 270) assumes the formation of an unstable hydroxyhydrazine which immediately loses water and nitrogen, thus:—

$$\begin{matrix} R & H \\ \dot{N}—H \\ H & OH \end{matrix} \rightarrow \begin{matrix} R{\cdot}H \\ N_2 \\ H{\cdot}O{\cdot}H \end{matrix} .$$

The presence of such a hydroxyhydrazine was not observed by Chattaway, as the oxidation always proceeded with immediate evolution of nitrogen, but striking confirmation of this hypothesis is afforded when phenylhydrazine (1 mol.) is oxidised by Caro's acid (equivalent to 1 atom of oxygen). When ice-cold, neutral, aqueous solutions (saturated with ether) of these agents are mixed together, a greenish-yellow coloration is immediately produced; this persists for some seconds, when vigorous evolution of nitrogen begins, the greenish-yellow coloration gives place to a yellow turbidity, and benzene appears on the surface of the liquid. On extraction with ether, the only products are benzene and azobenzene, no diazo-compound being formed. The same phenomenon is observed if equimolecular amounts of phenylhydrazine and oxygen (as Caro's acid) are used, or if the solutions are rendered slightly alkaline or acid before mixing. It appears highly probable that the greenish-yellow coloration is due to the presence of a hydroxyhydrazine as postulated by Chattaway, and that this then undergoes disruption into benzene and azobenzene.

No explanation is given by Chattaway of the mechanism by which azo-compounds are formed in the reaction, but it seems probable that two molecules of the hydroxyhydrazine may decompose according to the scheme:—

$$\begin{matrix} R{\cdot}NH{\cdot}\dot{N}H{\cdot}OH \\ R{\cdot}NH{\cdot}\dot{N}H{\cdot}OH \end{matrix} \rightarrow \begin{matrix} R{\cdot}NH \\ | \\ R{\cdot}NH \end{matrix} + \begin{matrix} N \\ \| \\ N \end{matrix} + 2H_2O,$$

giving rise (in the case of phenylhydrazine) to hydrazobenzene which would be immediately oxidised to azobenzene.

Confirmation of this is perhaps furnished by Chattaway's isolation, in one experiment using 100 grms. of phenylhydrazine, of a very small amount of a white, crystalline solid melting at 125°. As this substance was not recrystallised, it appears likely that it was hydrazobenzene, which melts at 131° (Gattermann, "Practical Methods of Organic Chemistry," gives 126°).

69. "*Some Reactions of Keten.*" By FRANCES CHICK and NORMAN THOMAS MORTIMER WILSMORE.

No better source for the preparation of keten by the "pyrogenic" method than acetic anhydride has been found. With this substance a yield of about 10 per cent of fairly pure keten is readily obtained. Acetone is more easily split up, but the resulting keten is too impure for most purposes. Glacial acetic acid is not attacked by the hot wire.

All attempts to prepare glycollaldehyde by the action of keten on water were unsuccessful, only acetic acid being formed. The aldehyde reactions previously mentioned (*Trans.*, 1907, xci., 1941) were found to be due to traces of formaldehyde in the crude keten. Carefully fractionated samples of keten, such as those used for analysis, did not give the aldehyde reactions. Similarly, with alcohol only ethyl acetate was formed.

Gaseous keten is slightly soluble at the ordinary temperature in benzene, chloroform, carbon tetrachloride, and ether, and very soluble in acetone and in acetic anhydride. Liquid keten is miscible without chemical reaction with most organic solvents which are liquid at its boiling-point, including alcohol.

By the action of liquid hydrogen chloride on liquid keten at the ordinary temperature, acetyl chloride, boiling at 51—52°, was obtained. There was no sign of the presence of chloroaldehyde or of dichloroethyl acetate, but a small quantity of an oil with a terpene-like smell was obtained from the residue. In the same way with liquid hydrogen sulphide, thioacetic anhydride, boiling at 55—58°, was formed.

Keten does not react with oxamide, benzamide, nitrosoaniline, acetyl chloride, amyl nitrite, or ethyl iodide. Also, liquid keten does not react at the ordinary temperature with liquid cyanogen. It reacts slowly, however, with anhydrous hydrocyanic acid, but does not appear to form acetyl cyanide.

70. "*Para- and Meta-nitrosoacetanilide.*" By JOHN CANNELL CAIN.

Para- and meta-nitrosoacetanilide have been prepared by oxidising the corresponding monoacetylphenylenediamine with Caro's acid.

p-*Nitrosoacetanilide* exists in two modifications: the unimolecular form is green, and melts at 176° with decomposition, whilst the bimolecular variety is colourless, and melts at 180—181° without decomposition.

This appears to be the first instance of both modifications of a nitroso-compound existing in the solid condition.

m-*Nitrosoacetanilide* also exists in two forms: the unimolecular modification, which was not isolated as it could not be obtained free from the bimolecular variety, remains as a green residue from its ethereal solution. This, on crystallisation from alcohol, furnishes the bimolecular form in pale, yellowish-brown needles melting at 111°.

71. "*Labile Isomerism among Acyl-salicylamides and Acyl-hydroxyamines.*" By ARTHUR WALSH TITHERLEY.

A reply to Auwer's criticism (*Ber.*, 1907, xl., 3506).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Mr. W. P. Byrne, C.B., Mr. Greville Douglas, Miss Forbes, Mrs. Hamilton, Mr. W. A. Johnstone, Dr. H. W. McConnel, Mr. A. K. Nicholson, Mr. J. Oswald, J.P., and Mr. J. E. Stead, J.P., F.R.S., were elected Members. The following are the lecture arrangements after Easter:—Mr. Gerald Stoney, two lectures on "The Development of the Modern Turbine and its Application"; Prof. F. T. Trouton, two lectures on (1) "Why Light is Believed to be a Vibration," (2) "What it is which Vibrates" (Experimental Course); Prof. William Stirling, two lectures on "Animal Heat and Allied Phenomena"; Mr. W. Bateson, three lectures on "Mendelian Heredity"; Dr. Alexander Scott, three lectures on "The Chemistry of Photography" (Experimental Course); Mr. G. F. Scott Elliot, two lectures on "Chile and the Chilians"; Mr. Laurence Binyon, two lectures on "Japanese Prints"; and Dr. H. W. Davies, two lectures on "The Art of Bach and Future Developments" (with musical illustrations). The Friday Evening Meetings will be resumed on May 1st, when Prof. Joseph Larmor will deliver a discourse on "The Scientific Work of Lord Kelvin" (with experiments and typical apparatus illustrative of his discoveries and inventions). Succeeding discourses will probably be given by Dr. J. Y. Buchanan, Dr. H. T. Bulstrode, Prof. Dr. J. C. Kapteyn, of the University of Groningen, Sir Ralph Payne-Gallwey, Bart, Prof. Sir James Dewar, and other gentlemen.

NOTICES OF BOOKS.

Stoichiometry. By SYDNEY YOUNG, D.Sc., F.R.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

IN many respects this is the most interesting of the series of text-books of physical chemistry yet published, and it seems likely to be the one which will have the widest circulation, for it deals with the fundamental principles of physical chemistry in an admirably clear way. Overlapping with the other volumes of the series has been skilfully avoided, although the title stoichiometry has been interpreted in a wide sense. The introductory chapters deal with the laws of chemical combination and the properties of gases, and then methods of determining atomic weights are described, and the results obtained are tabulated. The Periodic Law is discussed in considerable detail, Lothar Meyer's table being adopted as preferable to Mendeleeff's. The properties of liquids, the kinetic theory of gases, and the properties of solids are next treated, and the chapter on mixtures is perhaps the most difficult in the book; in it the author's own important researches are touched upon. The introduction to the series, by Sir William Ramsay, is printed in this volume, to which it properly belongs.

A Treatise on Chemistry. By H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Volume II. "The Metals." New Edition. London: Macmillan and Co., Ltd. 1907.

THE fourth edition of Sir Henry Roscoe and Prof. Schorlemmer's well known treatise on inorganic chemistry has been thoroughly revised and much enlarged. The second volume now contains the section on chemical crystallography, which was formerly included in the first volume on the non-metallic elements, and much new matter has been added, dealing with recent advances in our knowledge of the chemistry of the metals and their compounds. Thus a new section on the radio-active elements gives a *résumé* of the most important work which has been done on the subject, dating back to the investigation of the phenomena of high vacua in 1870. The metals of the rare earths are treated much more fully than before, and the outline of the methods of separating these elements includes a valuable table which shows very clearly the process of decomposing the original earths. As in the earlier editions, technical processes, for example, glass-making, are treated in sufficient detail for the student of general chemistry, who can base a specialised knowledge of any technical branch very satisfactorily upon the information he will find in the treatise, the most modern processes only being considered.

Technical Dictionary. Vol. II. By KURT DEINHARDT and ALFRED SCHLOMANN. Edited by CHAS. KINZBRUNNER, A.M.I.E.E. London: Archibald Constable and Co., Ltd. 1908.

THIS technical dictionary in six languages, English, French, German, Italian, Spanish, and Russian, will be a boon to engineers and scientific men generally who have occasion to refer to foreign periodicals and text-books. It is excellently planned and arranged, and although it contains an immense amount of matter, space has been so well economised that it is not by any means of unwieldly size. On the other hand, there is no niggardliness of explanation, nor are any baffling abbreviations used, which often waste much time and patience, and the dictionary is excellently illustrated by clear little diagrams. An alphabetical index is provided, showing where every word is to be found, and although this means looking up an unknown word twice it is undoubtedly the best plan. The present volume deals with all branches of electrical engineering with the exception of traction, which is deferred to a later volume on railway engineering. Telegraphy and telephony are included and a limited amount of electro-chemistry. The dictionary can be confidently recommended as one of the most valuable of its kind to be procured.

British Minerals and Where to Find Them. By J. STEPHEN NEIL, F.G.S., F.C.I.S. London: Thomas Murby and Co.

STUDENTS of geology will find this book handy as a reference list giving the minerals, rare and otherwise, which are to be found in Great Britain. It is divided into two parts. In the first the minerals are classified according to the localities in which they occur, so it is very easy for the mineralogist to ascertain what specimens he may expect to find in any district. The second part gives an alphabetical list of minerals, together with short descriptions of their crystalline form, their colour, lustre, and occurrence; some notes on the chemical composition of some of the commoner minerals would probably be appreciated, but the list as it stands will satisfactorily fulfil its chief aim of helping the student to identify specimens which are unknown to him.

Matriculation Directory, January, 1908. Cambridge: The University Tutorial Press.

THE Matriculation Directory, No. XLVIII., issued by the University Correspondence College, gives reprints of the papers set in the examination held in January this year, together with solutions of some of them and criticisms of the questions. In addition the book contains a good deal of sound advice on the choice of subjects and methods of preparation, given by tutors who are well acquainted with the scope of the examination and are thoroughly qualified to assist intending candidates.

Merck's 1907 *Index.* Third Edition. New York: Merck and Co.

THIS book, which is well known as a useful handbook for druggists and doctors, has been enlarged by the addition of the names, physical constants, physiological effects, doses, and therapeutic uses of the newest chemicals and drugs which have come into use recently. The products which can be obtained from the firm of Merck and Co. are all specially marked, but others are also included for the sake of completeness, and although a price list is not given a kind of key is provided by which the comparative costs of the preparations can be ascertained.

Man and His Future. By WILLIAM SEDGWICK. London: T. Werner Laurie. 1907.

A GENUINE attempt to put before the reading public the scientific facts which seem to show what may be man's ultimate destination and destiny is always to be treated with respect, and this book is a good example of a class of literature which attracts many readers. It is easily written, and the author is an adept at stating his arguments forcibly and driving them well home; he may, perhaps, be forgiven a tendency to didactic writing, for the sake of the obvious loftiness of his aim and the strength of his convictions. The book is well worth reading by those who are interested in endeavours to solve the riddle of the universe, and who like their science in easily digested forms and small quantities.

The Education of To-morrow. By JOHN STEWART REMINGTON. London: Guilbert Pitman. 1907.

THE author of this work describes his book as the disconnected notes of a man who has watched very carefully the results of modern English education, but such a view of it does not give an adequate idea of the value of the suggestions he has to offer. Unpretentious as the volume is, it discusses sensible practical views on the best ways of truly educating the mind of a child, and the criticisms of

modern methods, though sweeping and expressed with warmth, are, on the whole, justified. Many of the ideas are by no means new, and, in fact, have been put forward by the best known educationists of the day, who, rejecting traditional methods, aim before all things at the development of the reasoning power, the resourcefulness and initiative of the pupil; but as yet these ideas appear to have made but little headway. The misuse of examinations is another subject which the author discusses, and many of his readers will agree with his opinions, and will perhaps wish that he had explained rather more fully the remedies for a state of affairs which is undoubtedly unsatisfactory in the eyes of thoughtful men.

Technologie der Fette und Ole. ("Technology of Fats and Oils"). By GUSTAV HEFTER. Vol. II. Berlin: Julius Springer. 1908.

IN this comprehensive work the origin, raw material, preparation, properties, and uses of the animal and vegetable oils, fats, and waxes are discussed very fully. Methods of analysis are not included, but all other branches of the fat industry are treated with the greatest completeness, so that the work will be indisensable for chemists and manufacturers. Much statistical material is given, and modern processes are fully explained. Methods of preparation are considered at some length, especially if they are in any way unusual (*e.g.*, as in the case of cotton or palm oil) or otherwise deserving special attention.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

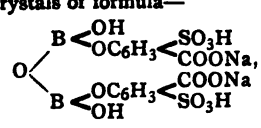
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 8, February 24, 1908.

Causes of the Allotropic Transformation of Yellow Phosphorus dissolved in Essence of Terebenthene.—Albert Colson.—Yellow phosphorus dissolved in essence of terebenthene is transformed into red phosphorus at 250—280°. This change does not appear to be due to a simple molecular condensation, but rather to be the result of a succession of chemical actions forming a closed cycle. Hydrogen compounds appear to be formed, and if their formation is stopped or diminished, the transformation is also either stopped altogether or retarded.

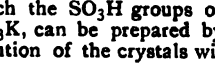
Isomeric Modification of Hydrated Hypovanadic Acid.—Gustave Gain.—Hydrated hypovanadic acid, $V_2O_4.2H_2O$, is red, but loses its colour when kept from contact with the moisture of the air, and becomes olive-green. This change is not due to hydratation, as it takes place in the perfectly dry acid, and it seems probable that the two hydrates are isomeric modifications. Moreover, the isomeric transformation persists in the salts which are obtained from the two forms. It is, however, possible to get to the same final state by adding to a solution of the sulphates the theoretical quantity of caustic potash necessary to saturate the sulphuric acid in the liquid. The liquid is then decolorised, potassium hypovanadate being formed, and it is no longer possible to distinguish between the two forms.

Action of Sulphosalicyclic Acid on Borax.—L. Barthe.—Borax and sulphosalicylic acid react together to form white crystals of formula—



which are decomposed by hydrochloric acid into sodium chloride, boric acid, and sulphosalicylic acid. The sodium potassium salt, in which the SO_3H groups of the above salt are replaced by SO_3K, can be prepared by saturating the boiling aqueous solution of the crystals with alcoholic potash.

Action of Nascent Hypolodous Acid upon Acids of General Formula R—CH=CH—CH$_2$—CO$_2$H.—J. Bougault.—*p*-Methoxyphenylisocrotonic acid, when dissolved in water containing sodium carbonate, gives with iodine the corresponding iodated lactone,—



In presence of large excess of sodium carbonate *p*-methoxybenzoylacrylic acid is obtained, $CH_3O—C_6H_4—CO—CH=CH—CO_2H$. Methylenedioxybenzoylacrylic acid can be obtained similarly, starting with methylene dioxyphenylisocrotonic acid. Thus, phenylisocrotonic acid and its derivatives substituted in the benzene nucleus, when treated with iodine in presence of a very large excess of sodium carbonate, have their side chains, $R—CH=CH—CH_2—CO_2H$, transformed into $R—CO—CH=CH—CO_2H$.

No. 9, March 2, 1908.

Lithium in Radio-active Minerals.—Sir William Ramsay and Alex. Cameron.—The authors do not think that lithium is the sole product obtained when salts of copper are treated with radium emanation, but that its presence can be explained only by supposing that such a change takes place. They have observed that the weight of the alkaline residue obtained is greater after than before treatment with the emanation, and that the spectrum of the residue shows the yellow sodium lines, and the potassium spectrum is also visible. Hence they are convinced that the decomposition of copper yields members of its group., *i.e.*, the alkaline series, and lithium is the most probable product. The sodium and potassium might be derived from the glass, and experiments to decide this question are in progress. The proportions of the products may depend upon unknown circumstances. It is possible that lithium is not a constant product of the action of the emanation on copper salts, but that the presence of other metals may determine its formation.

Direct Hydrogenation of Aromatic Quinones.—Paul Sabatier and A. Mailhe.—The aromatic quinones may be directly hydrogenated in contact with finely divided nickel at 200°, a good yield of the corresponding hydroquinones being obtained. When the temperature of hydrogenation is lowered the diphenols, which are derived from hydroquinone and its homologues, may fix six atoms of hydrogen in the nucleus, and thus the diols of the cyclohexane series can be obtained.

Oxidation of Platinum.—C. Marie.—Platinum appears to be much more readily oxidised at the ordinary temperature than has hitherto been believed. Thus potassium persulphate, bichromate, chlorate, and permanganate in sulphuric acid solution, and the ferricyanide and permanganate in alkaline solution, all oxidise plates of the metal. Ferric chloride in acid solution and hydrogen peroxide appear to have no action, but hot concentrated (not fuming) nitric acid oxidises the metal. The oxide obtained (PtO_2 ?) is dissociated by heat. It is soluble in hydrochloric acid, and in dilute sulphuric acid in presence of reducing agents.

Syntheses by Mixed Organo-metallic Compounds of Zinc. Ketone Alcohols.—E. E. Blaise and I. Herman.—The acid chloride of oxypivalic acid is transformed by the action of $ZnIC_2H_5$ into acetoxypseudobutylethyl ketone,—

$$CH_3—CO—O—C(CH_3)_2—COCl + Zn\langle^{I}_{C_2H_5} = CH_3—CO—O—C(CH_3)_2—CO—C_2H_5 + ZnICl.$$

When this acetoxyketone is saponified with aqueous potash

the products are formic acid, formic aldehyde, and liquid products, which can be separated into two parts. The first part consists of a mixture of ketones which can be separated into ethyl isopropyl ketone and an unsaturated ketone; the other part is composed chiefly of a polymer of the unsaturated ketone. This latter contains seven atoms of carbon, and its formation can be explained only by supposing that a molecular transformation or else a secondary reaction takes place.

Preparation and Properties of Crystalline *d*-Talite.—Gabriel Bertrand and P. Bruneau.—By a slight modification of the details of E. Fischer's method of reducing *d*-talonic acid the authors have obtained pure crystalline *d*-talite. It forms a crust of crystalline prisms in supersaturated alcoholic solutions. It is very soluble in water and is deliquescent. It fuses at 86°. Its most characteristic compound is the tribenzoic acetal already described by E. Fischer.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xli., No. 4, 1908.

Ketenes.—H. Staudinger and H. W. Klever.—The simplest ketene, $CH_2 : C : O$, can be prepared by the action of zinc on bromacetic acid bromide:—$CH_2Br.CO.Br + Zn = CH_2 : C : O + ZnBr_2$. Ketene boils at −56° and melts at −151°. It has an unbearable odour, recalling chlorine and acetic anhydride. It is poisonous. Metallic chlorides make it polymerise, yielding (in ethereal solution) resinous masses. Tertiary bases also cause polymerisation. With water it gives acetic acid; it decolorises an ethereal solution of bromine, forming bromacetyl bromide. Since it does not react with sodium or potassium powder it is probably not an oxyacetylene, which might be expected to have acid properties, but a true ketene of formula $CH_2 : C : O$.

Quantitative Determination of Phenol-hydroxyl Groups.—J. Herzog and V. Hancu.—Diphenyl urea chloride with phenols gives crystalline urethanes, which when treated with caustic potash give diphenylamine. The preparation and saponification of the phenol urethanes provide a means of determining the phenol hydroxyl groups, for the weight of diphenylamine shows how many hydroxyl groups were present in the corresponding phenol. Since 1 OH (17) in the phenol gives one molecule of diphenylamine (169) the weight of diphenylamine divided by 169/17, gives the weight of hydroxyl.

MEETINGS FOR THE WEEK.

Wednesday, 15th.—Microscopical, 8. "Dendritic Growths of Copper Oxide in Paper," by J. Strachan. "Nature's Protection of Insect Life" (illustrated by Lantern Slides in Three-colour Photography), by F. Enock.

THE CHEMICAL NEWS.

VOL. XCVII., No. 2525.

ON THE ORIGIN OF JET.*

II.

By PERCY E. SPIELMANN, A.R.C.S., A.I.C., B.Sc. (Hons.) Lond.

THE present article is based on the results of an examination of some samples of Whitby jet, made at the Eidgenössische Prüfungranstalt für Brennstoffe at Zürich, under the direction of Prof. E. J. Constam.

The substance was considered from the point of view of of a fuel; chemical analyses and determinations of heating values were made for comparison with similar results for coals of various kinds, examined in the ordinary routine of such a laboratory.

The following analyses and heating values (published here for the first time through the courtesy of Prof. Constam) have been obtained :—

	I. Cals.	II. Cals.	III. Cals.
Heat of combustion of sample, per grm.	8884	8889	8861
Deduct—			
Heat of combustion of sulphur	29	29	28
Water condensed in bomb = 0·6848 grm., of which the heat of evaporation is	411	411	411
Heating power per grm.	8444	8449	8422

Average.. .. .. 8438 cals.

Chemical Composition of Sample.

Moisture (loss of weight, 103° C.)	2·12 per cent
Ash	0·47
Combustible matter	97·46
	100·05

Elementary Analysis (per cent)

	I.	II.	Mean.
C	81·54	81·74	81·64
H	7·33	7·41	7·37
O	6·20	5·99	6·09
N	1·03	1·02	1·03
S	1·31	1·25	1·28
Ash	0·47	0·47	0·47
Moisture	2·12	2·12	2·12
	100·00	100·00	100·00

By means of the formula $81\,C + 290\left(H - \frac{O}{8}\right) + 25S - 6W$ (a modification of Dulong's formula), the calculated heat of combustion works out to 8511 cals., in excellent agreement with the experimental value 8538 cals.

From the above analysis, one obtains :—

Composition of Combustible Matter (per cent).

C	83·81
H	7·57
O	6·25
N	1·06
S	1·31
	100·00

Heating value, 9084 cals.

* The first article appeared in the CHEMICAL NEWS, 1906, vol. xciv., p. 281.

Volatile Matter.

A determination was made by strongly heating a portion of the same sample in a platinum crucible :—

Volatile matter	74·62 per cent
Moisture	2·12
Ash	0·47
Fixed carbon	22·79
	100·00

The coke remaining behind possessed a graphitic lustre, and showed slight intumescence.

Another sample—from which the external shaly layer, which all jet possesses, was not removed—was extracted with CS_2. 1·9991 grm. of jet yielded 0·3424 grm. (= 17·13 per cent) of a yellow oil, which still contained some CS_2. After drying in vacuum over P_2O_5, until the weight had become constant, the residue consisted of 0·1427 (= 7·14 per cent) of a thick dark brown oil, smelling like petroleum.

The solid matter left behind was pulverised and examined.

	Cals.	Cals.	Cals.
Heat of combustion of sample, per grm.	6722	6715	6719
Deduct—			
Heat of combustion of sulphur	17	17	17
Water condensed in bomb = 0·531 grm., of which the heat of evaporation is	319	319	319
Heating power, per grm.	6386	6379	6383

Average.. .. .. 6383 cals.

Chemical Composition (per cent).

Moisture	2·02
Ash	22·01
Combustible matter	75·97
	100·00

Elementary Analysis.

	I.	II.	Mean.
C	63·81	63·56	63·69
H	5·62	5·74	5·68
O+N	5·80	5·93	5·86
S	0·74	0·74	0·74
Ash	22·01	22·01	22·01
Moisture	2·02	2·02	2·02
	100·00	100·00	100·00

Composition of Combustible Matter (per cent).

C	83·84
H	7·48
O+N	7·71
S	0·97
	100·00

This very closely approximates to the formula $C_{14}H_{16}O$; in which C = 84, H = 8, O = 8 per cent.

Heating value = 8823.

It has been shown that jet consists of approximately 93 per cent of solid matter and 7 per cent of oil. Assuming for a moment that the oil is actually petroleum, with an average heating-power of 11,100 cals. per grm., the total heating-power can be calculated :—

8823 × 92 per cent	= 8205 cals.
11,100 × 7 „	= 777 „
	8982

in good agreement with 9084 cals. found.

Comparing the results for the above sample of pure jet with those obtained for cannel coal, a great similarity between the two is seen.

Cannel Coal from Ruhr, Westphalia.

	I.	II.
Heat of combustion of sample, per grm.	8629	8646
Deduct—		
Heat of combustion of sulphur	17	17
Water condensed in bomb = 0·5719 grm., of which the heat of evaporation is ..	343	343
Heating power per grm.	8269	8286

Average.. .. .. 8277 cals.

Chemical Composition of the Sample (*per cent*).

Moisture	0·73
Ash..	5·50
Combustible matter	93·77
	100·00

Elementary Analysis (*per cent*).

C	81·44
H	6·27
O	4·11
N	1·20
S	0·75
Ash..	0·73
Moisture	5·50
	100·00

Heating value (calculated), 8281 cals.

Composition of Combustible Matter (*per cent*).

C	86·85
H	6·69
O	4·38
N	1·28
S	0·80
	100·00

Heating value, 9194 cals.

Volatile Matter (*per cent*).

Volatile matter	43·59
Moisture	0·73
Ash..	5·50
Fixed carbon	50·18
	100·00

(These analyses were also made at the Eidgenössische Prüfungsanstalt für Brenstoffe, Zürich).

That there should be a difference in the amount of fixed carbon is not surprising, since jet and cannel coal have been formed at different geological periods, probably from very different woods, and certainly under different conditions.

Comparing, in tabular form, the analyses and heating values of the combustible matter of jet and cannel coals from Ruhr and Wigan, the connection between the three is apparent.

	Cannel coal from Wigan (*a*).	Cannel coal from Ruhr.	Jet.
C	85·20	86·85	83·81
H	6·07	6·69	7·57
O	8·58	4·38	6·25
N		1·28	1·06
S		0·80	1·31
	99·85	100·00	100·00
Heating powers (cals.)		9194	9084

(*a*) Muspratt, "Handbuch der Technischen Chemie," 4th German edition, 1893, quoting from Percy's "Metallurgy."

Muck ("Chemie der Steinkohle," Second Edition, 1893) states that jet must be classed with cannel coal, but gives no reasons for it.

These results show that jet must be classed with cannel coal rather than with lignite (av. 5500 cals.), whose composition is very different from the above. Although analogous results for bitumen have not been published anywhere to my knowledge, a calculation made on an average sample gave, as result, a heating value of 10,019 cals.

From this, together with analyses (in my first paper), it is seen that jet is far removed from bitumen, compared with cannel coal.

Mr. McIntosh (Chemical News, 1906, xciv., p. 314) contributes some very interesting facts and suggestions in connection with the origin of jet, and although he is able to speak with a certain amount of authority, I would venture to oppose his attempt to connect jet and amber closely together when considering the former's origin. Taking his letter point by point the following suggestions occur to me :—

In forming a mental picture of the structure of jet on the basis of the extraction experiment mentioned above, it is not unjustifiable to consider each particle of jet to be surrounded by a film of the petroleum-like substance; this may cause all the difference between the electrifying power of jet and cannel coal, since the petroleum film would act as an insulator and prevent the escape of electricity, just in the same way as an insulating handle permits of the electrifying of a metal rod.

Mr. McIntosh must not think me carping if I consider that an authority about 125 years old to be somewhat out of date for the present argument, especially as Bishop Watson—though fairly correct in his description of the amber beds (compare Geikie, "Text-book of Geology," 1903, ii., p. 1257)—considers amber to be a mineral the production of which requires the aid of subterranean distillation and a mineral acid. Indeed, Mr. McIntosh favours throughout the destructive distillation theory for the origin of petroleum and natural bitumens, while no direct evidence of any source of heat—volcanic or otherwise—has been found when these and other connected substances are studied *in situ*. I do not know if he bases his contention on Neuburger and Noalhat's "Technology of Petroleum," as I was unable to consult this work when collecting authority for my first paper.

If there is any close connection between jet and amber (or resin), it can only be in the relation wood → jet → amber, because jet still contains some recognisable woody structure, which would be impossible if it were derived from amber; more especially as amber was originally a semi-liquid, able to catch up insects as it moved, and could therefore only exhibit either a flow or crystal structure.

Amber first appears in the Oligocene age. If jet is metamorphosed amber or resin, one would expect to find intermediate gradations between the two bodies in beds later than Upper Lias and earlier than Oligocene; but none are recorded. Considering, also, that pine resins (and I imagine the resins of all conifers) contain turpentine or some analogous substance of a germicidal character, it is scarcely likely that amber would suffer the particular kind of decomposition (very probably fermentation, and bacterial rather than fungoid) that has changed wood into jet (according to my idea). This, combined with the fact that in such trees as provide resins, these latter, which are waste-products, are thrown out down special ducts, and are not spread promiscuously throughout the cells making up the bulk of the tree, can be taken as strong evidence against Mr. MacIntosh's interpretation of the "jetisation" of the partially fossilised tree, as given in his postscript; and, indeed, against his general suggestion.

I scarcely agree with Mr. McIntosh's suggestion that the study—by destructive distillation—of possible substances would help in the elucidation of the origin of jet. Differences in the materials from which jet, coal, and amber

(for instance) are formed, to say nothing of the influence of the actual conditions under which the trials would be carried out, would prevent comparable results from being obtained. From what is known, however, the results of distilling the above substances are very different.

Finally, it really goes against the grain that Mr. McIntosh should claim my theory as "a plea for the resiniferous origin of petroleum and jet"! Considering the relative quantities of resin and the tree containing it, and the relative sizes and quantities of the lumps of amber and jet found, the former could only be responsible for a very small quantity of the jet found.

I follow Mr. McIntosh in hoping that the question will be attacked by chemists. So far as I could discover, up to the time of my first paper, no chemist had looked into the question of the origin of jet, only botanists or geologists; these latter have, I think, collected quite enough information for the chemists to work on.

ON THE CALCULATION OF THERMO-CHEMICAL CONSTANTS.

II.

By H. STANLEY REDGROVE, B.Sc. (Lond.).

Thermal Constants of Organic Halogen Compounds.

IT is evident from a consideration of the molecular heats of combustion and molecular heats of formation of the hydrocarbons (CHEMICAL NEWS, xcv., 301; xcvi., 188) that, in general, the former are more suitable for the calculation of constants than the latter, and constitute better criteria for the examination of any hypotheses on the subject. This is due to the fact that a small percentage error made in determining a molecular heat of combustion will very often occasion a large percentage error in the corresponding molecular heat of formation.

To take an example, consider benzene: the experimental molecular heat of combustion (corrected) is 797·9 cals. (Thomsen); suppose the mean error to be only 0·2 per cent, this would cause an error of 1·6 cals.; supposing the heats of combustion of carbon and hydrogen in the molecular condition to be known accurately, we get, even in this extreme case, a value, −13·7 cals., for the molecular heat of formation with a mean error of 1·6 cals.; that is to say, 11·6 per cent!

This increase in percentage error will be found in general. We shall therefore, in preference to molecular heats of formation, employ molecular heats of combustion (in all cases corrected for constant volume) upon which to base any arguments; however, for the sake of completeness the molecular heat of formation constants have been obtained, and the molecular heats of formation calculated therefrom.

1. *Molecular Heat of Combustion of Organic Halogen Compounds.*

All halogen substituted hydrocarbons can be theoretically obtained by replacing f hydrogen atoms by f halogen atoms, where f is some integer; we shall therefore require the following constant:—

χ = the algebraic sum of the following heats—(i.) due to the severance of a C.H link; (ii.) due to the combustion of a hydrogen atom (to liquid water), minus the algebraic sum of the following heats; (iii.) due to the severance of a C.Cl(C.Br,C.I) link; (iv.) one-half that due to the formation of a gaseous chlorine (bromine, iodine) molecule; or as it can be more simply written:—

χ = the sum of the following heats—(ii.) due to the combustion of a hydrogen atom (to liquid water); (iii.) due to the formation of a C.Cl(C.Br,C.I) link, minus the sum of the following heats; (i.) due to the formation of a C.H link; (iv.) one-half that due to the formation of a gaseous chlorine (bromine, iodine) molecule.

So that the general halogen substituted hydrocarbon,—

$$nC+2(n+1-a-2b-p-\tfrac{1}{2}f)H+(n+p-a-b-1)L_1+ +aL_2+bL_3+fC.Cl(C.Br, C.I) \text{ links} + fCl(Br,I),$$

can be written—

$$nC+2(n+1-a-2b-p)H+ +(n+p-a-b-1)L_1+aL_2+bL_3-f\chi(\chi_1,\chi_2)= =na-(n+p-a-b-1)\beta-a\gamma-b\delta-f\chi(\chi_1,\chi_2),$$

where χ is used for chlorine, χ_1 for bromine, and χ_2 for iodine.

Before proceeding to calculate the values of these constants, a few regularities in the molecular heats of combustion of the compounds under consideration will be pointed out, using the results of Thomsen, corrected for constant volume.

1. The effect on the molecular heat of combustion, by replacing a hydrogen atom in any hydrocarbon by a chlorine atom, is constant; similarly, the effects produced by replacing the chlorine by bromine, and the bromine by iodine, are respectively constant, as shown in Table I.

2. The effect on the molecular heat of combustion by replacing in turn 1, 2, 3 hydrogen atoms in any hydrocarbon by chlorine is constant. Apparently the replacement of a fourth hydrogen atom produces a less effect, but as the data is scanty, and the difference is in any case small, it has been neglected in the calculations to follow.

This regularity is shown in Table II.

3. The mere position of the halogen has no effect on the molecular heat of combustion. This is shown by the fact that the results for monochlorpropylene (=452·4 cals.) and for allyl chloride (=453·7 cals.) are practically equal, and the result for ethylene chloride (=295·8 cals.) identical with that for ethylidene chloride (=295·8 cals.).

In Table III. will be found the molecular heats of combustion (corrected for constant volume) of fourteen chlorine, four bromine, and two iodine compounds determined by Thomsen, from these the values of χ, χ_1, and χ_2 have been calculated; thus, methyl chloride is CH_3Cl, *i.e.*, $a-\chi$; M.H.C. found = 176·2 cals. Therefore, $\chi = a - 176{\cdot}2$ cals. $= (210{\cdot}8 - 176{\cdot}2)$ cals. $= +34{\cdot}6$ cals., &c.

The value thus obtained from each substance is given in the table; and means have been struck so as to give the lowest average error.

The values thus obtained are—

χ = 35·5 cals., χ_1 = 28·6 cals., χ_2 = 15·9 cals.

These are the fundamental molecular heat of combustion halogen constants.

Using these values, the molecular heats of combustion of all the halogen compounds given have been calculated, and the results, together with the difference between them and the experimental, and the percentage error are given in Table III.

Excepting chloroform, perchlorethylene, and carbon tetrachloride the results are quite satisfactory, although not exhibing the extraordinary exactness with which the molecular heats of combustion of hydrocarbons can be calculated by means of the author's "fundamental constants."

2. *Molecular Heat of Formation of Organic Halogen Compounds.*

The constants required will be entirely analogous to the molecular heat of combustion constants, so that:—

χ' = the algebraic sum of the following heats:—(i.). One-half that due to the decomposition of a hydrogen molecule; (ii.) due to the formation of a C.H link minus the algebraic sum of the following heats; (iii.) one-half that due to the decomposition of a chlorine molecule; (iv.) due to the formation of a C.Cl link; or as it can be more simply written—

χ' = the sum of the following heats—(ii.) due to the formation of a C.H link; (iii.) one-half that due to the formation of a chlorine molecule minus the sum of the following heats; (i.) one-half that due to the formation of

TABLE I.

	Hydride. Cals.	Difference. Cals.	Chloride. Cals.	Difference. Cals.	Bromide. Cals.	Difference. Cals.	Iodide. Cals.
Methyl	210·8	−34·6	176·2	+7·8	184·0	+11·4	195·4
Ethyl..	369·0	−35·9	333·1	7·7	340·8	11·9	352·7
Propyl	527·5	−36·4	491·1	7·9	498·0	—	—

TABLE II.

		M.H.C. Cals.	Difference. Cals.
Ethane	C_2H_6	369·0	
Ethyl chloride	C_2H_5Cl	333·1	35·9
Ethylene chloride	$C_2H_4Cl_2$	295·8	37·3
Monochlorethylene chloride	$C_2H_3Cl_3$	262·3	33·5
Methane	CH_4	210·8	
Methyl chloride	CH_3Cl	176·2	34·6
Chloroform	$CHCl_3$	107·2	2×34·5
Carbon tetrachloride	CCl_4	76·5	30·7

TABLE III.—Organic Halogen Compounds.

1. Substance.	2. Formula.	Molecular Heat of Combustion. 3. Formula.	4. M.H.C. found (Thomsen) constant vol. Cals.	5. χ Calculated. Cals.	6. M.H.C. calculated. Cals.	7. Difference between cols. 4 and 6. Cals.	8. Error. Per cent.	Molecular Heat of Formation. 9. Formula.	10. M.H.F. found (Thomsen) constant vol. Cals.	11. χ′ Calculated. Cals.	12. M.H.F. calculated. Cals.	13. Difference between cols. 10 and 12. Cals.
Chlorides.												
Methyl chloride	CH_3Cl	$a-\chi$	176·2	34·6	175·3	−0·9	−0·51	$a'-\chi'$	22·0	−0·8	22·9	+0·9
Ethyl chloride	C_2H_5Cl	$2a-\beta-\chi$	333·1	36·0	333·6	+0·5	+0·15	$2a'-\beta'-\chi'$	29·6	−2·2	29·1	−0·5
Propyl chloride	C_3H_7Cl	$3\beta-2\gamma-\chi$	491·1	36·3	491·9	+0·8	+0·16	$3a'-2\beta'-\chi'$	36·0	−2·4	35·3	−0·7
Isobutyl chloride	C_4H_9Cl	$4\alpha-3\beta-\chi$	648·5	37·2	650·2	+1·7	+0·26	$4a'-3\beta'-\chi'$	43·1	−3·3	41·5	−1·6
Monochlorethylene	C_2H_3Cl	$2a-\gamma-\chi$	297·6	35·0	297·1	−0·5	−0·17	$2a'-\gamma'-\chi'$	−2·5	−1·1	−1·9	+0·6
Monochlorpropylene	C_3H_5Cl	$3a-\beta-\gamma-\chi$	452·4	38·5	455·4	+3·0	+0·66	$3a'-\beta'-\gamma'-\chi'$	+7·3	−4·7	+4·3	−3·0
Allyl chloride	C_3H_5Cl	$3a-\beta-\gamma-\chi$	453·7	37·2	455·4	+1·7	+0·37	$3a'-\beta'-\gamma'-\chi'$	5·9	−3·3	4·3	−1·6
Ethylene chloride	$C_2H_4Cl_2$	$2a-\beta-2\chi$	295·8	$73·3\times\frac{1}{2}$	298·1	+2·3	+0·78	$2a'-\beta'-2\chi'$	33·1	$-5·7\times\frac{1}{2}$	30·8	−2·3
Ethylidene chloride	$C_2H_4Cl_2$	$2a-\beta-2\chi$	295·8	$73·3\times\frac{1}{2}$	298·1	+2·3	+0·78	$2a'-\beta'-2\chi'$	33·1	$-5·7\times\frac{1}{2}$	30·8	−2·3
Dichlorpropane	$C_4H_6Cl_2$	$3a-2\beta-2\chi$	453·0	$74·4\times\frac{1}{2}$	456·4	+3·4	+0·75	$3a'-2\beta'-2\chi'$	40·3	$-6·7\times\frac{1}{2}$	37·0	−3·3
Chloroform	$CHCl_3$	$a-3\chi$	107·2	$103·6\times\frac{1}{3}$	104·3	−2·9	−2·71	$a'-3\chi'$	23·5	$-2·3\times\frac{1}{3}$	26·3	+2·8
Monochlorethylene chloride.	$C_2H_3Cl_3$	$2a-\beta-3\chi$	262·3	$106·8\times\frac{1}{3}$	262·6	+0·3	+0·11	$2a'-\beta'-3\chi'$	32·8	$-5·4\times\frac{1}{3}$	32·5	−0·3
Carbon tetrachloride	CCl_4	$a-4\chi$	76·5	$134·3\times\frac{1}{4}$	68·8	−7·7	−10·07	$a'-4\chi'$	20·5	$+0·7\times\frac{1}{4}$	28·0	+7·5
Perchlorethylene	C_2Cl_4	$2a-\gamma-4\chi$	195·7	$136·9\times\frac{1}{4}$	190·6	−5·1	−2·61	$2a'-\gamma'-4\chi'$	−1·7	$-1·9\times\frac{1}{4}$	3·2	+4·9
		Mean		$\chi = 35·5$				Mean		$\chi' = -1·7$		
Bromides.				χ_1						χ_1'		
Methyl bromide	CH_3Br	$a-\chi_1$	184·0	26·8	182·2	−1·8	−0·98	$a'-\chi$	+14·2	+7·0	16·0	+1·8
Ethyl bromide	C_2H_5Br	$2a-\beta-\chi_1$	340·8	28·3	340·5	−0·3	−0·09	$2a'-\beta'-\chi_1'$	21·8	5·6	22·2	+0·4
Propyl bromide	C_3H_7Br	$3a-2\beta-\chi_1$	498·0	29·4	498·8	+0·8	+0·16	$3a'-2\beta'-\chi_1'$	29·1	4·5	28·4	−0·7
Allyl bromide	C_3H_5Br	$3a-\beta-\gamma-\chi_1$	461·1	29·8	462·3	+1·2	+0·26	$3a'-\beta'-\gamma'-\chi_1'$	−1·5	4·1	−2·6	−1·1
		Mean		$\chi_1 = 28·6$				Mean		$\chi_1' = +5·3$		
Iodides.				χ_2						χ_2'		
Methyl iodide	CH_3I	$a-\chi_2$	195·4	15·4	194·9	−0·5	−0·26	$a'-\chi_2'$	+2·8	18·4	+3·3	+0·5
Ethyl iodide	C_2H_5I	$2a-\beta-\chi_2$	352·7	16·4	353·2	+0·5	+0·14	$2a'-\beta'-\chi_2'$	9·9	17·5	9·5	−0·4
		Mean		$\chi_2 = 15·9$				Mean		$\chi_2' = 17·95$		

a hydrogen molecule; (iv.) due to the formation of a C.Cl link.

Similarly, χ_1' for bromine, and χ_2' for iodine.

It follows therefore that $\chi' + \chi = \chi_1' + \chi_1 = \chi_2' + \chi_2$ = the heat due to the combustion of a hydrogen atom (to liquid water), less half the heat due to the formation of a hydrogen molecule = the heat of combustion of 1 grm. molecular hydrogen to liquid water = $\frac{1}{2} \times 67{\cdot}5$ cals. = 33·75 cals.

Whence—

$$\chi' = (33{\cdot}75 - 35{\cdot}5) \text{ cals.} = -1{\cdot}75 \text{ cals.}$$
$$\chi_1' = (33{\cdot}75 - 28{\cdot}6) \text{ cals.} = +5{\cdot}15 \text{ cals.}$$
$$\chi_2' = (33{\cdot}75 - 15{\cdot}9) \text{ cals.} = 17{\cdot}85 \text{ cals.}$$

In Table III. will be found the molecular heats of formation of the halogen compounds under consideration, given by Thomsen; from these the values of χ', χ_1', and χ_2' have been calculated in a similar manner as were the molecular heat of combustion constants.

The values thus obtained are $\chi' = -1{\cdot}7$ cals., $\chi_1' = +5{\cdot}3$ cals., $\chi_2' = 17{\cdot}95$ cals., agreeing with the above.

Using the mean values—

$\chi' = -1{\cdot}7$ cals., $\chi_1' = +5{\cdot}2$ cals., $\chi_2' = 17{\cdot}9$ cals.,

which are the fundamental molecular heat of formation halogen constants, the molecular heats of formation of all the halogen compounds given have been calculated, and the results, together with the difference between them and experimental, are given in Table III.

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NOTE.—The following is probably the explanation why, in trying to find a formula for the carbon molecule (CHEMICAL NEWS, xcvii., 37) which would give a heat of combustion in agreement with the experimental, it was found invariably that the calculated was too great: constants were employed to determine the formula of a solid substance which were derived from the heats of combustion of gases; this ought only to be done if the latent heat of the solid substance (carbon in this case) were solely due to the splitting up of complex molecules into more simple ones, otherwise the calculated result must of necessity be too great, as in the above case,

ERRATA.—I find two insignificant clerical errors in Table I. (CHEMICAL NEWS, xcv., 301). The figures in Column 4 for di-isopropyl and *iso*-amylene should be 996·6 and 805·6 respectively; corresponding slight changes in the other columns for these two substances are thereby necessitated.

THE COMPOSITION OF THE RED CLAY.

By F. W. CLARKE.

IN the volume upon "Deep Sea Deposits" (pp. 198, 201, 425—35), issued as one of the reports of the *Challenger* expedition, there are published twenty-five analyses of the "red clays." This sediment is now recognised as the most extensive and important of all oceanic deposits, for it covers 51,500,000 square miles of the sea floor, and is characteristic of the greatest depths. It is therefore obviously desirable to know its average composition as exactly as possible, and for that reason the following investigation was undertaken.

Of the analyses above mentioned twenty-one were by Brazier, two by Hornung, one by Klement, and one by Renard. They are, however, not strictly comparable, as a glance at the recorded data will show, nor are they, from the point of view of the modern analyst, so complete as they should be. For example, that ubiquitous element, titanium, was not determined in any of the analyses, for at the time they were made its importance and relative abundance were not appreciated. Other substances which are common in clays were neglected for similar reasons, but their significance is now better understood, and improvements in analytical methods have made it easier to search for them. In Brazier's analyses the alkalis were not estimated, but were reported by the other analysts; an omission in the first group that was not due to oversight, but to the limitations of the purposes for which the work was done. The general nature of the red clay was well established, its great variability in composition was clearly shown, and its relations to other clays were made sufficiently plain to satisfy all ordinary requirements.

Of late years, however, it has become a matter of interest to determine the relative abundance and distribution of the chemical elements; and in an inquiry of that sort so notable a substance as the red clay could not well be neglected. A new and more elaborate analysis of it therefore seemed to be required, and to that end two methods of investigation were available. First, it was possible to make a number of individual analyses of separate samples, from which an average might be computed. Secondly, one composite sample could be analysed, giving the desired information once for all. The first method, evidently, would have involved much labour, too much, indeed, to be justifiable. The second method would solve the problem equally well, but with greater ease and vastly less expenditure of time. The second, therefore, was chosen. Through the kindness of Sir John Murray, and his secretary, Mr. James Chumley, fifty-one samples of the red clay, from as many localities, and approximately equal in weight, were combined into a single sample, and that was analysed by my associates in the Laboratory of the United States Geological Survey. (The analytical methods employed were those prescribed by Hillebrand, in *Bulletin* No. 305, U.S. Geological Survey). The results of the composite analysis will be given presently.

The composite sample, as made up by Mr. Chumley, contained thirty-five samples from the dredgings of the *Challenger* expedition, twelve collected by the *Egeria*, two by the *Waterwitch*, and two by the *Penguin*. Of these, eight samples were collected in the Atlantic, two in the Indian Ocean, and forty-one in the Pacific. The *Challenger* localities were stations Nos. 5, 9, 26, 27, 29, 160, 165, 181, 215, 221, 226, 228, 229, 230, 238, 240, 241, 244, 247, 251, 253, 254, 255, 256, 258, 259, 275, 277, 285, 286, 288, 294, 329, 330, and 353. These stations can be identified by reference to the published reports of the expedition. (A chart showing the position at which each sample was taken was also furnished with the material sent for analysis). The geographic range of the collection is evidently large enough to give a significant average, and the number of individual samples was also adequate. Twelve of the localities enumerated above are represented among the analyses already published in the volume on "Deep Sea Deposits," and are there indicated by their station numbers. The other localities furnished material hitherto unstudied chemically.

The new analysis of the clay was made made upon the air-dried and unwashed sample. It therefore included adherent sea salts, and hygroscopic moisture, varying in these respects from the earlier analyses. The magnitude of these variations, however, was determined, and appears in Table I. The final data are as follows:—

A. General analysis, by Mr. George Steiger.
B. Portion solution in cold water, by Mr. George Steiger.
C. Special determinations, by Dr. W. F. Hillebrand.
D. Special determinations, on material concentrated from 150 grms. of clay, by Dr. E. C. Sullivan.

These last determinations were checked by blank experiperiments upon equal quantities of the reagents employed in the research. Zirconia and the rare earths were sought for by Dr. Hillebrand, but not found. Titanium, chromium, vanadium, barium, strontium, nickel, copper[1] lead, zinc, arsenic, and molybdenum were not reported in the *Challenger* analyses. Their widespread distribution in the igneous rocks is, however, well recognised. The absence of lithium and fluorine is noteworthy. The unusually high

proportion of manganese suggests the presence of disseminated or incipient manganese nodules, like that so admirably analysed by Gibson ("Deep Sea Deposits," p. 422). In his work several of the rarer elements were determined; so that their existence in the oceanic sediments is no new discovery. The fact of their general distribution, however, remained to be proved.

TABLE I.

	A.	B.	C.	D.
SiO_2	45·32	none		
Al_2O_3	13·26	none		
Fe_2O_3	7·20	none		
FeO	0·70	none		
MgO	3·05	0·21		
CaO	6·82	0·19		
Na_2O	3·63	2·01		
K_2O	2·43			
H_2O at 106°	3·28	—		
H_2O above 106°	5·93	—		
TiO_2	0·82	—		
CO_2	3·91	—		
P_2O_5	0·25	—		
SO_3	0·48	0·39		
Cl	2·77	2·73		
F	none	—		
Cr_2O_3	0·01	—	0·011	
NiO, CoO	0·032	—		
MnO_2	1·01	—		
BaO	0·17	—	0·16	
SrO	0·046	—		
Li_2O	none	—		
V_2O_3	0·023	—	0·035	
MoO_3	—	—	trace	
CuO	—	—	—	0·02
PbO	—	—	—	0·007
ZnO	—	—	—	0·004
As_2O_3	—	—	—	0·0007
	101·141	5·53		
Less O = Cl	0·62	0·62		
	100·521	4·91		

In order to establish the true composition of the clay substance, some deductions must be made from the analysis as it is now stated. Hygroscopic water and soluble matter must be eliminated, and also the calcium carbonate which is represented by the CO_2. The composition of the aqueous extract, as given by Mr. Steiger's figures, is very near that of the sea salts. I have therefore taken Dittmar's analysis of sea salts as a standard, and subtracted their equivalent, as measured by the chlorine in the unleached clay, from the analysis of the latter. A slight excess of SO_3 remained, which I have also thrown out as representing gypsum. In short, from the general analysis I have withdrawn the water lost below 106°, the sea salts, the calcium carbonate, and a little gypsum, and re-calculated the remainder to 100 per cent.

For comparison, I have combined the twenty-five analyses of the *Challenger* report into an average, from which similar subtractions, so far as they were needed, have been made. In this case only gypsum and calcium carbonate were rejectable. As for the combination, its value is not very great, because of the inequality shown by the individual analyses. Only in four of the latter were alkalis determined, and the mean of those four I have assumed to be representative of all. The ferrous oxide is even more doubtful, for it was only determined in one of Hornung's analyses and neglected in the others. Still, as will be seen in Table II., the comparison is not without significance, and even if it is not perfect, it is better than none at all.

The minor elements, not shown in the *Challenger* analyses, only sum up, altogether, to 1·36 per cent. Apart from these the comparison is satisfactory in some respects, not so in others. In silica, alumina, and water, the agreement is fairly good, but in iron the old analyses range much higher than the new. Possibly for the individual analyses, the reddest and therefore the most ferruginous samples were chosen for examination, as being presumably the most typical.

TABLE II.—*Reduced Analyses.*

	Composite analysis.	Challenger average.
SiO_2	54·48	54·28
TiO_2	0·98	—
Al_2O_3	15·94	16·41
Cr_2O_3	0·012	—
Fe_2O_3	8·66	13·58
FeO	0·84	1·26
NiO, CoO	0·039	—
MnO_2	1·21	1·62
MgO	3·31	1·76
CaO	1·96	0·74
SrO	0·056	—
BaO	0·20	—
K_2O	2·85	1·61
Na_2O	2·05	1·37
V_2O_3	0·035	—
As_2O_3	0·001	—
MoO_3	trace	—
P_2O_5	0·30	0·35
CuO	0·024	—
PbO	0·008	—
ZnO	0·005	—
H_2O	7·04	7·02
	100·000	100·00

On the proximate or mineralogical composition of the red clay I have no important suggestions to offer. That problem was discussed at some length, in the *Challenger* report, on the basis of Brazier's analyses. In those analyses there was discrimination between the portion of the clay soluble in strong hydrochloric acid and the portion insoluble. In nearly every case the soluble ferric oxide was reported in excess of the insoluble; from which I am inclined to suspect that the iron of the clay is present, at least partially, in limonitic or glauconitic combination. The new composite analysis shows a quantity of potash, which suggests the presence of glauconite. The latter compound may well exist in a diffused form, quite unlike its common granular variety, and therefore not so readily recognised. This is a mere suspicion, not entitled to much weight at present, but worth considering in future investigations. My specific problem has been to study the distribution of the chemical elements in nature, and to that end the composite analysis of the red clay is a step forward.

Addendum.

Since the foregoing was written I have received from Sir John Murray a composite of fifty-two "Terrigenous" clays, dredged up from oceanic depths ranging from 140 to 2120 fathoms. In the nomenclature of the *Challenger* expedition, forty-eight of the individual samples are classified as "blue muds" and four as "green muds." Twenty-three of the clays were collected by the *Challenger*; the others were brought in from voyages of the *Buccaneer*, *Dart*, *Egeria*, and *Rambler*. The range of collection, as in the case of the "red clay," was world-wide, and all of the great oceans are represented in the composite sample.

Molybdenum and zirconium were not detected. Nickel, cobalt, lead, zinc, and arsenic, which were reported in the red clay, were not looked for. Apart from these trivial omissions, the red and Terrigenous clays are fairly comparable. The red clay is lower in silica and alumina, but higher in iron than the muds, and other minor differences appear. The high manganese of the red clay may be correlated with the abundance of manganese nodules in the greater oceanic depths. The results of analysis appear in Table III.

TABLE III.

A. General analysis by Mr. Steiger.
B. Portion soluble in water.
C. Analysis reduced to standard form by rejecting soluble salts, calcium carbonate, and hygroscopic water, and re-calculation of the remainder to 100 per cent.

	A.	B.	C.
SiO_2	46·64		57·09
TiO_2	1·04		1·27
Al_2O_3	14·08		17·24
Cr_2O_3	0·044	0·14	0·05
Fe_2O_3	4·14		5·07
FeO	1·88		2·30
MnO	0·10	—	0·12
MgO	1·95	0·18	2·17
CaO	7·20	0·38	2·04
SrO	0·25	—	0·03
BaO	0·05	—	0·06
K_2O	1·84	—	2·25
Na_2O	2·98	2·12	1·05
V_2O_3	0·028	—	0·03
P_2O_5	0·17	—	0·21
CO_2	4·05	—	—
SO_3	0·32	0·32	—
S.	0·11	—	0·13
Cl	2·25	2·25	—
CuO	0·016	—	0·02
C	1·38	—	1·69
H_2O at 105°	4·73	—	—
H_2O above 105°	5·86	—	7·18
	100·883		100·00
Less O = Cl	0·56		
	100·323		

—*Bulletin U.S. Geological Survey.*

THE IODOMETRIC DETERMINATION OF COPPER.*

By F. A. GOOCH and F. H. HEATH.

(Concluded from p. 176).

WE have now to study the effect of free acid upon potassium iodide (Table III.).

So it appears that a trifling amount of iodine is in every case set free, due no doubt to presence of traces of iodate. It appears also that no more than 2 cc. of concentrated sulphuric acid or hydrochloric acid may safely be present with 2 grms. of potassium iodide in 50 cc. of solution, and the presence of 1 cc. of pure nitric acid makes error. The tendency to liberate iodine is manifestly less at the higher dilution, and it appears that in a volume of 100 cc. of solution containing 5 grms. of potassium iodide 3 cc. of concentrated sulphuric acid, hydrochloric acid, or nitric acid free from nitrogen oxides may safely be present. Acetic acid of 50 per cent strength may apparently make up half the solution at either dilution. When either sulphuric acid, hydrochloric acid, or nitric acid is present, obviously the higher dilution is preferable.

Table IV. gives the results of experiments in which various amounts of copper were determined by titration of the iodine set free in a volume of 100 cc. in presence of 5 grms. of potassium iodide and free acid.

It appears that so much as 50 cc. of 50 per cent acetic acid may be present with 5 grms. of potassium iodide in 100 cc. of solution without interfering appreciably with the estimation of 0·0010 grm. of copper, and that the error introduced by the presence of 1 cc., 2 cc., and 3 cc. of sulphuric acid, hydrochloric acid, and nitric acid (free from nitrogen oxides) in 100 cc. of solution is scarcely appreciable.

* From the *American Journal of Science*, [4], xxiv., p. 65.

TABLE III.—*Effect of Acids upon Potassium Iodide.*

KI. Grms.	Acid. Cc.	Volume. Cc.	Copper equivalent to I set free. Grms.
	H_2SO_4 (conc.).		
2	1	50	0·0002
2	2	50	0·0005
2	3	50	0·0007
2	5	50	0·0019
5	1	100	0·0002
5	2	100	0·0002
5	3	100	0·0002
5	5	100	0·0014
	HCl (conc.).		
2	1	50	0·0002
2	2	50	0·0003
2	3	50	0·0006
2	5	50	0·0016
5	1	100	0·0002
5	2	100	0·0002
5	3	100	0·0002
5	5	100	0·0008
	HNO_3 (conc., purified).		
2	1	50	0·0025
2	2	50	0·0094
2	3	50	0·0230
5	1	100	0·0002
5	2	100	0·0002
5	3	100	0·0002
5	5	100	0·0294
	$HC_2H_3O_2$ (50 per cent).		
2	25	50	0·0002
5	25	100	0·0002
5	50	100	0·0003

TABLE IV.—*Effects of Acids upon the Determination of Small Amounts of Copper.*

Copper taken as $Cu(NO_3)_2$. Grm.	KI. Grms.	Acid. Cc.	Total volume. Cc.	Copper found. Grm.	Error. Grm.
		H_4SO_4 (conc.).			
0·0010	5	1	100	0·0016	+0·0006
0·0010	5	2	100	0·0014	+0·0004
0·0010	5	3	100	0·0019	+0·0009
		HCl (conc.).			
0·0010	5	1	100	0·0014	+0·0004
0·0010	5	2	100	0·0014	+0·0004
0·0010	5	3	100	0·0015	+0·0005
		HNO_3 (conc., purified).			
0·0010	5	1	100	0·0014	+0·0004
0·0010	5	2	100	0·0015	+0·0005
0·0010	5	3	100	0·0015	+0·0005
		$HC_2H_3O_2$ (50 per cent).			
0·0010	5	10	100	0·0012	+0·0002
0·0010	5	20	100	0·0012	+0·0002
0·0010	5	30	100	0·0010	—
0·0010	5	40	100	0·0010	—
0·0010	5	50	100	0·0010	—

In Table V. are given the results of similar procedure applied to larger amounts of copper.

In the experiments of Series B and C the material for each test was metallic copper standardised electrolytically. Portions of this material were weighed and converted to the nitrate by acting with nitric acid. The solution of the nitrate was evaporated nearly to dryness and the residue dissolved and titrated in the manner indicated.

The N/10 sodium thiosulphate used in estimating the iodine liberated added appreciably to the initial volume, 100 cc., of the solution. In Series A the increase of volume, less than 20 cc., did not affect appreciably the accuracy of the determinations. In Series B the increase of volume to 140 cc., without corresponding increase in

TABLE V.—*Effect of Acids upon the Determination of Larger Amounts of Copper.*

Copper taken as $Cu(NO_3)_2$.	KI present.	KI, approximate excess.	Acid.	Volume at beginning of titration.	Volume at end of titration.	Copper found.	Error.
Grm.	Grms.	Grms.	Cc.	Cc.	Cc.	Grm.	Grm.
A.—Final volume between 110 and 120 cc.							
			H_2SO_4 (conc.).				
0·1200	5·0	4·5	2·5	100	119	0·1200	—
0·0900	5·0	4·5	3·0	100	114	0·0903	+0·0003
0·0900	5·0	4·5	3·5	100	114	0·0905	+0·0005
			HCl (conc.).				
0·0900	5·0	4·5	2·0	100	117	0·0897	−0·0003
0·1200	5·0	4·5	2·0	100	119	0·1195	−0·0005
0·0900	5·0	4·5	3·0	100	114	0·0901	+0·0001
0·1200	5·0	4·5	3·0	100	119	0·1200	—
0·1200	5·0	4·5	3·5	100	119	0·1197	−0·0003
0·0900	5·0	4·5	4·0	100	114	0·0903	+0·0003
			HNO_3 (conc.).				
0·0900	5·0	4·5	1·0	100	114	0·0900	—
0·1050	5·0	4·5	1·5	100	117	0·1051	+0·0001
0·0900	5·0	4·5	2·5	100	114	0·0901	+0·0001
			$HC_2H_3O_2$ (50 per cent).				
0·1200	5·0	4·5	3·0	100	119	0·1195	−0·0005
0·0900	5·0	4·5	5·0	100	114	0·0898	−0·0002
0·1050	5·0	4·5	10·0	100	117	0·1048	−0·0002
B.—Final volume between 140 and 155 cc. without increase of KI.							
			H_2SO_4.				
0·3336	5·0	3·5	3	100	153	0·3315	−0·0021
			HCl.				
0·2818	5·0	4·0	2	100	144	0·2797	−0·0021
			HNO_3.				
0·3320	5·0	3·5	3	100	152	0·3290	−0·0030
			$HC_2H_3O_2$.				
0·2541	5·0	3·5	6	100	140	0·2523	−0·0018
C.—Final volume increased to 132 and 150 cc., with corresponding increase of KI.							
			H_2SO_4 (conc.).				
0·2218	7·0	6·0	2	100	135	0·2214	−0·0004
0·3231	8·0	6·4	3	100	150	0·3226	−0·0005
			HCl (conc.).				
0·2023	7·0	6·0	2	100	132	0·2016	−0·0007
0·2581	7·8	6·7	3	100	141	0·2574	−0·0007
			HNO_3 (conc., purified).				
0·2023	8·0	7·0	1	100	132	0·2017	−0·0006
0·2520	10·0	8·5	3	100	148	0·2512	−0·0008
			$HC_2H_3O_2$ (50 per cent).				
0·2125	7·5	—	5	100	133	0·2119	−0·0006
0·2064	8·0	—	8	100	132	0·2058	−0·0009

the amount of potassium iodide present, did affect the indications unfavourably.

In Series C, however, the unfavourable effect of similar dilution was overcome by the addition of more potassium iodide.

It is apparent that at any volume a very considerable excess of potassium iodide above the theoretical equivalent involved in the reaction is necessary, and that the necessary excess increases very materially with the dilution of the solution. It appears also that the noted small amounts of sulphuric acid, hydrochloric acid, and nitric acid (free from nitrogen oxides) exert no appreciable influence upon the indications of the process carried out at a volume approximately 100 cc.; and that acetic acid may be present in amount equivalent to at least 25 per cent of the absolute acid.

We find no ground for the inference of Moser that the presence of acid (*Zeit. Anal. Chem.*, 1904, xliii., 597), best sulphuric acid, is necessary to the attainment of good results at all volumes excepting the most concentrated; and there appears to be no reason why the addition of small amounts of acid should increase the amount of iodine liberated if the potassium iodide is free from iodate or other oxidiser. We are wholly unable to offer any explanation for Moser's extraordinary observation, quite contrary to our own, that variation in the amounts of 10N/1 H_2SO_4, from 1 cc. to 100 cc. (0·49 grm. to 49 grms.) for 50 cc. of a solution of copper sulphate, is practically without effect in the treatment by potassium iodide.

The best general procedure in determining by the iodometric method amounts of copper not exceeding about 0·3 grm. seems to us to be covered by the following directions:—The solution of the cupric salt, containing no more than 3 cc. of concentrated sulphuric acid, hydrochloric acid, or nitric acid (free from nitrogen oxides), or 25 cc. of 50 per cent acetic acid, is to be made up to a volume of 100 cc., 5 grms. of iodate-free potassium iodide are to be added, and the titration of the free iodine is to be made by sodium thiosulphate in the usual manner with the use of the starch indicator at the end. In case the end reaction has not appeared when 25 cc. of the thiosulphate have been added, 2 to 3 grms. more of potassium iodide are to be added before continuing the titration.

The error of the process, properly conducted, should not exceed a few tenths of a milligrm. in terms of copper.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 27th, 1908.

Dr. CHARLES CHREE, F.R.S., President, in the Chair.

DR. C. V. DRYSDALE exhibited a Vacuum Tube Apparatus for demonstrating the Propagation of Alternate Current Waves in Cables.

The propagation of alternate current waves in conductors has been frequently exhibited by the aid of a helix, notably by Prof. Fleming and Dr. G. Scibt, and the former has proposed the use of vacuum tubes to show the distribution of potential. The author had noticed that in a tube laid parallel to the helix the brightness was proportioned to the slope of potential and hence to the current. The apparatus therefore consisted of a wooden stand which supported a helix about six feet long, a vacuum tube just above it, and a series of eighteen vertical tubes below it. On feeding the helix frum a high-frequency resonance circuit nodes and loops of potential and current were simultaneously visible in the two sets of tubes, and these were approximately in quadrature with one another. Experiments were shown in which the frequency of the supply was varied, and the capacity of the helix was altered by introducing an earthed wire inside it. Resistance, capacity, and inductance were also connected successively to the receiving end, and the effects were approximately in agreement with theory.

Mr. W. DUDDELL expressed his interest in the experiments, and asked why the points of zero potential were not more clearly marked. Was it due to absorption of energy by the tubes or to the superposition of oscillations with higher frequencies? Had the author used a single long tube with a strip of tinfoil on the outside? He also asked what gas the author used in the vertical tubes, and whether he had tried helium.

Dr. DRYSDALE in reply said that the tubes were filled with CO_2. It was somewhat difficult to ensure their equality, and no attempt had therefore been made to use rare gases. Doubtless still better results could be obtained, but the CO_2 tubes were sufficiently bright for most purposes. He believed that the energy taken by so many tubes was the cause of the absence of complete darkness at the nodes, as with a single tube sharper results had been obtained. For this reason the single tube with a strip of tinfoil on the side had not been used.

Dr. C. V. DRYSDALE read a paper entitled "*Notes on the Plug Permeameter.*"

The author briefly described the instrument, in which a drill is employed to cut a conical hole in a casting or forging, at the same time leaving a pin one-tenth inch diameter standing in the middle. A wrought-iron plug carrying a bobbin with magnetising and search coils completes the magnetic circuit, forming a miniature permeameter. The readings are taken by means of an ammeter and ballistic galvanometer in the ordinary way, or by the aid of a portable direct-reading test set. When this instrument was first described it was found, as would be expected, that the values of the induction given by it were too low, and it had been supposed by some that this was due to imperfection in the magnetic joint. The author, on the other hand, had attributed it to end effects and to the shortness of the specimen. Investigations had been made confirming this view, and showing that the amount of this end effect could be fairly closely compensated by correcting the value of H in the same ratio for all specimens. These investigations had been carried out by obtaining some rings of cast- and wrought-iron and steel, testing them by the ring method, and afterwards cutting them into quadrants which were drilled and tested with the plug. Curves were given showing the results obtained by the plug permeameter when the instrument had been empirically calibrated from the foregoing tests. These showed that the instrument was accurate within two or three per cent, which was as satisfactory as most other permeameters.

Prof. S. P. THOMPSON said the author's instrument commended itself for its usefulness and ingenuity. He would like to know how far its results were comparable with those obtained from ring and double yoke methods. He was not sure that the author's explanation that the discrepancies were due to end effects was the correct one. In drilling the hole in the casting the magnetic properties of the iron were altered and the hysteresis increased.

Mr. A. CAMPBELL remarked that from his experience of several varieties of permeameters he was not at all surprised to find that Dr. Drysdale had had to calibrate his permeameter by the purely experimental method of comparison with the trustworthy ring method. By averaging the different calibrations given by various types of material he appeared to be able to obtain fairly good results, but there were other permeameters which gave as satisfactory results without any empirical calibration.

Mr. A. RUSSELL said he appreciated the ingenuity displayed in the Drysdale permeameter. He suggested the following as the probable cause of part of the discrepancy between the magnetisation curves got by the ring method and by the permeameter. In the former method the mean flux and the mean magnetising force over the cross section of the ring were measured. The ring experimented on was of appreciable radial depth, so that the magnetic force on the inner circumference of the ring was about 50 per cent greater than that on the outer circumference. The permeability of the iron at the greater force would probably be very different from that at the smaller force. The mean value, therefore, of the flux density over the cross sectional area of the ring might possibly be something quite different from the value it would have if the magnetic force were constant and equal to the mean magnetic force. The errors due to this cause in the ring method, even when the ring was narrow, were sometimes very appreciable. The criticism also applied to many cases in which electricians apply what they call the fundamental magnetic equation.

Mr. W. DUDDELL asked if it was assumed that all the pins had the same diameter.

Dr. C. V. DRYSDALE, in reply to Prof. Thompson, said that the end effect was not of the same nature as an air-gap or it would have had a more marked influence at high permeabilities. When the instrument was first introduced, a few tests had been made by drilling a specimen and testing it, and afterwards annealing and re-testing. No change had been observed, but possibly a greater number of tests would have shown variations. The size of the pin seemed not to vary by more than a mil whatever metal was drilled. As to Mr. Campbell's remarks, he quite agreed that other permeameters were equally or more accurate, but this was the only one that could be used on the actual forging or casting, and it was surprising and gratifying to find that it was as accurate as it seemed to be. The thickness of the ring mentioned by Mr. Russell was an important point. It was necessary in order to permit of drilling, but he was inclined to think that there would be little error from this cause except at low inductions.

Dr. C. V. DRYSDALE read a paper on "*The Use of Shunts and Transformers with Alternate Current Measuring Instruments.*"

Owing to the limited range of most alternate current instruments shunts and transformers have come into considerable use, but they are liable to cause errors both in the magnitude and phase of the current. The paper deals with these errors mathematically and experimentally. In the case of shunts, the condition for accuracy at all frequencies is that the time constants of the instrument and shunt should be equal, but formulæ are given for the multiplying power and phase displacement in other cases.

For current transformers the best results are obtained by keeping the magnetising and core-loss currents as small as possible. The best uniformity of ratio for different loads is obtained with a non-inductive or leading load; but the lowest phase displacement with a lagging load. P.D. transformers are much more satisfactory than current transformers, both for ratio and phase displacement. Experimental tests using a wattmeter as indicator approximately confirmed the theory.

Mr. A. CAMPBELL expressed his interest in the thorough manner in which Dr. Drysdale had gone into the question of the use of transformers with measuring instruments. With regard to the author's criticism of his (Mr. Campbell's) work on the subject (which was carried out twelve years ago) he should like to mention several points. The main object of the first quoted paper was to show that with air-core transformers the transformation ratio becomes more and more constant (for various frequencies) the higher we make the time-constant of the secondary circuit; thus high inductance and low resistance are wanted. Mr. Campbell stated that in his paper he also gave several experiments to show that iron-ring transformers "may in many cases be used in a similar way," care being taken to have the resistance of the secondary circuit small enough. In a later paper he stated that to make the ratio sufficiently constant and independent of frequency we require relatively low resistance and high inductance in the secondary circuit. Dr. Drysdale showed that, for the special case of constant frequency, relatively high inductance does not give the most constant ratio. His (Mr. Campbell's) experiments were not complete enough to settle this point, and he was careful not to dogmatise on the matter. He was glad that Dr. Drysdale had elucidated it.

Mr. A. RUSSELL expressed his interest in the paper. He suggested that the author should take the mutual inductance between the shunt and the instrument into account. If L_1, R_1 be the constants of the instrument and L_2, R_2, those of the shunt, and if M be the mutual inductance between them, the multiplying factor for the reading will be the same whatever the frequency provided that $\frac{L_1 - M}{R_1} = \frac{L_2 - M}{R_2}$.

Mr. KENELM EDGCUMBE referred to the fact that the author recommended small core-losses, and pointed out that he had seen it stated that in special cases it was possible to improve the ratio and phase errors by increasing the core-losses.

Dr. DRYSDALE, in reply to Mr. Campbell, said his praise of the air-core transformer was justified, but in practice instrument-makers were forced to use iron for commercial reasons. Similarly, the ring form of transformer was generally impossible, as in practice instrument transformers were used to insulate the observing instrument from high pressure mains, and considerable insulation between the windings was necessary. The reason why an iron-cored transformer behaved differently to one with an air-core chiefly resided in the core-loss current which was not proportional to the magnetising current. The method of testing the transformers would be shown in operation in the laboratories.

A paper on "*Dynamometer Wattmeters*" was read by Dr. C. V. DRYSDALE.

The author gives a somewhat complete investigation of the theory of the Wattmeter, including the effects of shunt inductance and capacity, mutual inductance, eddy currents, wave-form, and of iron. It is pointed out that the theory of the wattmeter is much obscured by the use of the correction factor. On sine wave forms the true power $\omega = W \cos \phi$, while the reading of the wattmeter—

$$\omega' = \frac{R}{I} W \cos(\phi - a) = W \cos a \cos(\phi - a);$$

where W is the apparent power, R and I the resistance and inductance of the shunt respectively, and a the angle of lag in the shunt. This leads to the simple relation—

$$\omega = \frac{\omega'}{1 + T^2 p^2} - T p W \sin \phi;$$

where T is the time constant of the shunt and $p = 2\pi \times$ frequency. In practice $T^2 p^2$ can be neglected in comparison with unity, and hence $d\omega = \omega' - \omega = T p W \sin \phi$, which is perfectly determinate at all power factors. This shows that the correction of a wattmeter should always be applied as a difference and not as a ratio. It is practically as absurd to apply a correction factor to a wattmeter as to an instrument with a zero displacement. The paper also contains a description of some single and double forms of standard wattmeter and of deflectional wattmeters containing iron. Also of the method of testing wattmeters for various errors and of a phase-shifting transformer for facilitating these tests. Various forms of wattmeters and phase-shifters were shown in operation.

Mr. W. DUDDELL expressed his interest in the paper, referring especially to the author's remarks upon the application of a correction factor. In some ways he thought a correction factor was preferable to the addition of a zero correction. He was interested in the wattmeters exhibited, which resembled in many features an instrument he had designed some years ago.

Mr. RAYNER, referring to the accuracy of the instruments, asked if Hooke's law held to one part in 500 over a whole turn of the torsion head.

Mr. TINSLEY remarked that the instrument shown resembled those of Mr. Duddell in the mechanical details because the design adopted was the only practical one.

Dr. DRYSDALE, in reply, said he still maintained that the only rational way of correcting wattmeter readings was by adding a correcting term instead of applying a correction factor. Mr. Beattie's device was unnecessary and of little use, as the inductive coil would not give any indication of the error due to capacity in the shunt, which might be considerable. He had not troubled about astaticism in his instruments as they were for use as standards, and it was easy to eliminate the effect of stray fields. He was surprised and gratified to find that Mr. Duddell recognised the strong resemblance between the wattmeter described in the paper and his own. The author's first paper on the subject appeared in the *Electrician* in March, 1901, and was available to anyone interested in the matter.

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).
Ordinary Meeting, April 6th, 1908.

Dr. J. LEWKOWITSCH in the Chair.

"*Considerations affecting the 'Strength' of Wheat Flours.*" By JULIAN L. BAKER and H. F. E. HULTON.

It is improbable that any one chemical or physical determination can be correlated with the "strength" of flours, as the generally accepted definition of "strength" includes two distinct qualities, viz., size and shape of loaf. If the bakers would apportion marks independently for size and shape—and there appears to be no reason why this cannot be done—then it would be possible to correlate data obtained in the laboratory with these two factors. We believe that it is in this direction that advances will be made.

The authors were unable to show the presence in flour of a proteolytic enzyme capable of degrading the gluten, and so influencing the character of the loaf, but there are small quantities of an erepsin; that is, a protease capable of degrading the products of pepsin hydrolysis, such as "Witte peptone," and which is characterised by the formation of tryptophane.

The *rôle* played by yeast enzymes in bread making is

discussed, and it is shown that yeast can effect partial proteolysis of gluten. It is probable that the physical character of the gluten may in this way be modified during the early stages of doughing without the production of large quantities of decomposition products.

The importance of amylolytic enzymes in flours is referred to, and evidence is adduced to prove that maltose is the sugar formed during the doughing period. The products of hydrolysis closely resemble those of the action of barley diastase on starch. The character of diastase in flour has been studied, and it is shown that as regards aqueous flour extracts there is a considerable departure from Kjeldahl's law of proportionality. In determining the diastatic power of wheats and flours the reducing power of the solution in terms of maltose should not exceed 20 per cent. No direct relation can be traced between the diastatic power of a flour as measured by Lintner's method and the baker's marks. It is well known that in some cases flours improve on keeping; in this connection it is interesting to note that the diastatic powers of flours also change. Doughs have a greater diastatic activity than either the aqueous extract of the flour or the flour itself, and this diastatic activity varies inversely with the amount of water with which the flour is wetted. This activity increases on keeping the dough at a temperature of 40° C.

The signification of gas production and its relation to "strength" is considered, and it is shown that the gas production follows fairly closely the maltose formed during doughing, which may occasionally rise to 8 per cent. This in conjunction with the circumstance that flour diastase will gradually liquefy flour pastes, suggested the presence of a liquefying enzyme. The malt extract, which is so often used by bakers, is considered to have its main significance as furnishing this liquefying diastase, adequate saccharifying enzyme being already present in the flour. A trace of powdered malt added to flours increases the volume of gas liberated from the dough, and this increase in volume is greater the less the original volume of gas liberated when malt is absent. The percentage increase of gas from malt-activated flours varies from 88 in the case of a flour giving very little gas to nil. This last flour produced a very large original volume of carbon dioxide.

The toxic action of flour and its aqueous extract on yeasts, in view of Lange's work, suggested that different flours might vary in their behaviour to yeast as regards their relative toxicity. Experiment did not confirm this.

The gliadin-glutenin ratio is discussed, and the formation of gluten from these two substances is shown to be independent of enzymic activity, as has sometimes been suggested. It appears to be a hydration phenomenon. Gliadin separated from flour by alcohol was re-combined with the residual gluten and starch, and from this the gluten was recovered by washing out, but in a weakened condition, due partly, doubtless, to the weakening effect of alcohol. The diastatic activity of gluten is confirmed and considered, and this activity is shown to reside in the glutenin moiety.

"*Note on Murexide as a Quondam Dye-stuff and Printing Colour.*" By WATSON SMITH.

The author exhibited a specimen of commercial murexide manufactured about the year 1861 or 1862, before magenta was able to crush it, as it subsequently did, and also a specimen of calico printed with it which had been carefully preserved from the light, and thus still exhibited the bright rose tints characteristic of it after nearly fifty years. This murexide was manufactured by Robert Rumney, of Manchester, from Peruvian guano, and at one time at the rate of 12 cwts. per week.

It was also pointed out that, although Himmer and Stieglitz indicate the constitution of murexide, and of its basis, purpuric acid, yet thirty years earlier Schorlemmer had pointed to the self-same constitution in his "Chemistry of the Carbon Compounds," published in 1875.

"*The Occurrence of Cyanogenetic Glucosides in Feeding Stuffs.*" By T. A. HENRY, D.Sc., and S. J. M. AULD, Ph.D.

It has long been known that a considerable number of plants are capable of yielding prussic acid when ground up and placed in contact with water. In association with Prof. Dunstan the authors have fully investigated a number of these plants, and have shown that the prussic acid is formed by the interaction of a glucoside and an enzyme which decomposes it, liberating prussic acid. Several of these plants are employed as sources of feeding-stuffs, notably Java beans, and it is to this liberation of prussic acid that the numerous cases of poisoning of cattle by Java beans are due. Linseed cake also contains a cyanogenetic glucoside, but the high temperature to which the cake is heated in the course of manufacture destroys the enzyme originally present in the seed, so that on placing the ground cake in water the glucoside is not decomposed, and no prussic acid is liberated.

The seed of the para rubber tree, sometimes used for feeding purposes in the tropics, also yields small quantities of prussic acid.

It is suggested that in estimating the amount of prussic acid obtainable from products of this type analysts should adopt the plan of extracting the whole of the cyanogenetic glucoside from the product under examination by means of a suitable solvent, and then estimate the prussic acid obtained by hydrolysing the extracted glucoside with acids.

NOTICES OF BOOKS.

Dairy Laboratory Guide. By CHARLES W. MELICK, B.S.A., M.S. London: Archibald Constable and Co., Ltd. 1907.

THE student who is taking a course of practical dairy work will find this little book very helpful from some points of view. The routine work of a dairy or creamery is described in a series of practical exercises, in which the directions for experimental work are clearly stated, and the student is encouraged to make the greatest possible use of his powers of observation and reasoning. The later part of the book is devoted to the testing of dairy produce for purity and quality. Since the book is intended mainly for students who have time for a short course of laboratory work only, the tests are often mere quick rule-of-thumb methods, and no attempt is made to explain the chemical reactions upon which they are based. None but the simplest processes are included; hence accuracy has had to be sacrificed in some cases, as in the testing of butter for foreign fats. In many respects the book can be regarded only as a satisfactory introductory manual, but its use by the student will save both the time and labour of the dairy instructor who is teaching the making of cheese, butter, &c., to a large class.

Detection of the Common Food Adulterants. By EDWIN M. BRUCE. London: Archibald Constable and Co., Ltd. 1907.

THIS little book is one of unquestionable utility. It is devoted exclusively to simple qualitative tests for adulterations in all common articles of food, and it will enable students of chemistry to get useful practice in qualitative analysis, and to become acquainted with the most common adulterants and their detection. The tests are well chosen for simplicity of manipulation and for sensitiveness, and although a great choice of methods is not given, all the commoner adulterants of each substance are taken into consideration. Microscopical work is touched upon, but it is a difficult branch of the subject to learn from any book however excellent, and the absence of illustrations adds to the difficulty. Quantitative tests are not included. The book will be found an excellent introduction to the analysis of foods, and it also provides interesting supplementary work in qualitative analysis.

The Paper-mill Chemist. By Henry P. Stevens, M.A., Ph.D., F.I.C. London: Scott, Greenwood, and Son. 1908.

The chemist employed in paper-mills will never regret adding this volume to his library, but, on the contrary, will probably find that it becomes indispensable to him after a short use. The book treats not so much of the manufacture of paper as of the analysis of the raw materials and finished product, and all tables and analytical data which the analyst is likely to require are arranged in a very convenient form. In the chapter on the detection of adulterations and impurities an account is given of the analysis and valuation of the more important materials used in the manufacture of paper and pulp. The most suitable dyeing materials for colouring pulp, and the best modern methods of applying them, are discussed in much detail, and an illustrated outline of microscope work is included. Methods of performing chemical and physical tests to determine the purity and value of papers are described in clear language which will enable all ordinary analytical operations to be carried out without any possibility of mistake.

Die Englischen Elektrochemischen Patente. ("English Electro-chemical Patents") By Dr. P. Ferchland. Vol. I. Halle-a-S.: Wilhelm Knapp. 1907.

This is the companion volume to No. XXIV. of the series of Monographs on Applied Electro-chemistry, which treats of the German electro-chemical patents. As English electro-chemical patents date further back than, and far exceed in number, those granted in Germany on the same subject, it has been found necessary to limit the processes included in this volume to those relating to the oldest branch of electro-chemistry (electrolysis), and to reserve for a later volume electrothermic processes. A chronological order has been adopted, and the specifications are so well indexed, both under subjects and patentees' names, that there can be no difficulty in finding any patent, if either its number, inventor's name, or subject is known. A short introduction to the volume gives an outline of the essential points of English patent law, special stress being laid upon the important details in which it differs from German law.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Berichte der Deutschen Chemischen Gesellschaft. Vol. xli., No. 5, 1908.

Liquid Hydrosol of Palladium Hydride.—C. Paal and Josef Gerum.—The authors have found that colloid palladium solutions absorb only insignificant quantities of oxygen from the air. The absorptive power of different colloid palladium solutions for hydrogen varies within wide limits, but no explanation has yet been found for this phenomenon. Liquid palladium hydrosols possess a higher power of absorption for hydrogen than has yet been observed for palladium.

Palladium Hydride.—C. Paal and Josef Gerum.—Palladium black in aqueous suspension takes up much more hydrogen than when the gas is allowed to act upon the solid between $-10°$ and $110°$. The composition of the hydride corresponds almost exactly with the formula PdH.

Determination of Lead, Copper, and Silver in Complicated Organic Salts.—M. Rindl and H. Simonis.—Lead is best determined in its salts of complicated organic acids by evaporation with concentrated sulphuric acid. In compounds containing sulphur in which more than one atom of sulphur is present to one of lead, the determination of lead can be combined with that of the sulphur by Carius's method; the sulphuric acid not combined with the lead is precipitated in the filtrate from the lead sulphate by means of barium chloride. The usual methods of determining copper are very unreliable; evaporation of easily decomposed compounds with concentrated sulphuric acid gives the most satisfactory results. Accurate values are found for silver in compounds containing halogens when the salt is heated in a tube with fuming nitric acid and potassium haloid. Dupont and Freundler's method of evaporation of the substance with aqua regia is quicker.

Classification of Ketenes.—H. Staudinger and H. W. Klever.—Ketenes can be divided into two classes:—(1) Those compounds which do not undergo autoxidation. These are colourless; pyridine and quinoline do not form ketene bases with them, but make them polymerise. To this class belong ketene, methyl ketene, ethyl ketene, and carbon suboxide. (2) The coloured compounds which readily undergo autoxidation. With pyridine and quinoline they form ketene bases, compounds of two molecules of ketene with one of base. Disubstituted ketenes such as diphenyl and dimethyl ketene belong to this class. Both classes readily fix water, alcohol, and amines at the carbon double bond, and form acids and their derivatives. They also fix chlorine and bromine at this double bond. The ketenes of the first-class polymerise very easily. The first-class may be called aldoketenes or aldenes, $\begin{matrix}R\\H\end{matrix}\!\!>\!C{:}CO$, and the second keto ketenes, $\begin{matrix}R_1\\R_2\end{matrix}\!\!>\!C{:}CO$.

Refractometer Proof of the Composition of Carbon Suboxide.—Arthur Michael.—Diels and Blumberg have stated that the author's formula for carbon suboxide is probably incorrect, basing their opinion on the results of determinations of the molecular refraction and dispersion of the compound. The author now points out that the optical constants of the acetylene bond vary very considerably, and the optical method does not appear to be trustworthy for distinguishing between the two proposed constitutional formulæ of carbon suboxide. The structure of the oxide can be determined only by experimental methods.

MISCELLANEOUS.

Royal Society of Arts.—It is announced that Mr. William Burton, in consequence of the pressure of other work, is unable to fulfil his engagement to deliver the course of Cantor Lectures on "The Nature and Structure of the Porcelains," announced for Mondays, May 4, 11, and 18. The course will therefore not be given this Session.

The Chemical Laboratory Fresenius at Wiesbaden.—During the Winter Term, 1907-08, the Chemical Laboratory Fresenius was attended by 26 students. Of these, 13 were from Germany, 3 from the United States of America, 2 from Russia, 1 from England, 1 from Belgium, 1 from France, 1 from Holland, 1 from Austria, 1 from Spain, 1 from Argentina, and 1 from East India. There were two assistants in the Instruction Laboratory, and twenty in the private laboratories (Versuchsstationen). To the teaching staff of the institution belong the Directors, Geh. Regierungsrat, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Heintz, and also Prof. Dr. med. G. Frank, Dr. L. Grünhut, Dr. R. Fresenius, and J. Huber (Architect). The next Summer Term begins on April 24th. From the beginning of next Summer Term ladies are admitted as students. During the Winter Term, 1907-08, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Vessuchsstationen) on behalf of trade, manufacture, mining, agriculture, hygiene, justice, and government.

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THE CENTENARY OF DAVY'S DISCOVERY OF THE METALS OF THE ALKALIS.*

By Prof. T. E. THORPE, C.B., Ph.D., LL.D., D.Sc., F.R.S.

A hundred years ago last October, there happened one of those events to which the term epoch-making may, without cavil or question, be fittingly applied.

As it was an occurrence with which the name and fame of the Royal Institution are inseparably bound up, the Managers have thought it only proper that its centenary should not pass unnoticed here, and it is by their wish therefore that I appear on this the first possible opportunity after the actual date of its hundredth anniversary to give you some account of it, and to state, so far as I am able and within the limits of an hour, the fruitful consequences that have flowed from it.

Let me, in the first place, attempt to recall the circumstances which led up to that cardinal discovery of which to-night we celebrate the centenary. These are connected partly with the Institution itself, and partly with the state of science in the early years of the Nineteenth century.

In the year 1807 this Institution was entering upon the eighth year of its existence. As you doubtless know, the Royal Institution grew out of a proposal to deal with the question of the unemployed—namely, by forming in London by private subscription an establishment for feeding the poor and giving them useful employment, and also for furnishing food at a cheap rate to others who may stand in need of such assistance, connected with an institution for introducing and bringing forward into general use new inventions and improvements, particularly such as relate to the management of heat and the saving of fuel, and to various other mechanical contrivances by which domestic comfort and economy may be promoted. Such was the original prospectus, but like many other prospectuses it failed to equal the promise its projectors held out.

Eventually the promoters decided, on the initiation of Count Rumford, that the Associated Institution would, as they expressed it, be "too conspicuous and too interesting and important, to be made an *appendix* to any other existing establishment," and therefore it ought to stand alone, on its own proper basis.

Accordingly, the problem of the unemployed still remains with us, whilst the new institution took the form of converting Mr. Mellish's house in Albemarle Street into a place where, by regular courses of philosophical lectures and experiments, the applications of the new discoveries in science to the improvement of the arts and manufactures might be taught, so as to facilitate the means of procuring the comforts and conveniences of life.

The Royal Institution had a troubled infancy. Like the poor it was originally designed to succour, it suffered much in the outset from lack of nourishment. To add to its miseries, the little starveling was caricatured by Gillray, lampooned by Peter Pindar, and ridiculed by Lord Brougham; and it was literally in the throes of dissolution when new life was breathed into it by the opportune arrival, in 1801, of a small spare youth of twenty-two, from Bristol, whom the Managers had engaged at a salary of 100 guineas a year. The youth was Humphry Davy, who had acted as assistant to Dr. Beddoes, of the Pneumatic Institution, and who had already made some slight stir in scientific circles by his discovery of a characteristic property of nitrous oxide. In announcing his arrival to the Managers, Count Rumford reported that he had purchased a cheap second-hand carpet for Mr. Davy's room, together with such other articles as appeared to him necessary to make the room habitable, and among the rest a new sofa-bed, which, in order that it may serve as a model for imitation, had been made complete in all its parts. Six weeks after his arrival Davy was called upon to lecture, and a descriptive paragrapher of the period thus chronicles his success in the *Philosophical Magazine* for 1801:—

"It must give pleasure to our readers to learn that this new and useful institution, the object of which is the application of Science to the common purposes of life, may be now considered as settled on a firm basis. . . .

"We have also to notice a course of lectures, just commenced at the institution, on a new branch of philosophy—we mean the Galvanic Phenomena. On this interesting branch, Mr. Davy (late of Bristol) gave the first lecture on the 25th of April. He began with the history of Galvanism, detailed the successive discoveries, and described the different methods of accumulating galvanic influence. . . . . He showed the effect of galvanism on the legs of frogs, and exhibited some interesting experiments on the galvanic effects on the solution of metals in acids. Sir Joseph Banks, Count Rumford, and other distinguished philosophers were present. The audience were highly gratified, and testified their satisfaction by general applause. Mr. Davy, who appears to be very young, acquitted himself admirably well; from the sparkling intelligence of his eye, his animated manner, and the *tout ensemble*, we have no doubt of his attaining a distinguished eminence."

And what was of more immediate consequence, this confident assurance was shared also by the Managers, for at a subsequent meeting they unanimously resolved "that Mr. Humphry Davy, Director of the Chemical Laboratory, having given satisfactory proofs of his talents as a lecturer, should be appointed, and in future denominated, Lecturer in Chemistry at the Royal Institution, instead of continuing to occupy the place of Assistant Lecturer, which he has hitherto filled."

That such shrewd experienced men of the world as Sir Joseph Banks and Rumford, who were the moving spirits in the management of the Institution and genuinely solicitous for its welfare, should thus entrust its fortunes, then at their lowest ebb, to the power and ability of a young and comparatively unknown man, barely out of his teens, seems, even in an age which was familiar with the spectacle of "a proud boy" as a Prime Minister, like the desperate throw of a gambler.

But Banks and Rumford had, doubtless, good reason for the faith that was in them. For a happy combination of circumstances had served to bring the Cornish youth within the range of many who could be of service to him in that search for the fame for which he hungered. His connection with the Beddoes brought him the friendship of the Edgeworths, and it is amusing to trace how the good-humoured patronage of the gifted Maria quickly passed into amazement and ended in awe as her acquaintance with him ripened. Living in Bristol, he was at once brought into that remarkable literary coterie which distinguished that city at the close of the Eighteenth Century. Southey spoke of him as a miraculous young man, whose talents he could only wonder at. Cottle, the publisher, on one occasion said to Coleridge, "You have doubtless seen a great many of what are called the cleverest men—how do you estimate Davy in comparison with these?" Mr. Coleridge's reply was strong and expressive. "Why, Davy can eat them all! There is an energy, an elasticity, in his mind which enables him to seize on and analyse all questions, pushing them them to their legitimate consequences. Every subject in Davy's mind has the principle of vitality. Living thoughts spring up like turf under his feet."

Davy's experimental work on "the pleasure-giving air" had made him known to the Watts and the Wedgewoods. Priestley, then in exile, and Hope, of Edinburgh, were

* A Discourse delivered before the Royal Institution, January 17, 1908.

greatly impressed with the philosophical acumen of the author of phosoxygen, and he had a powerful friend in his own countryman, Davies Gilbert, who succeeded him in the Presidential Chair of the Royal Society. We need be in no doubt, therefore, as to the influences which conspired to bring Davy into what he termed "the great hotbed of human power called London."

The mention of Davy's first course of lectures in this Institution brings me at once to the proper subject of this discourse.

The first year of the last century is memorable for the invention of the voltaic battery, and for its immediate application by Nicholson and Carlisle in this country to the electrolytic decomposition of water.

Davy himself has said, "The voltaic battery was an alarm bell to experimenters in every part of Europe; and it served no less for demonstrating new properties in electricity, and for establishing the laws of this science, than as an instrument of discovery in other branches of knowledge; exhibiting relations between subjects before apparently without connection, and serving as a bond of unity between chemical and physical philosophy."

We owe it to Sir Joseph Banks that Volta's great discovery was first made known to English men of science, and the study of the phenomena of Galvanic Electricity was at once entered upon by a score of experimenters in this country. Among them was Davy. Even before he left Bristol he was hard at work on the subject, sending the results of his observations to *Nicholson's Journal* in a series of short papers. He resumed his inquiries immediately on his arrival in London, and was doubtless well prepared, therefore, for his opening course of lectures.

In 1801 he sent his first communication to the Royal Society on "An Account of some Galvanic Combinations Formed by the Arrangement of Single Metallic Plates and Fluids, Analogous to the New Galvanic Apparatus of Mr. Volta." Although the work was continually interrupted by requests made to him by the Managers to carry out their own ideas of facilitating the means of procuring the comforts and conveniences of life, he never lost sight of the subject of voltaic electricity, and in spite of innumerable distractions due to the precarious position of the Institution, he gradually accumulated the material, out of which grew his first Bakerian Lecture "On some Chemical Agencies of Electricity," read before the Royal Society on November 20th, 1806. I have ventured elsewhere to express my opinion of this paper. In my judgment it constitutes, in reality, Davy's greatest claim as a philosopher to our admiration and gratitude, for in it he, for the first time, succeeded in unravelling the fundamental laws of electro-chemistry, and thereby imported a new order of conceptions, altogether unlooked for and undreamt of, into science.

I am only at the moment concerned with this memoir in its relation to the discovery of which to-night we celebrate the centenary. The isolation of the metals of the alkalis was unquestionably an achievement of the highest brilliancy, and as such appeals strongly to the popular imagination. But it was only the necessary and consequential link in a chain of discovery which, had Davy neglected to make it, would have been immediately forged by another.

The publication of Davy's first Bakerian Lecture produced a great sensation, both at home and abroad. Berzelius, years afterwards, spoke of it as one of the most remarkable memoirs that had ever enriched the theory of chemistry. Very significant, too, of the impression it made on the world of science was the action of the French Institute. Bonaparte, then First Consul, had announced his intention of founding a medal "for the best experiment which should be made in the course of each year on the galvanic fluid," and a committee of the Institute, consisting of Laplace, Halle, Coulomb, Hauy, and Biot, was appointed to consider the best means of giving effect to the wishes of the First Consul. To the young man, with the little brown head, like a boy (as Lady Brownrigg described him), now twenty-eight years of age, was awarded the medal. All the Institute got from the founder of the medal was, what Maria Edgeworth termed, "a rating all round in imperial Billingsgate." There was no *entente cordiale* in those days; indeed, the feeling of animosity was intense. Of course, there were persons who said that patriotism should forbid the acceptance of the award. Davy's own view was more sensible and politic:—"Some people," he said to his friend Poole, "say I ought not to accept this prize; and there have been foolish paragraphs in the papers to that effect; but if the two countries or governments are at war, the men of science are not. That would, indeed, be a civil war of the worst description; we should rather, through the instrumentality of men of science, soften the asperities of national hostility."

Thanks to the kindness of Dr. Humphry Davy, Rolleston, the grandson of Dr. John Davy, the brother of Sir Humphry, who has also been so good as to lend me this admirable bust of the great chemist by Chantrey, and this charming portrait by Jackson, I am able to show you this evening this historically interesting medal.

What Davy looked like at this period of his life may be seen from the picture I now project upon the screen. It is a reproduction of the large portrait which hangs in the vestibule, and which the Institution owes to the thoughtful kindness of the late Mr. Graham Young.

As the applications of voltaic electricity seemed in 1806 to have no immediate bearing on the comforts and conveniences of life, Davy, during the greater part of the following year, was required to direct his attention to other matters. But in the late summer of 1807 he was able to resume his work with the voltaic battery, and he commenced to study its action on the alkalis.

That the alkalis—potash and soda—would turn out to be compound substances was not an unfamiliar idea at the time, and it is significant that almost immediately after Nicholson and Carlisle had resolved water into its elements by the action of voltaic electricity, Henry, of Manchester, the friend and collaborator of Dalton, should have made the attempt to apply the same agency to the separation of the presumed metallic principle of potash. The conception that what the older chemists called "earths" might be made to yield metals was at least as old as the time of Boyle, and probably dates back from the earliest days of alchemy. The relation of the earths to the metals was part of the doctrine of Becher and Stahl; it was no less a part of the antiphologistic doctrine of Lavoisier, although the points of view were diametrically opposed. Neumann attempted to obtain a metal from lime, Bergman considered that baryta was, like lime, a metallic calx, and Baron that alumina contained a metal. From their many analogies to these substances it was not unreasonable, therefore, to surmise that potash and soda might also contain metallic principles.

I have elsewhere pointed out that there is some evidence that whilst at Bristol Davy had already attacked the problem of the resolution of the alkalis by means of voltaic electricity. What precise idea he had in again attacking it, or what expectation he had of a definite result, is difficult to determine. In one of his lectures on Electro-chemical Science, delivered some time subsequently, he said he had a suspicion at the time that potash might turn out to be "phosphorus or sulphur united to nitrogen," conceiving, that as the volatile alkali was composed of the light inflammable hydrogen united to nitrogen, so the fixed and denser alkalis might be composed of the denser inflammable bodies—phosphorus and sulphur—also united to nitrogen.

Davy once said that "analogy was the fruitful parent of error," and few more striking instances of perverted analogy are to be met with in science than this. In another of his lectures he said of the alchemists that "even their *failures* developed some unsought-for object partaking of the marvellous"; and if such had been his reasoning, the statement is no less true of himself.

So far as can be ascertained, it was on October 19, 1807, that he obtained his first decisive result. This is thus

described in Davy's own handwriting in the Laboratory Journal, which has been preserved for us by the pious care of Faraday, and which is one of the most precious of the historical possessions of the Royal Institution:—"When potash was introduced into a tube having a platinum wire attached to it, so [fig.], and fused into the tube so as to be a conductor—*i.e.*, so as to contain just water enough, though solid—and inserted over mercury, when the platina was made negative, no gas was formed, and the mercury became oxydated, and a small quantity of the alkaligen was produced round the platina wire, as was evident from its quick inflammation by the action of water. When the mercury was made the negative, gas was developed in great quantities from the positive wire, and none from the negative mercury, and this gas proved to be pure oxygen—a capital experiment, proving the decomposition of potash."

On the 19th of the following month he delivered what is generally regarded as the most memorable of all his Bakerian Lectures. It is entitled "On some New Phenomena of Chemical Changes produced by Electricity, particularly the Decomposition of the fixed Alkalis; and the Exhibition of the New Substances which Constitute their Bases; and on the General Nature of Alkaline Bodies."

Few discoveries of like magnitude have been made and perfected in so short a time, and few memoirs have been more momentous in result than that which, put together in a few hours, gave the results of that discovery to the world.

The whole work was done under conditions of great mental excitement. His cousin, Edmund Davy, who at the time acted as his assistant, relates that when he saw the minute globules of the quicksilver-like metal burst through the crust of potash and take fire, his joy knew no bounds; he actually danced about the room in ecstasy, and it was some time before he was sufficiently composed to continue his experiments.

The rapidity with which he accumulated results, after this first feeling of delirious delight had passed, was extraordinary, and he had obtained most of the leading facts concerning the physics and chemistry of the new substances before the middle of November.

He began his lecture with a felicitous reference to the concluding remarks of one of the previous year, namely:—"That the new methods of investigation promised to lead to a more intimate knowledge than had hitherto been obtained concerning the true elements of bodies. This conjecture, then sanctioned only by strong analogies, I am now happy to be able to support by some conclusive facts."

In the first attempts he made to decompose the fixed alkalis he acted upon concentrated aqueous solutions of potash and soda with the highest electrical power he could then command at the Royal Institution, viz., from voltaic batteries containing 23 plates of copper and zinc of 12 inches square, 100 plates of 6 inches, and 150 of 4 inches, charged with solutions of alum and nitric acid; but although there was high intensity of action, nothing but hydrogen and oxygen was disengaged. He next tried potash in igneous fusion, and here the results were more encouraging; there were obvious and striking signs of decomposition; combustible matter was produced, accompanied with flame and a most intense light. He had observed that, although potash, when dry, is a non-conductor, it readily conducts when it becomes damp by exposure to air, and in this state "fuses and decomposes by strong electrical powers."

Let me state in his own words, for the words are classical, what followed:—

"A small piece of pure potash, which had been exposed for a few seconds to the atmosphere, so as to give conductive power to the surface, was placed upon an insulated disc of platina, connected with the negative side of the battery of the power of 250 of 6 and 4 [that is 100 plates of 6 inches square and 150 plates of 4 inches square] in a state of intense activity: and a platina wire communicating with the positive side was brought in contact with the upper surface of the alkali. . . . Under these circumstances a vivid action was soon observed to take place. The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the lower or negative surface, there was no liberation of elastic fluid; but small globules, having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces."

He goes on to say:—

"Soda, when acted upon in the same manner as potash, exhibited an analogous result; but the decomposition demanded greater intensity of action in the batteries, or the alkali was required to be in much thinner and smaller pieces.

"The substance produced from potash remained fluid at the temperature of the atmosphere at the time of its production; that from soda, which was fluid in the degree of heat of the alkali during its formation, became solid on cooling, and appeared having the lustre of silver."

It would seem from this description of its properties that the potassium Davy first obtained was alloyed with sodium owing to the fact that the potash contained soda. Potassium is solid up to 143° F., whereas, as Davy was the first to show, an alloy of potassium and sodium is fluid at ordinary temperatures.

On account of their alterability in contact with air, Davy had considerable difficulty in preserving and confining the new substances so as to examine their properties. As he says, like the Alkahests imagined by the Alchemists, they acted more or less upon almost every body to which they were exposed. Eventually, he found they might be preserved in mineral naphtha.

The "basis" of potash were described by him as a soft malleable solid with the lustre of polished silver.

"At about the freezing-point of water it becomes harder and brittle, and when broken in fragments exhibits a crystallised texture which in the microscope seems composed of beautiful facets of a perfect whiteness and high metallic splendour. It may be converted into vapour below a red heat, and may be distilled unchanged, and is a perfect conductor of heat and electricity. Its most marked difference from the common run of metals is its extraordinary low specific gravity." At the time of its discovery it was the lightest solid known.

The "basis" of soda was found to have somewhat similar properties. It was slightly heavier than the "basis" of potash, and fused at a higher temperature.

Davy next examined the behaviour of the new substances towards a large number of reagents, but as his observations are now the common property of the text-books, it is unnecessary here to dwell upon them.

He then enters upon some general observations on the relations of the "bases" of potash and soda to other bodies:—

"Should the bases of potash and soda be called metals? The greater number of philosophical persons," he says, "to whom this question has been put, have answered in the affirmative. They agree with metals in opacity, lustre, malleability, conducting powers as to heat and electricity, and in their qualities of chemical combination.

"Their low specific gravity does not appear a sufficient reason for making them a new class; for amongst the metals themselves there are remarkable differences in this respect. . . . In the philosophical division of the classes of bodies, the analogy between the greater number of properties must always be the foundation of arrangement.

"On this idea, in naming the bases of potash and soda, it will be proper to adopt the termination which by common consent has been applied to other newly discovered metals, and which, though originally Latin, is now naturalised in our language.

"Potasium (*sic*) and sodium are the names by which I have ventured to call the new substances; and whatever changes of theory, with regard to the composition of bodies, may hereafter take place, these terms can scarcely express an error; for they may be considered as implying simply the metals produced from potash and soda. I have consulted with many of the most eminent scientific persons in this country upon the methods of derivation, and the one I have adopted has been the one most generally approved. It is perhaps more significant than elegant. But it was not possible to found names upon specific properties not common to both, and though a name for the basis of soda might have been borrowed from the Greek, yet an analogous one could not have been applied to that of potash, for the ancients do not seem to have distinguished between the two alkalies."

Such, then, are the more significant features of one of the greatest discoveries ever made by a British chemist, as these are set forth in one of the most remarkable papers in the *Philosophical Transactions of the Royal Society*.

(To be continued).

EXPLOSIVE COMBUSTION, WITH SPECIAL REFERENCE TO THAT OF HYDROCARBONS.*

By Professor WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S.

It is hardly necessary to remind you that the subject of my discourse will be ever associated with the illustrious name of Davy. Davy turned his attention to the phenomena of flame in the year 1815, in response to an urgent appeal on the part of a committee formed in the North of England, to investigate the causes of accidents arising from the explosion of fire-damp in coal mines, and to devise means for their prevention. The perennial interest of his researches, however, lies not so much in their immediate practical success, great as this undoubtedly was, as in the broader theoretical issues which were disclosed, and brought within the region of experimental enquiry, by so splendid an exercise of genius.

Davy insisted on the necessity of considering flames in all cases "As the combustion of an *explosive mixture* of inflammable gas, or vapour, and air," and he defined flame as "aëriform, or gaseous matter, heated to such a degree as to be luminous." For the starting and propagation of a flame in an explosive mixture, he showed that each successive layer of gas must be raised to a certain definite temperature, called the "ignition point," and he investigated both the ignition temperatures and the explosion limits of a large number of the commoner combustible gases. He then proceeded to his famous discovery that, notwithstanding the extremely high temperatures of flames, which, in the case of cyanogen, he estimated to be "above 5000° of Fahrenheit," they can be readily extinguished by contact with a cooling surface of sufficient area and heat conducting power, and that for this purpose metal surfaces are by far the most efficient. How he developed and applied this discovery to the construction of his "safe-lamp" for miners is, of course, a matter of history.

In experimenting upon the ignition temperatures of explosive mixtures, Davy made the important and far-reaching discovery that combustible gases combine with oxygen at lower temperatures without any appearance of flame whatever. He emphasised the importance of a complete investigation of the chemical aspects of this flameless combustion, and he himself was led to ask whether, seeing that the temperatures of flames far exceed those at which solids become incandescent, a metallic wire can be raised to incandescence by the slow combustion of two gases "without actual flame, but producing heat enough to keep the wire ignited." In this way he discovered the remarkable property of platinum and other metallic wires of inducing surface combustion, and in the course of his further experiments on this subject, he made two notable observations respecting the burning of compounds containing carbon and hydrogen. He found "much carbonic oxide" produced when a platinum wire was kept incandescent by the slow combustion of a mixture of ethylene and oxygen, rendered non-explosive by an excess of the hydrocarbon, and in a similar experiment with ether vapour, he recorded the appearance of "a pale phosphorescent light" accompanied by "the formation of a peculiar acrid volatile substance possessed of acid properties."

Finally, in speculating upon the difficult and thorny subject of the luminosity of hydrocarbon flames, he was "led to imagine" that it "might be owing to the *decomposition* of part of the gas towards the interior of the flame where the air was in smallest quantity, and the deposition of solid charcoal, which, first by its *ignition*, and afterwards by its *combustion*, increased in a high degree the intensity of the light." It is important to observe that not only did Davy rightly attribute the luminosity of a hydrocarbon flame to the presence therein of incandescent carbon, but also that he avoided the error of attributing the separation of carbon to a supposed preferential burning of hydrogen.

In considering the propagation of a flame through an explosive mixture of gases, it is necessary to distinguish between two well-defined conditions. When such a mixture is ignited, the flame travels for a certain limited distance (a few feet only) at a fairly uniform slow velocity, which in the case of a mixture of hydrogen and oxygen in their combining ratios is approximately thirty-four metres (thirty-eight yards) per second. This initial stage of the combustion is called "*inflammation*."

After traversing a few feet, however, the flame begins to vibrate, and alters in character. The vibrations become more and more intense, the flame swinging backwards and forwards with oscillations of increasing amplitude. Then one or other of two things happens; either the flame is extinguished, or it goes forward with an exceedingly great and constant velocity, producing the most violent effects. The new condition thus set up is termed "*Detonation*," and the forward movement of the flame is called the "*Explosion Wave*."

The discovery of "*detonation*" in gaseous mixtures was made simultaneously by M. Berthelot and MM. Mallard and Le Chatelier, in the year 1881; Berthelot proved that the velocity of the explosion wave is independent of the length of the column of gas traversed, and that for the same gaseous mixture under given physical conditions it always has a constant value. In this connection I would mention Prof. H. B. Dixon's exhaustive researches on the "*rates of explosion*" of gaseous mixtures, which have extended in so many ways our knowledge of explosive combustion.

Experiment I.

Perhaps the best illustration of the outward difference between ordinary "*inflammation*" and "*detonation*" is afforded by the case of a mixture of carbonic oxide and oxygen in their combining ratios. When ignited in an open tube four or five inches long, the mixture burns quietly with the familiar blue flame. Far otherwise is it, however, when a long column of the mixture is fired in a leaden coil, where the brief initial period of *inflammation* is succeeded by the *explosion wave*, which dashes onwards through the gases at a rate of 1700 metres (about a mile) per second with shattering effect.

Another notable feature of "*detonation*" is the extremely short duration of the flame. In the course of some experiments carried out under Prof. Dixon's direction, it was found that the duration of luminosity in each successive layer of gas in the detonation of electrolytic gas does not exceed 1/5000th part of a second. But short as this time is, it is something like a million times longer than the

* Discourse delivered before the Royal Institution, February 28, 1908.

interval between successive molecular collisions in a gaseous mixture.

The question of how a hydrocarbon burns, that is to say, precisely how it is attacked by the oxygen, has been the subject of much discussion during the past fifteen years. A hydrocarbon is a compound of the two combustible elements, carbon and hydrogen, and in a sufficient supply of oxygen, both of these are ultimately burnt to carbon dioxide and steam, respectively. Thus, for example, in the case of ethane :—

$$\underset{2\text{ vols.}}{2C_2H_6} + \underset{7\text{ vols.}}{7O_2} = \underset{4\text{ vols.}}{4CO_2} + \underset{6\text{ vols.}}{6H_2O}.$$

On kinetic grounds, however, it seems inconceivable that the passage from the initial system of ethane and oxygen to the final system of carbon dioxide and steam can be immediate and direct. It is, therefore, universally recognised that the process involves a number of successive stages. But opinion has been sharply divided as to the nature and sequence of these stages, and I will now endeavour to put before you the main points in dispute. They may be conveniently summarised under three heads.

1. During the greater part of last century the belief prevailed that the hydrogen is much the more combustible of the two elements of a hydrocarbon, and that consequently when combustion occurs in a limited supply of oxygen, the hydrogen is preferentially burnt, as follows :—

$$C_2H_4 + O_2 = 2C + 2H_2O.$$

Who was the author of this view, or what was originally its experimental basis, is not quite clear, but it received the active support of two such eminent authorities as Thomas Graham and Michael Faraday, and for fifty years it was regarded as one of the most certain articles of chemical faith. Its final overthrow by Dixon and Smithells in the year 1892 caused no small stir in chemical circles.

2. The second theory originated with Kersten in 1861, who as the outcome of experiments on the explosion of a mixture of ethylene and electrolytic gas, asserted that "before any portion of the hydrogen is burnt, all the carbon is burnt to carbonic oxide, and that the excess of oxygen then divides itself between the carbonic oxide and the hydrogen." In other words, Kersten attempted to substitute the idea of the preferential burning of carbon for that of the preferential burning of hydrogen. His views, however, received no serious attention until they were revived and endorsed by Dixon and Smithells in 1892.

The chief experimental basis for this theory is the behaviour of ethylene and acetylene when exploded with their own volume of oxygen. More than a century ago, Dalton found that a mixture of equal volumes of ethylene and oxygen yields mainly carbonic oxide and hydrogen on explosion, without any separation of carbon, in conformity with the equation :—

$$\underset{1\text{ vol.}}{C_2H_4} + \underset{1\text{ vol.}}{O_2} = \underset{2\text{ vols.}}{2CO} + \underset{2\text{ vols.}}{2H_2}.$$

This fact, after being overlooked for nearly eighty years, was re-discovered by Dixon in 1891 ; moreover, a few years later, when it was proved that acetylene behaves in a precisely similar manner :—

$$\underset{1\text{ vol.}}{C_2H_2} + \underset{1\text{ vol.}}{O_2} = \underset{2\text{ vols.}}{2CO} + \underset{1\text{ vol.}}{H_2},$$

the advocates of the theory were able to claim a strong body of evidence in support of their case.

3. But the idea of a "*preferential*" combustion, whether of carbon or of hydrogen, seemed repugnant to well-established principles concerning the nature and conditions of chemical interactions in gaseous systems. Moreover, whilst the assumption of a *direct* passage from an initial system of ethylene and oxygen, $C_2H_4 + O_2$, to the system carbonic oxide and hydrogen, $2CO + 2H_2$, implied a simple transaction from the kinetic standpoint, an extension of the idea to the case of such a hydrocarbon as propylene—

$$2C_3H_6 + 3O_2 = 6CO + 6H_2,$$

would at once raise serious difficulties.

It therefore remained to consider whether the solution of the problem might not lie in the assumption of an initial *association* of the hydrocarbon and oxygen forming an unstable "oxygenated" molecule, which subsequently rapidly decomposes. Thus, for example, the changes involved in the explosive combustion of an equimolecular mixture of ethylene and oxygen might conceivably be represented somewhat as follows :—

$$C_2H_4 + O_2 = \underset{\text{Unstable.}}{[C_2H_4O_2]} = 2CO + 2H_2.$$

Many years ago, indeed, Prof. H. E. Armstrong suggested that the combustion of a hydrocarbon takes place under the conjoint influence of water and oxygen, and involves the successive formation of intermediate "*hydroxylated*" molecules, which at high temperatures rapidly decompose into simpler products. Little notice was taken of his suggestion at the time, but recent researches have shown that "*hydroxylated*" molecules are probably formed, even in flames, although I think it doubtful whether water vapour is an essential factor in the process.

The researches recently carried out at the Manchester University have covered the entire range of conditions under which hydrocarbons can be burned, from the slow flameless combustion discovered by Davy, right up to the extreme conditions of detonation. An exhaustive study of the slow combustion of methane, ethane, ethylene, and acetylene, at temperatures between 250° and 400° C., afforded decisive evidence against the preferential burning, whether of carbon or of hydrogen. Large quantities of aldehydic intermediate products were isolated, and the balance of evidence was decidedly in favour of the "*hydroxylation*" theory, with the proviso, however, that the oxygen is directly active. Finally, the following scheme was put forward for the slow combustion of ethane, and ethylene at 250° to 350° C. :—

$$\underset{\text{Ethane}}{CH_3.CH_3} \rightarrow \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} \rightarrow \underbrace{CH_3.CH(OH)_2}_{H_2O + \overbrace{CH_3.CHO}^{\text{Acetaldehyde}}} \rightarrow \underbrace{CO + H_2O + \overbrace{H.CHO}^{\text{Formaldehyde}}}_{\overbrace{CO + H_2O}^{\text{Formic acid}}} \rightarrow \underbrace{H.COOH}_{\overbrace{CO + H_2O}^{\text{Formic acid}}} \rightarrow \underbrace{CO(OH)_2}_{\overbrace{CO_2 + H_2O}^{\text{Carbonic acid}}}.$$

$$\underset{\text{Ethylene}}{CH_2:CH_2.} \rightarrow H_2C:CH(OH) \rightarrow \underbrace{(HO)CH:CH(OH)}_{\overbrace{2H.CHO}^{\text{Formaldehyde}}} \rightarrow \underbrace{H.COOH}_{\overbrace{CO + H_2O}^{\text{Formic acid}}} \rightarrow \underbrace{CO(OH)_2}_{\overbrace{CO_2 + H_2O}^{\text{Carbonic acid}}}$$

Translated into words, this means that, in the case of ethane, the initial oxidation product is probably *ethyl alcohol* $C_2H_5.OH$. The alcohol has not, indeed, been actually isolated during the slow combustion at 300° C., chiefly because it is much more rapidly oxidised under these conditions than is ethane itself; it is, however, formed in quantity when ethane is oxidised by means of ozone at 100° C. The second stage involves the rapid oxidation of the alcohol to the unstable $CH_3.CH(OH)_2$, which at once decomposes into steam and *acetaldehyde*. The acetaldehyde is in turn burnt to carbonic oxide, steam, and *formaldehyde* (possibly through the unstable $\begin{matrix} .H \\ HO.C.H \\ HO{\cdot}\dot{C}{:}O \end{matrix}$), and finally the formaldehyde is burnt to steam and oxides of carbon, probably through *formic acid* and *carbonic acid*.

As the temperature rises, the intermediate products become more and more unstable, and to an increasing extent decompose into simpler products, which then undergo independent oxidation. Thus *ethyl alcohol* decomposes into ethylene and steam, *acetaldehyde* either into methane and carbon monoxide, or into carbon, hydrogen,

methane, and carbon monoxide, according to the temperature, and *formaldehyde* is resolved into carbon monoxide and hydrogen, as follows:—

Ethyl Alcohol.	Acetaldehyde.	Formaldehyde.
C_2H_5OH.	$CH_3.CHO$	$H.CHO$
$C_2H_4+H_2O$.	CH_4+CO / $C+2H_2+CO$	$CO+H_2$

With the extension of the research to the conditions existing in hydrocarbon flames and explosions, it became increasingly evident that the mechanism of combustion is essentially the same above as below the ignition point. I do not mean, of course, that the phenomena observed at low temperatures, in slow combustion, are exactly reproduced in flames, but rather that the result of the initial molecular encounter between the hydrocarbon and oxygen is probably much the same in the two cases, namely, the formation of an "oxygenated" molecule. At the higher temperatures of flames, secondary thermal decompositions undoubtedly come into operation at an earlier stage, and play a more important *rôle* than in slow combustion, but they do not precede the onslaught of the oxygen upon the hydrocarbon, but arise in consequence of it. I am aware that there are eminent critics who, whilst admitting the validity of these views as applied to slow combustion, hesitate to accept entirely their extension to explosive combustion. They find it difficult to believe that such compounds as ethyl alcohol, acetaldehyde, formaldehyde, and the like, which are undoubtedly very unstable at high temperatures, can possibly be formed in flames. But surely this objection involves some confusion of thought as to the factors which govern the formation and stability of chemical compounds; the fact that a substance cannot permanently exist at a given temperature does not justify the assertion that it cannot be formed at that temperature by the operation of factors which are not concerned in its decomposition. Therefore, I am not prepared to admit that because the acetaldehyde molecule does not long remain intact at high temperatures, it necessarily follows that it cannot be brought into actual existence as the result of the interaction of ethane and oxygen in flames.

Professor Smithells, in his recent presidential address to the Chemical Section at the British Association (1907), expressed his dissent from my views, as applied to flames, on the ground that "The isolation of an intermediate product under one set of circumstances is in itself no proof that this product is transitorily formed when the reaction is proceeding under another set of circumstances. . . ." To this I would reply, that whilst the isolation of (say) acetaldehyde in the slow oxidation of ethane is not *by itself* sufficient proof of its transitory formation in the explosive combustion of the hydrocarbon, yet if it can be demonstrated, not only that the facts of explosive combustion can be *best* interpreted on the assumption of its formation, but that, so far as can be judged at present, no other interpretation can be advanced, and, moreover, that aldehydes are actually produced in flames, then it may be justly claimed that the assumption is well founded, and that the onus of its experimental disproof rests with the sceptics.

(To be continued).

APPARATUS FOR SUBLIMATION.

By W. G. LLEWELLYN.

Purification of a substance by sublimation is very easily and rapidly carried out in the apparatus here described.

It consists of an open tube about five and a-half inches long fitting closely inside a six-inch test-tube. The open tube is conveniently made from a large test-tube by cutting the closed end off.

The substance to be sublimed is placed in the test-tube, warmed, and condensed on the inner tube. This is removed, scraped, and the substance obtained free from any charred residues.

A plug of glass-wool fitting loosely into the open end of he apparatus prevents the escape of vapour.

MARIGNACITE.*

A New Variety of Pyrochlore from Wausau, Wisconsin.

By S. WEIDMAN and VICTOR LENHER.

In the north-central part of Wisconsin, within the general pre-Cambrian area, there are widespread occurrences of igneous rocks intrusive in the Huronian sedimentaries. ("Geology of North Central Wisconsin," *Bull.* No. xvi., Wisconsin Geological and Natural History Survey). Chief among these intrusives is a complex magma, consisting of various phases of granite, quartz-syenite and nepheline-syenite. Pegmatitic modifications are a characteristic feature of the granite-syenite magma, both nepheline and quartz-bearing pegmatites being developed in considerable quantity. In several phases of the quartz-bearing pegmatite a small octahedral mineral was observed that proved upon investigation to be a variety of the rare group of pyrochlore minerals, the principal constituents of which are the metals of the rare earths.

The minerals associated with the pyrochlore in the pegmatite consist mainly of quartz, alkali-felspar, and acmite. Other minerals in the pegmatite veins of the locality are lithia-mica, lepidomelane, varieties of acmite-pyroxene high in alumina and potassium, rutile, fluorite, and several zirconium-bearing minerals. The pegmatite and associated-granite and syenite are closely related in composition, and are characterised by a relatively high content of alumina and soda. In most respects the granite and nepheline-syenite are similar to the well-known occurrences of nepheline-bearing and associated rocks of Arkansas, Ontario, Canada, Essex County, Mass., and the Christiania region of southern Norway.

The pyrochlore was found in the pegmatite occurring along the road in the S.W. 1/4 of Sec. 22, T. 29, R. 6 E., about nine miles north-west of Wausau. It occurs only in small crystals of nearly perfect octahedral form, varying in form up to about one-eighth inch (3 mm.) in diameter. The mineral was found in small quantity, and although after its identification further search was made for it, only a small additional amount was secured. It is likely, however, that the pyrochlore will be found elsewhere in the pegmatite veins of the immediate locality, although very probably only in small quantity.

The only form of the mineral observed was the simple octahedron (Fig. 1). Some of the crystals occur in aggregates (Figs. 2 and 3) and some show a slightly distorted form, but no combinations with other crystal forms were observed. Under the microscope inclusions of quartz and felspar were seen. This examination showed the mineral to be homogeneous, with none of the characteristic features of alteration or of replacement.

Chemical Analysis.—The pyrochlore used for analysis was first picked out by hand from the crushed rock. As the latter was somewhat disintegrated, many of the small octahedral crystals were readily separated from the associated minerals by crumbling the rock under pressure of the hand. Before the mineral was powdered each crystal was examined with a hand lens and all adhering minerals were rubbed off so far as possible. After being powdered and passed through a 100-mesh sieve, the powdered material was subjected to separation by a specific gravity solution of silver-thallium nitrate, and by this method the adhering and included particles of quartz, felspar, and acmite were separated from the pyrochlore. The relatively high specific gravity of the pyrochlore furnished conditions favourable for the separation by the specific gravity method, and for this reason, as well as others later described, the mineral analysed is believed to have been essentially pure.

The analysis of the pyrochlore made upon 3·15 grms., and the molecular ratio of the constituents, is as follows:—

* Published by permission of the Director of the Wisconsin Geological and Natural History Survey. From the *American Journal of Science*, xxiii., p. 287.

Analysis of Pyrochlore (Marignacite) from Wausau, Wisconsin.

	Analysis.	Molecular Ratio.
Cb_2O_5	55·22	0·198
Ta_2O_5	5·86	0·013
SiO_2	3·10	0·051
TiO_2	2·88	0·036
Fe_2O_3	0·50	0·003
FeO	0·02	
Ce_2O_3	13·33	0·040
Yt_2O_3	5·07	0·022
ThO_2	0·20	0·001
CaO	4·10	0·073
MgO	0·16	0·004
Na_2O	2·52	0·041
K_2O	0·57	0·006
F	none	
H_2O at 110°+ ..	5·95	0·331
H_2O at 110°− ..	0·45	
	99·93	

Al_2O_3, MnO, SnO_2, WO_3, Di_2O_3, La_2O_3, Er_2O_3, occur in traces, while F, ZrO_2, BeO, UO_2, Li_2O, could not be detected. The mineral shows no radio-activity.

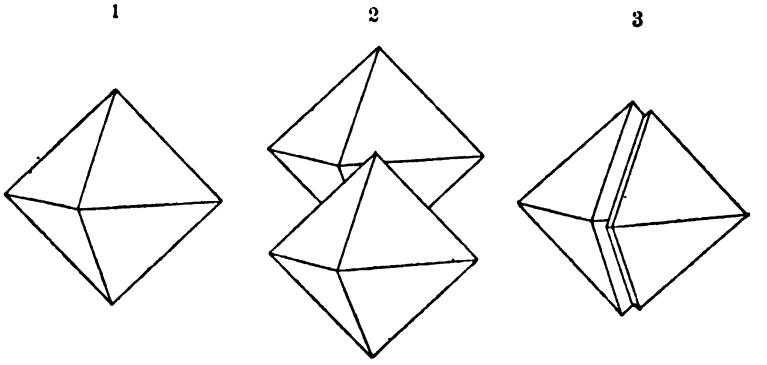
The mineral has a hardness of 5 to 5·5, a specific gravity of 4·13. The cleavage is indistinct, the mineral is brittle and breaks with a conchoidal fracture. The lustre is resinous on fractured surfaces. The streak is light brown to yellowish-brown. The colour varies from a light to dark brown in the hand specimen, while under the microscope a yellow brown to red brown is shown.

It is sub-translucent to transparent. The index of refraction is relatively high and anomalous double refraction is characteristic. Before the blowpipe it is infusible and unchanged. In the borax or salt of phosphorus bead, it dissolves with a yellow colour while hot, and is colourless when cold. The mineral is very refractory to the acids, and is only slightly attacked by fused sodium carbonate. It is attacked in the cold by hydrofluoric acid, and can be decomposed by fusion with either potassium acid sulphate or potassium acid fluoride.

For analysis the mineral can be decomposed either by fusion with potassium acid sulphate, in which case the silica and metallic acids can be separated from the earths, &c., or it can be decomposed by treatment with hydrofluoric acid, when the metallic acids pass into solution, leaving the earthy fluorides insoluble.

Silica was estimated in the residue obtained from repeated extractions of a bisulphate fusion by volatilisation with hydrofluoric acid in the presence of sulphuric acid. The columbic and tantalic acids were tested for tin, molybdenum, tungsten, titanium, and the earths. The titanium was separated from them by a bisulphate fusion, and the metallic acids were separated by the Marignac method of crystallising the double potassium fluorides from each other. It is perfectly well appreciated that the results for columbium and titanium are only closely approximate, for as shown by Hall (*Journ. Am. Chem. Soc.*, xxvi., 1235), Smith (*Ibid.*, xxvii., 1369), and Warren (*Am. Journ. Sci.*, 1906, xxii., 520), it is impossible by present methods to obtain a perfect separation of these two elements. Six crystallisations were made to separate the columbium and tantalum.

The earths after being precipitated together were treated in acid solution with ammonium oxalate. The oxalates were ignited, dissolved in nitric acid, and the excess of acid removed by evaporation. The nitrates were treated with a saturated solution of potassium sulphate. The thoria was separated by means of the thiosulphate and ammonium oxalate methods. The ceria was purified by suspending the hydrate in a solution of potassium hydroxide and treating with chlorine. The weighed oxide was of a salmon colour, and when dissolved as nitrate its solution showed no absorption bands. Didymium and lanthanum could be detected only in traces. In the soluble yttrium group the nitrate solution showed the erbium bands quite markedly. Fluorine, zirconium, beryllium, uranium, and lithium were carefully tested for, but found to be absent. The basic portion of this mineral is largely composed of the cerium and yttrium metals, while silica and the oxide of titanium appear to the extent of nearly 6 per cent. From the careful manner with which the mineral used for analysis was selected and purified, and from the microscopic character of the fragments used, it appears as though the silica and titanium oxide were normal constituents of the mineral.



Fluorine could not be detected by even the most careful examination. The high content of water, 5·95 per cent, given off above 110 degrees and the absence of fluorine may be due to the fact that fluorine and hydroxyl are mutually interchangeable in this group of minerals, as they are in the lithia fluorine micas, and in triploidite and related minerals of the wagnerite group. The isomorphism between hydroxyl and fluorine was first demonstrated by the late Prof. Penfield, who showed its existence for the first time in triploidite, and later in many other minerals in which these radicals occur.

The analyses of marignacite and the several members of the pyrochlore group given in the table show the presence of either or both of these radicals in each of the completed analyses. While a careful determination of the hydroxyl in the analyses of these minerals has apparently not been carried out, it seems reasonable to apply the principle of isomorphism of these radicals in this group.

The presence of an appreciable content of silica, 3·10 per cent, in the pyrochlore from Wausau, perhaps needs further discussion. As already stated, the pyrochlore is associated in the rock with quartz, felspar, and varieties of aluminous acmite containing 5 per cent Al_2O_3 and above, and these minerals to a slight extent were necessarily included in the powdered material prepared for the

specific gravity separation. Previous to powdering the material, however, each pyrochlore crystal was examined and all material clinging to the latter was rubbed off so far as possible. The relatively high specific gravity of the pyrochlore, namely, 4·13 as compared with 2·6 of quartz, 2·6 of felspar, and 3·5 of acmite, should furnish a favourable means for separation by the method adopted. The fact that the chemical analysis shows only a trace of alumina indicates the essential absence of felspar and aluminous pyroxene in the material analysed. And if these minerals were successfully removed from the powdered material in the process of separation by the specific gravity method, it seems reasonable to believe also that the quartz was removed at the same time and to the same extent. Hence it seems probable that the silica is a normal constituent of this mineral.

If the SiO_2 is an original constituent of this pyrochlore, it differs in this respect from other varieties of pyrochlore. Silica is shown in the analysis of some of the members of the columbate-tantalate groups, but it is usually considered of secondary origin. However, if the silica with the titanium oxide are normal constituents, they indicate an interesting relation in the composition of this pyrochlore to many of the titano-silicate minerals, such as tscheffkinite, johnstrupite, mosandrite, rinkite, and also to dysanalyte. In content of cerium oxide this pyrochlore from Wausau is higher than in any of the other pyrochlores, and in its high content of cerium oxide it also resembles the titano-silicates referred to. This pyrochlore with appreciable content of SiO_2, believed to be a normal constituent, therefore, shows an interesting relation in composition between the titano-silicates on the one hand and of the columbate-tantalates on the other.

In the table the analysis of the pyrochlore from Wausau is shown in comparison with the analyses of the typical varieties described by various investigators. By comparison of the several analyses in the table it may be seen that the pyrochlore from Wausau differs from the others in the proportion of each of the several acid and basic radicals. The principal difference in composition with respect to individual constituents appears to be the relatively higher content in the Wausau pyrochlore of cerium and yttrium, and the lower content of lime and iron as compared with the other members of the pyrochlore group. The presence of silica in the Wausau pyrochlore is also a distinctive feature, as already stated.

The name *marignacite* is proposed for this variety of pyrochlore in honour of Marignac, who besides making other valuable contributions to chemistry, developed the method for separating columbium and tantalum through the agency of the difference of solubility of their double fluorides in hydrofluoric acid, which is to-day the most satisfactory method of separating these two elements.

Analyses of Varieties of Pyrochlore.

1. Pyrochlore from Brevik, Norway: Analyst, C. F. Rammelsberg; cited by Brögger, *Zeit. Kryst.*, xvi., p. 512.
2. Koppite, from Schelingen, Baden: G. H. Bailey, *Journ. Chem. Soc.*, 1886, xlix., p. 153.
3. Marignacite from Wausau, Wisconsin: Analyst, V. Lenher, 1906.
4. Hatchettolite from Mitchell Co., N. Carolina: O. D. Allen, *Am. Journ. Sci.*, 1877, xiv., p. 128.
5. Pyrochlore from Batum: G. P. Tschernik, *Zeit. Kryst.*, 1904, xxxix., 624.
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	1.	2.	3.	4.	5.	6.
Cb_2O_5 . .	58·27	61·64	55·22	34·24	26·22	7·74
Ta_2O_5 . .	—	—	5·86	29·83	27·39	68·43
TiO_2 . .	5·38	0·52	2·88	1·61	4·20	—
SiO_2 . .	—	—	3·10	—	—	—
Fe_2O_3 . .	—	—	0·50	—	0·26	0·42*c*
FeO . .	—	3·01	0·02	2·19	6·32	—
CaO . .	10·93	16·61	4·10	8·87	6·00	11·80
MgO . .	—	1·62	0·16	0·15	—	1·01
Na_2O . .	5·31	3·58*f*	2·52	1·37	3·15	3·15*d*
K_2O . .	—	0·36*g*	0·57	Trace	—	—
ThO_2 . .	4·96	—	0·20	—	—	—
Ce_2O_3 . .	5·50	6·89*b*	13·33	—	12·34	0·17*e*
Yt_2O_3 . .	—	—	5·07	—	—	0·23
Di_2O_3 . .	—	—	—	—	0·63	—
La_2O_3 . .	—	—	—	—	0·71	—
UO_2 . .	5·53*a*	—	None	15·50	8·33	1·59
SnO_2 . .	—	—	Trace	0·30	—	1·05
WO_3 . .	—	—	Trace	—	—	0·30
BeO . .	—	—	—	—	—	0·34
ZrO_2 . .	—	3·39	None	—	—	—
F. . . .	3·75	Trace	None	—	1·90	2·85
H_2O 110°+	1·53	—	5·95	4·49	1·45	1·17
H_2O 110°−			0·45			
Total . .	101·16	—	99·93	98·55	98·90	100·25

a, with FeO; *b*, with La,Di; *c*, with 0·13 Al_2O_3; *d*, with 0·29 K_2O; *e*, with Di; *f*, calculated as Na; *g*, calculated as K.

THE REPORTED SOLIDIFICATION OF HELIUM.

THE following letter from Sir James Dewar appeared in *The Times* of the 16th inst.:—

Sir,—As I was responsible for communicating to *The Times* a telegram from Professor Kamerlingh Onnes announcing the solidification of helium, I should like to lay before your readers an important correction resting upon the authority of a written detail of the Leiden experiments which I have recently received.

Professor Onnes has found that the helium operated upon, though purified with due care, had by some unexplained accident got mixed with a small percentage of hydrogen. The transient solidification witnessed on rapidly expanding the mixed gas from a state of high compression at a very low temperature was due to the hydrogen, of the presence of which Professor Onnes was unaware. The net result is that we are as far as ever from achieving the liquefaction or solidification of helium even as a momentary phenomenon. On the other hand, if the critical temperature of helium is no higher than 5° absolute, as Professor Onnes infers from a study of its isothermals at temperatures reached by the use of liquid hydrogen, then we may confidently predict, as stated in my Presidential Address to the British Association in 1902, that unless with costly expenditure it would be hopeless to anticipate any success in obtaining the liquid or solid in the static condition. My hopes of the Royal Institution method of attacking the problem leading to a satisfactory result were based on the assumption that the critical temperature of helium would not be lower than about 8° absolute; but if Professor Onnes is right, then it is clear that any resources I can at present command would be inadequate to settle the question.

JAMES DEWAR.

Royal Institution of Great Britain, April 14.

Royal Institution.—On Tuesday next, April 28, at 3 o'clock, Mr. Gerald Stoney begins a course of two lectures at the Royal Institution on "The Development of the Modern Turbine and its Application"; on Thursday, April 30, Mr. William Bateson commences a course of three lectures on "Mendelian Heredity" (these are the Tyndall Lectures); and on Saturday, May 2, Mr. G. F. Scott Elliot delivers the first of two lectures on "Chile and the Chilians." The Friday Evening Discourse on May 1 will be delivered by Professor Joseph Larmor, on "The Scientific Work of Lord Kelvin"; on May 8, by Mr. John Young Buchanan, on "Ice, and its Natural History"; and on May 15, by Mr. Herbert Timbrell Bulstrode, on "The Past and Future of Tuberculosis."

VOLUMETRIC METHOD FOR THE DETERMINATION OF ZINC.*

By WM. HERBERT KEEN.

SEVERAL schemes have been advanced for the estimation of zinc by titration with potassium ferrocyanide, but so far no one of them has found universal application, The methods which have found favour are either so complicated or so difficult in manipulation that a large personal error is always introduced, and it seldom happens that very close checks are obtained by different operators, even when the same procedure is followed. Nearly a year ago I became interested in the volumetric determination of this metal with the idea of substituting it for the rather tedious gravimetric method which has always been in use in the laboratory of Booth, Garrett, and Blair, of Philadelphia.

At first, and for quite a long time in fact, I was not very successful, and encountered numerous difficulties. The samples which I used in this preliminary work were spelters, the zinc content of which had been very carefully determined by difference. Finally, after a trial of all the methods which seemed reliable, with varying successes, I concluded that changes might be made to good advantage in nearly all of them, so with what experience I had already gained, I attempted to work up a scheme which would embody the good points of all of these methods, and as far as possible none of the bad ones. The method which I am about to describe, therefore, is not new, but is rather a re-modelling of the older ones. The scheme is one which is identical in certain parts for almost every condition, but there are some slight variations which are necessary for different products, and, if accuracy is desired, they should be observed. Accordingly, I will describe the method, applying it to typical cases.

Preparation of the Ferrocyanide Solution.—Dissolve crystals of chemically pure potassium ferrocyanide in water in the proportion of 22 grms. to the litre. If the solution is not clear, it should be filtered before it is diluted to the desired volume. It is a good plan to make up several litres at a time, as the solution remains constant almost indefinitely, and if many determinations are necessary, a bottle of 15, or even 20, litres of solution will not last very long.

Preparation of the Standard Zinc Solution.—This solution should be made up with the greatest care, as all subsequent work depends on its accuracy. In order to make up 2 litres, weigh very carefully, and transfer to an 800 cc. beaker 10 grms. of chemically pure zinc or an equivalent weight of the oxide (12·4465 grms.)—if the latter is used, it must be freshly ignited, cooled in a desiccator—and dissolved in 50 cc. of hydrochloric acid diluted with water. Heat until solution is complete, and then dilute to about 300 cc., and add a considerable excess of bromine water. Heat until the bromine is entirely expelled. Wash the cover-glass and the sides of the beaker, and add an excess of ammonia. Put in a warm place on the hot plate where it will remain just below the boiling-point, or boil very gently for about fifteen minutes. By this time the small amount of iron, which is nearly always present, should be completely precipitated. Filter carefully into a graduated litre flask, washing the beaker and precipitate once with water containing a little ammonia, and then several times with hot water. Replace the flask under the funnel by a small beaker (about 250 cc. capacity), and dissolve the iron precipitate in hot dilute hydrochloric acid. Re-precipitate the iron with ammonia, and filter again, adding the filtrate to the main solution. Burn the filter-paper containing the iron precipitate, and ignite. Weigh as Fe_2O_3 and calculate to Fe, deducting this weight from the original 10 grms. of zinc. Sometimes small amounts of silica and dirt are also present in the so-called chemically pure zinc, and the weight of this should also be deducted. These are small corrections, and make very little difference as a rule, but it is always well to make them, as it gives the operator more confidence in his results, and leaves no loop-hole for inaccuracy in later work. Now make the solution barely acid, using a small piece of litmus-paper as an indicator, and add 30 cc. of hydrochloric acid in excess for each litre of solution. Add also 10 grms. of ammonium chloride for each litre. Dilute to the mark with water, after cooling, and pour carefully into a *dry* 2-litre bottle. Do not wash out the flask, but after it has drained as much as it will, fill it to the mark with distilled water, and add this to the rest of the solution. Shake until thoroughly mixed, and the solution is ready for use. Its value will be 0·0050 grm. of zinc per cc. of solution—less a small correction due to the impurities deducted from the original weight.

Standardisation.—By means of standard pipettes, measure out three portions of the zinc solution of 20 cc. each, three portions of 50 cc., three of 70 cc., and three of 100 cc., into 400 cc. beakers of the wide shallow type, which will greatly lessen the amount of stirring necessary in order to obtain a homogeneous solution after each addition of the ferrocyanide. Add about 1 cc. of hydrochloric acid to each of the smaller portions. Dilute each to 150 cc., and all are ready for the titration. Except for very accurate work it is not necessary to take more than three or four portions altogether (one for each amount) to determine the average value of the ferrocyanide solution, but it has been found that a slightly different factor should be used for different amounts of zinc (*Journ. Am. Chem. Soc.*, xxix., 205), hence the necessity in accurate work for establishing these factors for amounts of solution likely to be used most frequently. Fill a clean burette with ferrocyanide, heat one of the portions of zinc chloride nearly to boiling, and titrate as follows:—Pour off about 20 cc. of the hot zinc solution into a small beaker, and set it aside. Titrate the remainder by running in ferrocyanide, a few cc. at a time, until a drop tested on a porcelain tile with a drop of 5 per cent solution of uranium acetate shows a decidedly brown colour. Now add all but about 2 cc. of the reserved portion, and having tested to be sure that the end-point is not now overstepped, add the ferrocyanide in portions of half a cc. at a time until the end-point is again passed. Finally, add the last of the reserved portion, washing it all out with distilled water, and carefully washing down the sides of the titration beaker, and finish the titration by adding two drops at a time, testing after each addition. The end-point at this time will be sharper if instead of one drop two or three drops are added to the drop of uranium acetate on the tile. The amount of zinc lost at this stage of the titration will be so small as to be insignificant. When the final distinctly brown tinge is obtained, wait a minute and observe if one or more of the preceding tests do not also develop a colour. Note the number of spots by which the end-point has been overstepped, and since each test means an addition of two drops, or 0·1 cc. of solution, make the necessary correction when reading the burette. A blank should also be made, and the final reading and all other readings corrected by this amount. The blank should be made with a solution containing 10 cc. of hydrochloric acid, neutralised with ammonia, made acid again, and after 3 cc. of acid have been added in excess, diluted to 150 cc., and heated nearly to boiling. This will usually require about 0·2 cc. to give a decided test. Run all the titrations in the same way, and calculate the values for 1 cc. of the solution for the different portions, taking the average of the three results in each case if they are close enough (it is easy to obtain checks within 0·1 cc.), thus obtaining the different factors for the varying amounts of zinc—or what is equivalent to the same thing, for varying amounts of ferrocyanide. In actual work later, the factor should be used for the amount of solution which corresponds most nearly to that required for the titration. Ordinarily, however, the one average factor for three or four different amounts of zinc will be accurate enough for all determinations.

* *Journal of the American Chemical Society*, xxx., No. 2.

The last solution which I standardised had the following factors :—

Standard zinc solution.	Grms. of zinc.	Ferrocyanide solution.	Factors.
20	0·09995	19·4	0·005152
50	0·24988	48·1	0·005195
70	0·34983	67·2	0·005206
100	0·49975	95·5	0·005233

Greater accuracy could be obtained with a slightly weaker solution, say, 15 or 18 grms. to the litre, but for general application I find a solution of the above strength the most convenient.

Determination of Zinc in a Spelter.

Method of Sampling.—There are several methods in common use, but probably the most accurate one is to break off small pieces from slabs in different parts of the pile until enough has been obtained to make a fair average—say, five pounds for each car load, if the shipment is homogeneous. The sample thus obtained should then be heated in an ordinary clay crucible until just melted, when it should be poured into a wooden box, previously rubbed with chalk—and shaken violently. A box suitable for this must be made with tight joints and no cracks, and should be supplied with a cover. This treatment should result in a finely granulated sample. Screen out the coarser pieces by passing through a 20-mesh, and reduce the bulk of the fine stuff by coning and quartering until a small working sample is obtained. This not only will be found very easy to weigh, but will in addition almost perfectly represent the whole consignment.

Analysis.—Weigh 5 grms. of the sample of spelter, place in a 600 cc. beaker, cover with a watch-glass, and dissolve in 50 cc. of hydrochloric acid (1·20) diluted with water. Heat until completely dissolved. The evolution of hydrogen, occasioned by the solution of the zinc, precipitates such metals as copper, lead, and tin; but the heating should be continued until these metals go into solution again, as they occlude small amounts of zinc. When solution is complete, neutralise with ammonia, and re-acidify with hydrochloric acid (1·20), adding 5 cc. in excess, dilute to about 300 cc., and pass a current of hydrogen sulphide gas through the warm solution for about twenty minutes. If the precipitated sulphides do not settle readily, allow the solution to stand for an hour or so at a temperature just below the boiling-point. This will not be necessary unless tin is present. Filter off the sulphides, allowing the filtrate to run into an 800 cc. beaker, and wash the filter thoroughly with hot water. Heat the filtrate to gentle boiling, and after the free hydrogen sulphide has been expelled add a large excess of bromine water, and continue the boiling until the bromine has been expelled. Now add a large excess of ammonia, and boil gently for about fifteen minutes. If the amount of iron is considerable, it will not be necessary to boil so long, as it is only in the case of very small amounts that the precipitation is likely to be incomplete, unless the boiling is continued. Filter into a graduated litre flask, washing first with dilute ammonia—both the beaker and the filter—and then with hot water. Put about 10 cc. of hydrochloric acid (1·20) in the beaker, dilute with hot water, and pour it over the precipitate on the paper, allowing it to run through into a small beaker of about 250 cc. capacity. Re-precipitate with ammonia, and filter into the main solution in the flask, washing as before. If the amount of iron is very large large, a third precipitation will be necessary, but in the ordinary spelter this is not the case. Put a small piece of litmus-paper in the flask, and add hydrochloric acid (1·20) until the solution is just acid, and then add 30 cc. in excess. Cool to room temperature, and then make up to the mark with water. After mixing the solution thoroughly by several decantations back and forth from the flask to a beaker, measure out several portions of 100 cc. each (equivalent to one-half grm. of spelter) by means of a pipette. I find it convenient to use a 400 cc. beaker for the titration. Usually only one portion is necessary, but it is well to have a second one in reserve. Dilute to 150 cc., heat nearly to boiling (about 85°), and titrate with ferrocyanide, as described in the procedure for standardisation. Calculate the percentage of zinc by multiplying the standard value of 1 cc. by the number of cc. required (less the blank), and divide by 0·5, the weight of spelter taken as a sample.

If manganese is present in the spelter—a rare occurrence—the above result will be too high. If time is an object, the quickest way to overcome this difficulty is to make a separate determination of the manganese, although it may be removed before titration in a way I shall describe later. To determine the manganese, the best and most rapid way is to use the bismuthate method as applied to steels. Dissolve 1 grm. of the spelter in a 150 cc. Erlenmeyer flask in 50 cc. of nitric acid (1 to 3), and boil off the nitrous fumes. Cool in ice-water, and add about a grm. of sodium bismuthate. If manganese is present, the pink colour of permanganic acid will develop at once. If such is the case, filter through an asbestos filter into a 300 cc. Erlenmeyer, washing with 100 cc. of ice-cold 3 per cent nitric acid. Add a measured amount of ferrous sulphate solution (12 grms. to the litre) until the solution is perfectly colourless; titrate the excess with a standard permanganate solution (1 grm. to the litre). Subtract the volume of permanganate required from the amount of the latter equivalent to the volume of ferrous sulphate used and multiply by the manganese value of the permanganate solution. The factor is about 0·00035 for a solution of this strength. This will give the percentage of manganese in the spelter. The chemical equivalent of this amount in zinc should be deducted from the percentage of zinc previously obtained.

If cadmium is present, it will also remain in solution with the zinc, and will affect the titration in a manner similar to the manganese. It is usually present in such very small amounts that it is not readily precipitated by hydrogen sulphide except from a nearly neutral solution, in which part of the zinc is also precipitated. It is therefore necessary to make a separate determination of the cadmium and correct the apparent amount of zinc, as was done in the case of manganese. Another alternative, which has given me doubtful success in the case of such small amounts, is to boil the solution for a few minutes with a piece of aluminium foil, just previous to titration. The aluminium thus introduced into the solution does not affect the result. Usually, however, unless specially asked for, cadmium is always counted as zinc.

(To be continued).

NOTICES OF BOOKS.

Fertilisers and Feeding Stuffs. By BERNARD DYER, D.Sc. Fifth Edition. London: Crosby Lockwood and Son. 1908.

THIS handbook is intended for the practical farmer, and in consequence the subject is treated from a more popular point of view than would be necessary or desirable if it were for the use of men who had had the advantage of some scientific training. It is extremely difficult to provide for agriculturists the information which will be immediately and practically useful to them, without wrapping it up in a covering of general preliminary explanation, which sometimes to the unskilled seems to obscure the scientific truths altogether, but the author has succeeded admirably in this little book. His evidently wide knowledge of farming practice will no doubt encourage his readers to accept his statements not as theories based upon experiments, but as facts accumulated in actual work. Of the former the farmer is suspicious, but now-a-days he is generally willing to accept the help of science if the services rendered by it on a scale comparable with his own are put definitely and clearly before him, as in

this book. The Fertilisers and Feeding Stuffs Act of 1906 is quoted in full, and notes upon it have been added by A. J. David, B.A, Ll.M.

Analytical Notes. 1907. London and Liverpool: The Laboratories of Evans Sons, Lescher, and Webb, Ltd. 1908.

THIS pamphlet contains an alphabetical list of the various drugs and chemicals which have been examined in the laboratories of Messrs. Evans Sons, Lescher, and Webb, Limited, together with notes upon the degree of purity of the different products. It gives a very good indication of what are the likely adulterations in the substances considered, and of what likelihood there is of obtaining a perfectly pure product in the market. The results of the analysis of pure specimens are compared with those of adulterated products, and in addition some methods of assay which have been perfected in the laboratories are described fully. The pamphlet will be of use to pharmaceutical chemists, who will find in it information relating to the probable adulterations and impurities in commercial samples of many important drugs.

Les Produits Industriels des Goudrons de Houilles et leurs Applications. ("The Industrial Products of Coal-Tar and their Applications"). By VLADIMIR DE VULITCH. Paris: Gauthier-Villars.

THE most important products obtained from coal-tar are considered in this book more from a commercial than scientific point of view. The reader is supposed to be acquainted with the chemical nature and properties of the substances dealt with, and only the industrial uses are discussed. These, however, are treated very fully, and practical methods of testing, which make up in speed for what they lack in accuracy, are specially emphasised. The adulteration of each product is considered, and also its valuation, while the principal conditions which a good marketable sample must fulfil are carefully explained. The applications of the various classes of products are enumerated, and chemists and manufacturers interested in coal-tar products will find that the little book contains much that will aid them in detecting the purity and estimating the value of specimens of the different products.

MISCELLANEOUS.

Tantalite in Australia.—In the Wodgina district in Western Australia a tantalite-bearing dike of pegmatite has been found near McCarthy's creek. In places the dike is almost entirely composed of the soda felspar albite, while elsewhere it is very largely quartz. Tantalite is very freely visible in the albite, in coarse pieces, often many pounds in weight. By ground-sluicing below the dike some heavy lumps have been obtained, one weighing about 500 lbs., evidently derived from the weathering-down of the pegmatite. The quantity of tantalite produced by the placer mining is 34·1 tons. The mines were worked energetically for a short time until the consumers' stocks were filled, and then the mineral could not be sold. The industrial uses of tantalite are at present very limited, and the demand for the mineral small.—*Mining and Scientific Press*, Toronto.

Vapour Densities of P_4S_3, P_4S_7, P_2S_5.—Alfred Stock.—Victor Meyer's apparatus was used to determine the vapour densities of the three sulphides of phosphorus from 600° to 1000°. All three sulphides decompose at a red heat, P_2S_5 in the neighbourhood of its boiling-point (520—530°), while P_4S_3 and P_4S_7, which boil at about 400°, have normal densities between fairly wide limits. Thus the vapour density of P_4S_3 at 700° is found to be 219 and of P_4S_7 337, while that of P_2S_5 is 185. P_4S_7 decomposes very rapidly between 750 and 800°.—*Berichte*, xli., No. 4.

MEETINGS FOR THE WEEK.

TUESDAY, 28th.—Royal Institution, 3. "The Development of the Modern Turbine and its Application," by Gerald Stoney, M.Inst.C.E., &c.
—— Royal Society of Arts, 8. "Lace as a Modern Industry," by Miss Isemonger.
WEDNESDAY, 29th.—Royal Society of Arts, 8. "Modern Roumania," by Alfred Stead.
—— Society of Dyers and Colourists, 8. "Dyeing and Colouring of Paper Pulp," by R. W. Sindall. "Germicidal Value of Petroleum Benzine," by F. J. Farrell and F. Howles.
THURSDAY, 30th.—Royal Institution, 3. (The Tyndall Lectures). "Mendelian Heredity," by William Bateson, F.R.S., &c.
—— Royal Society of Arts, 4.30. "Reminiscences of Indian Life," by the Rt. Hon. Lord Lamington, G.C.M.G., &c.
FRIDAY, May 1st.—Royal Institution, 9. "The Scientific Work of Lord Kelvin," by Prof. Joseph Larmor, Sec.R.S.
— — Royal Institution, 5. Annual Meeting.
SATURDAY, 2nd.—Royal Institution, 3. "Chile and the Chilians," by C. F. Scott Elliot, M.A., &c.

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THE CHEMICAL NEWS.

VOL. XCVII., No. 2527.

A SCHEME FOR THE SEPARATION OF THE RARE EARTHS.

By C. JAMES.

IN this communication a comparatively simple scheme for the separation of mixtures of the rare earths is offered in the hope that it may prove of value to anyone who is desirous of entering this very interesting field of research. The conclusions presented are the results of several years' investigation upon the various methods proposed for fractionation, and personal trial of the applicability of many other compounds which had not previously been employed for the separation of these elements. Only those methods which proved valuable will be mentioned.

It might be as well to state in the beginning, for the benefit of those who have had little cause to study this subject, that there is no quantitative method for the separation of any of the rare earths. The true members of this family comprise those elements that are included in the cerium and yttrium groups, and are characterised by their trivalency, and the fact that they form oxalates that are insoluble in dilute acids and in cold ammonium oxalate solution.

The nearest approach to a quantitative separation is found in the case of cerium. This is due to the fact that the properties of the metals of all these earths and of their salts, with the possible exception of cerium itself, vary among themselves by very minute differences.

Bearing these observations in mind, the following scheme is presented :—The mineral is decomposed either by hydrochloric acid, sulphuric acid, bisulphate of potassium, sodium hydroxide, or hydrofluoric acid. When hydrochloric acid is used the whole is evaporated to dryness to render the silica insoluble. It is then warmed with a little concentrated hydrochloric acid, after which the mass is treated with water and filtered. The filtrate may then be precipitated either by oxalic acid or ammonium oxalate. If the liquid contains a lot of mineral acid, ammonium oxalate is to be preferred. When sulphuric acid or potassium bisulphate has been used to break up the mineral, it is necessary to stir with cold water to obtain the solution of the desired elements.

Fusion with sodium hydroxide and washing with water gives a residue of oxides. These are dissolved in hydrochloric acid. Hydrofluoric acid decomposes many minerals, such as niobates, tantalates, &c., in the cold, giving a residue of rare earth fluorides, while silicon, niobium, tantalum, &c., go into solution. The insoluble fluorides are decomposed by means of sulphuric acid.

The sulphate or chloride solutions are then precipitated either by ammonium oxalate or oxalic acid, as mentioned above.

Having obtained the earths in the form of oxalates they are treated as follows :—

Zirconium and Thorium.

Should the rare earth oxalates contain these elements, they may be separated by boiling with a solution of ammonium oxalate, when the whole of the zirconium and nearly all of the thorium pass into solution. The residue is filtered off and washed with ammonium oxalate solution. On the addition of an excess of hydrochloric acid to the filtrate, thorium oxalate alone is precipitated, while the whole of the zirconium is held in solution by the oxalic acid produced by the action of the hydrochloric acid on ammonium oxalate.

As zirconium oxalate is soluble in an excess of oxalic acid, this reagent alone may be used in the absence of thorium. In this connection it should be remembered that the oxalates of cerium and of the earths of the yttrium group are somewhat soluble in hot concentrated ammonium oxalate solution, so that varying amounts go into solution. Thorium can, however, easily be separated from the yttrium earths which remain with it by means of the double sulphate of thorium and potassium, which is insoluble in a solution of potassium sulphate, while the corresponding compounds of the yttrium group are soluble. The crude thorium oxalate is converted into sulphate, and the cold solution is stirred with solid potassium sulphate. Sulphate solutions of the earths are the best to work with for this purpose, for if other compounds are used care must be taken to keep the solution from being too concentrated, since members of the yttrium group may be precipitated also.

After the removal of the yttrium earths cerium earths are still present, and thorium may be separated from these by means of the solubility of its oxalate in ammonium oxalate, or, according to Glaser, by the solubility of thorium oxalate in ammonium acetate (*Journ. Am. Chem. Soc.*, xviii., 782); also by the method of Wyrouboff and Verneuil, in which thorium is precipitated by hydrogen peroxide (*Bull. Soc. Chim.*, [3], xix., 219). These methods are given under the separation of cerium and thorium, because under usual conditions they separate together from the rest of the rare earths.

In the next step there are three alternatives which depend upon the composition of the oxalates as approximately determined by the solubility of the double sodium or potassium sulphates in potassium or sodium sulphate solution, viz. :—(*a*) If containing 20 per cent or more of the yttrium earths and only a trace of thorium; (*b*) if containing 20 per cent or more of the yttrium earths together with thorium; (*c*) if containing less than 20 per cent of the yttrium earths.

(*a*) When the material consists of 20 per cent or more of the yttrium earths and practically no thorium, the oxalates are converted into sulphates by mixing with strong sulphuric acid and carefully igniting until fumes of sulphuric acid are no longer evolved. The residue is then powdered and dissolved in *ice-cold* water. The resulting sulphate solution is stirred with solid sodium sulphate, which throws down the double sulphates of sodium and the cerium earths.

NOTE.—Another method, which is simpler if the oxides will dissolve in acid, is to ignite the oxalates, and dissolve the oxides so obtained in hydrochloric acid or nitric acid, dilute the solution, and treat with solid sodium sulphate until the double sulphates are precipitated. However, when oxalates rich in cerium are ignited, the oxides which are formed dissolve with great difficulty in hydrochloric or nitric acid, and so in this case it is better to treat the oxalates with sulphuric acid as mentioned above. Extra care must be taken when the chlorides or nitrates in solution are stirred with solid sodium sulphate, for if the solution is too concentrated metals from the yttrium group will be precipitated also.

This precipitate contains some of the yttrium group of earths, while small amounts of samarium, gadolinium, and europium remain in solution. The precipitate is separated by filtration and washed with a solution of sodium sulphate. The insoluble double sulphates consist chiefly of cerium, lanthanum, praseodymium, neodymium, samarium, europium, and gadolinium, together with small amounts of the yttrium earths in which the terbium, dysprosium, and holmium contents are considerably increased. These double sodium sulphates constitute Fraction A. The filtrate, on the addition of an excess of oxalic acid, throws down the oxalates of terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium, and scandium, together with some samarium, europium, and gadolinium. This precipitate forms Fraction B.

(*b*). The composition of the oxalates in this case is very similar to (*a*), the only difference being the thorium content.

The sulphate or chloride solution is treated with sodium sulphate and the insoluble double sodium cerium group sulphates, forming Fraction A, filtered off. Since sodium thorium sulphate is somewhat soluble in sodium sulphate solution, the filtrate is saturated with potassium sulphate, when the remaining thorium is precipitated as thorium potassium sulphate insoluble in potassium sulphate solution. After separating the precipitate, the filtrate is treated with an excess of oxalic acid, the insoluble oxalates being filtered off and washed. This material is added to Fraction B.

(*c*). In this, the third and last alternative, the oxalates consist almost entirely of the cerium metals, and it is best to start the work of separation from the point A.

Cerium and Thorium.

The next operation consists of separating cerium together with thorium, if the latter is present, from the other elements forming Fraction A. This is best carried out by treating the nitrate solution with an excess of zinc oxide and potassium permanganate. If the material is in the form of the insoluble double sodium sulphates it should be boiled with sodium hydroxide in excess. The resulting hydroxides are filtered off, well washed with hot water, and dissolved in nitric acid. In dealing with oxalates that contain large amounts of lanthanum, praseodymium, and neodymium, it is only necessary to ignite, when the oxides so obtained will readily dissolve in nitric acid. As a rule, when cerium is present in large amounts, since the oxide dissolves with great difficulty, the oxalates are converted into sulphates. The sulphate solution is then poured into fairly strong and boiling sodium hydroxide. The rare earth hydroxides formed under these conditions filter rapidly, and after washing with boiling water are dissolved in nitric acid. The nitrate solution obtained by any of the above methods is neutralised, stirred rapidly by a motor, and an *excess* of zinc oxide added. On the addition of potassium permanganate cerium peroxide is precipitated, and the addition is continued until the liquid, after continued stirring, remains red. This method leaves a little cerium in solution, which is separated later. The precipitate, consisting of cerium and manganese peroxides, together with thorium and a small amount of lanthanum, praseodymium, and neodymium, makes Fraction C. The filtrate is saturated with sodium sulphate, causing a precipitate of the double sulphates of sodium with lanthanum, praseodymium, neodymium, &c. This, after filtering and washing with sodium sulphate solution, constitutes Fraction D. To this last filtrate, containing small amounts of the yttrium group, an excess of oxalic acid is added. The oxalates so obtained are united with those forming B.

Thorium.

Although thorium is not now considered as a rare earth, methods for its purification do not seem to be altogether out of place. The cerium peroxide contains large amounts of manganese, which is first removed by dissolving in strong hydrochloric acid and precipitating the earths by means of solid sodium sulphate until no more insoluble double sulphates separate. The liquid is then filtered, and the precipitate washed with sodium sulphate solution. A portion of the thorium remains in the filtrate, but this can be separated either by means of oxalic acid or else by stirring with solid potassium sulphate.

The cerium sodium sulphate is boiled with an excess of sodium hydroxide, the residue filtered off, washed with boiling water, and dissolved in nitric acid. The nitrate solution is then neutralised by means of ammonia, after which peroxide of hydrogen is added (Wyrouboff and Verneuil, *Bull. Soc. Chim.*, [3], xix.-xx., No. 6; and CHEMICAL NEWS, lxxvii., 245), and the whole boiled for a few minutes. Some of the filtered solution should then be tested by treating with an equal volume of hydrogen peroxide and boiling, and the process repeated until no precipitate is thus obtained. The filtrate is reserved for he preparation of pure cerium, The thorium precipitate, having the composition $Th_4O_7N_2O_5$, is very impure, and may have a yellow or even an orange colour after standing for a short time.

NOTE.—It is highly important that the peroxide of hydrogen be free from phosphoric acid, otherwise an insoluble cerous phosphate may be thrown down with the thorium.

The crude thorium obtained above may be purified by treating the nitrate solution with an excess of warm ammonium oxalate. The soluble portion can then be converted into the oxalate, and treated again with warm ammonium oxalate.

Thorium can be separated from cerium (Glaser, *Journ. Am. Chem. Soc.*, xviii., 782) by the solvent action of ammonium acetate on thorium oxalate. This, as well as the ammonium oxalate method, can be applied to the cerium precipitate. The whole is dissolved in strong hydrochloric acid and precipitated by means of oxalic acid. Glaser says:—"Thorium is separated best by converting the oxalates into sulphates, the greater part of the free acid neutralised 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 solution of ammonium acetate is 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 (F); in the filtrate precipitate thoria with ammonia in excess, filter, and wash." All the thorium precipitates are accumulated at E. Another treatment or two with hydrogen peroxide in neutral nitrate solution gives a very good thorium product.

Thorium can be obtained very pure in the following manner:—Thorium hydroxide is first prepared by adding a slight excess of ammonium hydroxide to a solution of thorium nitrate and washing well the precipitate thrown down. This is then added to a solution of acetyl acetone in absolute alcohol, and the mass heated on the water-bath for a short time, after which it is filtered and allowed to crystallise. The acetyl acetonate is then placed in a very small retort and carefully distilled in a vacuum. The portion that condenses in the neck of the retort and in the receiver is dissolved in concentrated nitric acid, boiled for a short time, diluted with water, filtered, and precipitated by means of oxalic acid. Thorium oxide obtained by igniting this oxalate is absolutely snow-white, even after long ignition. A determination of the equivalent gave an atomic weight of 232·3. Thorium may also be purified by the sulphate method as follows:—Anhydrous thorium sulphate is dissolved in ice-cold water until the liquid is saturated. (According to Urbain, ammonium acetate aids the solution).

The filtered liquid is then heated to 20° C., when nearly pure thorium sulphate separates. It is then dehydrated, and the treatment repeated two or three times.

Cerium.

F is the starting-point for the preparation of pure cerium. If Wyrouboff and Verneuil's method for separating thorium has been used, the purification is easily carried out by slightly modifying the zinc oxide and potassium permanganate method. If other methods have been used it is best to convert the oxalates, &c., into nitrates. The liquid is neutralised by ammonia, and treated with hydrogen peroxide in order to remove the last of the thorium. To the solution of cerium nitrate, freed from thorium, sufficient ammonium nitrate is added to form the double salt. An excess of potassium permanganate is run in, and only enough cream of zinc hydroxide added to precipitate most of the cerium, being sure to leave some in solution, for otherwise praseodymium and neodymium will accompany the precipitate. The whole is then heated by steam, filtered, and washed with water containing a little ammonium nitrate. The precipitate is dissolved in concentrated hydrochloric acid, the solution diluted, and the cerium precipitated with oxalic acid (G). The oxalate

obtained by this method usually contains a little zinc and manganese, the latter colouring the oxide brown; so for the final purification the oxalate is treated with a slight excess of sulphuric acid, and the whole heated until the fumes of sulphuric acid are no longer given off. The resulting sulphate is dissolved in cold water, and the filtered solution heated on the water-bath. The sulphate that separates is washed with boiling water. This material should give an oxide with only a pale yellow tint.

Note.—Praseodymium is a very common impurity found in cerium. This has been pointed out many times by different investigators, so that if very pure cerium is required one must be on his guard against this substance.

The mother-liquor is treated with oxalic acid, the oxalate which is thrown down being worked up with the next lot. The filtrate from the cerium peroxide still contains cerium, which is removed by adding an excess of zinc oxide, and more potassium permanganate should the colour be discharged. The precipitate obtained here is mixed with F. The filtrate is precipitated with an excess of oxalic acid, and the insoluble oxalates, consisting of lanthanum, praseodymium, neodymium, &c., constitute Fraction H.

Lanthanum, &c.

Fractions H and D contain lanthanum, praseodymium, neodymium, samarium, europium, and gadolinium, together with small amounts of the yttrium earths and some cerium.

These are best separated from each other by the fractional crystallisation of certain double nitrates, such as those formed by the rare earth nitrates with ammonium, magnesium, manganese, or nickel nitrate. For the separation of lanthanum and praseodymium the double ammonium nitrates are by far the best, and for separating praseodymium from neodymium the manganese salts are to be preferred. However, where one is working on the large scale it is better to start with the double magnesium nitrates, as the more soluble portions crystallise more readily than is the case with the double ammonium nitrates.

The double magnesium nitrates,—

$$2[M'''(NO_3)_3] \cdot 3[Mg(NO_3)_2] + 24H_2O$$

(Demarçay, *Comptes Rendus*, cxxx., 1019), are prepared by dissolving the rare earth oxides in a known amount of nitric acid. An equal amount of nitric acid is then neutralised by magnesium oxide, after which the two solutions are mixed and evaporated until after blowing on the surface small crystals form. Water is sprayed over the surface, and the whole allowed to crystallise for about twenty-four hours. The mother-liquor is then poured off and evaporated further, while the crystals are heated with water until dissolved, the correct amount to use being soon learned by experience. Both fractions are again allowed to crystallise for a like period, the concentration of the solutions being such that half of the solid separates on cooling. Two fractions have thus been obtained, and in subsequent fractionations the more soluble moves in one direction and the less soluble in the opposite. After the crystallisation of the second series is complete, the liquid from the most soluble portion is poured off and evaporated, while the liquid from Fraction I. is used as the solvent for the crystals forming Fraction II., adding water or evaporating as may be necessary. The least soluble portion, Fraction I., is again dissolved by heating with water. The above is repeated many times. When the fractions at either end become too small to work they should miss one crystallisation, and then be added to the next lot. After a few series of crystallisations the least soluble portion becomes very light coloured, later growing nearly colourless, and finally takes a faint green tinge. When the fractions at this end no longer show the characteristic absorption bands of neodymium, they should be placed aside and mixed together according to the amount of praseodymium contained therein; in other words, fractions of the same colour are united.

The most soluble portion changes very rapidly. It soon takes a yellow colour, and shows a samarium spectrum, together with the bands of dysprosium, holmium, and erbium. Sometimes at this stage the liquid refuses to crystallise, or else a precipitate may form. If either of these things happens it is best to dilute with water and saturate with solid sodium sulphate to separate the yttrium earths and impurities that have accumulated and interfere with the crystallisation. The insoluble double sodium sulphates are converted back to the double magnesium nitrates in the same manner as already described, and the solution will be found to crystallise readily on evaporation. The filtrate from the double sodium sulphates is precipitated with an excess of oxalic acid, and the oxalates of the yttrium group which are thrown down are added to lot B. The neodymium bands finally become very weak in the most soluble fractions, and these are set aside for the preparation of samarium, europium, and gadolinium. After the samarium has been separated in this manner the more soluble portion of the remaining fractions rapidly turns to a beautiful amethyst, and when this occurs it is separated from the rest as neodymium. After the process has been continued a little longer it will be found that the material has been split up into four groups according to the order of their solubilities. Commencing with the least soluble, we have:—

1. Lanthanum and praseodymium.
2. Praseodymium and neodymium.
3. Neodymium.
4. Samarium, europium, and gadolinium, together with small amounts of terbium, dysprosium, &c.

Lanthanum.

Lanthanum and praseodymium are best separated from each other according to the method of Auer von Welsbach (*Monatsh. Chem.*, vi., 477), which consists of the fractional crystallisation of the double ammonium nitrates of the type $M'''(NO_3)_3.2(NH_4NO_3)+4H_2O$. These compounds are crystallised from water containing nitric acid to the extent of one-tenth the weight of the dissolved solid. To prepare the double salts the oxides are dissolved in the required amount of nitric acid, and for every three parts of acid required for the oxides two additional parts are neutralised by ammonium hydroxide. The resulting solutions are mixed, filtered, and evaporated until small crystals form on blowing over the surface of the liquid. A little water is sprayed over the surface, and the whole set aside for twenty-four hours. The process of fractionation is then carried out similarly to the double magnesium nitrates. By this method lanthanum ammonium nitrate is soon obtained perfectly colourless, and a saturated solution gives no praseodymium absorption spectrum even when observed through very thick layers. The lanthanum ammonium salt does not enclose anything like the amount of mother-liquor that the double magnesium compound does. Both cerium and praseodymium accumulate in the more soluble portion.

The colourless lanthanum salt is dissolved in water, the solution acidified and precipitated by means of oxalic acid. This oxalate is treated with a slight excess of concentrated sulphuric acid, and the whole gently ignited until all free acid has been driven off. The sulphate is powdered and dissolved in water at about 1° C. until the liquid is saturated, after which it is filtered, placed in a water-bath, and gradually raised to 32° C. The solution soon changes to a solid mass, which is placed on a Buchner funnel and washed with hot water. The few grms. that remain in solution are thrown out by means of oxalic acid. The crystallised sulphate may be rendered anhydrous and submitted once again to the sulphate method. This lanthanum gives a fine white oxide.

Praseodymium.

There are two sources for praseodymium; firstly, from the more soluble portion obtained from the purification of lanthanum, and, secondly, from those fractions of the

double magnesium nitrates which show a strong praseodymium spectrum. These are not mixed but treated separately.

In the first case the crystallisation is carried on until no more colourless crystals separate, praseodymium accumulating in the more soluble fractions together with a little cerium.

In the second case the double magnesium salts are converted into the corresponding manganese compounds, which are finally fractionally crystallised from nitric acid of specific gravity 1·3 (Lacombe, *Bull. Soc. Chim.*, [3], xxxi., No. 10; and CHEMICAL NEWS, lxxxix., 277). In order to do this, the magnesium double salts are dissolved in water, the solution acidified, and the rare earths thrown down by oxalic acid. The oxalates obtained are washed, dried, and ignited to oxides. The oxides are then dissolved in a known amount of nitric acid. An equal amount of nitric acid is then neutralised by manganese carbonate, after which the two solutions are mixed. A precipitate of manganese peroxide is sometimes obtained at this point, but it is easily removed by adding a little oxalic acid and warming. The least soluble portion from this fractional crystallisation that no longer gives any neodymium bands in the spectroscope, is dissolved in water, acidified, and thrown down with oxalic acid. The fractions of praseodymium ammonium nitrate that are free from lanthanum are also dissolved and precipitated by oxalic acid. The praseodymium oxalate from the two sources is then united. This material may be impure owing to the presence of cerium.

Cerium can be separated in several different ways. One method consists in treating the nitrate solution with potassium permanganate and a little sodium carbonate. A separation is obtained according to Wyrouboff and Verneuil (*Bull. Soc. Chim.*, [3], xix., No. 6; and CHEMICAL NEWS, lxxvii., 254) by adding a solution of sodium acetate to a solution of the nitrates, and precipitating the cerium by hydrogen peroxide. The above methods throw down a certain amount of praseodymium also, so the precipitate should be worked up again. (Meyer and Koss, *Ber.*, xxxv., 672, recommend magnesium acetate in place of sodium acetate).

Neodymium.

Pure neodymium is obtained by continuing the crystallisation of the neodymium magnesium nitrate obtained somewhat earlier. After a few more series of crystallisations the liquid assumes a beautiful bluish lilac colour, which is seen better when some of the solution is diluted with water. On observing the spectrum, the absorption bands in the blue stand out clearly. When the solution contains samarium or praseodymium, these weaker neodymium bands are usually a little hazy. An excellent test of the purity of neodymium is found by observing the colour of the oxide, which is blue only when pure.

Samarium and Europium.

Samarium, europium, and gadolinium are contained in the mother-liquors which were obtained during the fractionation of the double magnesium nitrates. The solutions are evaporated, and the residue fractionally crystallised from nitric acid of 1·3 specific gravity (Demarçay). The addition of the isomorphous bismuth magnesium nitrate aids enormously in the separation of these elements, as Urbain and Lacomb have shown (*Comptes Rendus*, cxxxvii., 792; cxxxviii., 84). Its solubility places it between samarium and europium, and it also assists in the crystallisation of the syrupy mother-liquors, inasmuch as it carries down with it the more crystallisable portions. Samarium is obtained from the least soluble fractions. Europium is separated from the excess of bismuth magnesium nitrate which is found between the samarium and gadolinium fractions. The bismuth is thrown down by hydrogen sulphide, and the mother-liquor precipitated by means of oxalic acid.

Gadolinium.

The fractions between europium and dysprosium, &c., consist mainly of gadolinium magnesium nitrate. These solutions are acidified, and the gadolinium thrown down as oxalate. This is then washed and ignited to oxide. The resulting oxide is converted into the double nickel nitrate of the type $2Gd(NO_3)_3.3Ni(NO_3)_2+24H_2O$ (Urbain, *Comptes Rendus*, cxl., No. 9), which is then fractionally crystallised from nitric acid of density 1·3. Terbium is left in the most soluble portion.

NOTE.—The writer is applying the bromate method to a complicated mixture of samarium, gadolinium, terbium, dysprosium, and holmium, and is obtaining interesting results.

Fraction B contains oxalates of terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium, and scandium. This material is converted into the anhydrous sulphate, the latter dissolved in cold water, and poured over an excess of barium bromate (James, *Journ. Am. Chem. Soc.*, xxx., 182; and CHEMICAL NEWS, xcvii., 61). The whole is well stirred and placed on the water-bath. After the double decomposition is complete, *i.e.*, when the clear liquid gives no precipitate with barium bromate solution after diluting and boiling, the mass is filtered and evaporated until a drop removed on the end of a glass rod nearly solidifies when stirred on a watch-glass. A little water is then sprayed on the surface, and the whole submitted to fractional crystallisation. The absorption spectrum soon shows that a rapid change is taking place. Small amounts of samarium and gadolinium are rapidly separated in the least soluble portion, while the next fractions contain terbium, and give oxides of a deep red brown colour. Dysprosium and holmium are more soluble than terbium. Yttrium places itself between holmium and erbium.

NOTE.—The writer, in a previous paper describing the serial order of the bromates, made an error in the position of yttrium (CHEMICAL NEWS, xcvii., p. 61). This element, as stated above, ranges itself in the fractions between holmium and erbium. The cause of the error was due to the fact that the material on which the serial order was worked out contained only a little yttrium and a fair amount of gadolinium. At the time gadolinium was not suspected, and the colourless bromate crystals were supposed to be due to yttria.

The most soluble portion contain erbium, thulium, and ytterbium.

Terbium, Dysprosium, and Holmium.

These elements are extremely difficult to separate. Operations with the bromates are still in progress. Terbium separates in the least soluble, together with samarium and gadolinium. The separation of dysprosium from holmium is extremly slow, and so much so that the bromate method is of no value for this work. Urbain recommends the fractionation of the double nickel nitrates from nitric acid of density 1·3 to separate samarium and gadolinium from terbium, dysprosium, and holmium. The more soluble portion, consisting of terbium, &c., with some gadolinium, is converted into the simple nitrate, and fractionally crystallised from concentrated nitric acid in the presence of bismuth nitrate. Terbium collects with the bismuth nitrate in the fractions between gadolinium and dysprosium. Fractional crystallisation of the ethyl sulphates gives dysprosium. Small amounts only of dysprosium and terbium have been separated. The preparation of pure holmia has not yet been accomplished.

Yttrium.

Yttrium is obtained from the bromate fractions between holmium and erbium. Some fractions show holmium bands in addition to erbium. It is most easily prepared from the fractions that are free from holmium. The earths are precipitated from dilute boiling solutions of the bromates by the addition of boiling potassium hydroxide solution. The hydroxides are filtered off, washed, and

converted into the nitrates. Yttrium is then separated by the method of Muthmann and Rolig (*Ber.*, xxxi., 1718) as follows:—The concentrated neutral nitrate solution is boiled, and a thick cream of magnesium oxide added until the liquid no longer gives the absorption bands of erbium. The fractions that contain holmium in addition to erbium can be put through the same process. Yttrium oxide, obtained by the bromate and magnesium oxide methods, is snow-white, and absolutely free from terbium, &c.

Erbium, Thulium, Ytterbium, and Scandium.

These elements are separated from each other by the continued fractionation of the most soluble portion of the bromates. The erbium solutions become of a beautiful rose tint. Thulium collects between erbium and ytterbium. The mother-liquor contains ytterbium with a very little scandium. The neutral solution is saturated with potassium sulphate when scandium potassium sulphate separates, as it is insoluble in potassium sulphate solution. The filtrate, on the addition of oxalic acid, gives a precipitate of ytterbium oxalate.

The fractionation of the least basic earths is still being carried on with the object of preparing pure thulium for a determination of the atomic weight, and also to confirm Urbain's lutecium.

In conclusion, I again thank the Welsbach Company for large amounts of material received through the courtesy of Dr. H. S. Miner. I also tender my thanks to the Christiania Minekompani, of Christiania, Norway, for many mineral specimens for examination.

New Hampshire College, Durham, N.H.
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THE ATOMIC WEIGHT OF TELLURIUM.

By H. BRERETON BAKER, M.A., D.Sc., F.R.S.

In December, 1907, a paper on this subject (*Journ. Chem. Soc.*, xci., 1849) was published by Mr. A. H. Bennett and myself, showing that the atomic weight was unchanged when the element was subjected to eight different methods of purification, each of which might have been expected to separate any foreign element present. The atomic weight of the highly purified element was determined by two independent methods, one of which gave the number 127·60 and the other 127·61. Simultaneously there appeared a paper by Prof. W. Marckwald (*Berichte*, 1907, xl., 4730) describing experiments on the fractional crystallisation of telluric acid. This was one of the methods tried by us, and in the hands of Prof. Marckwald, as in ours, it led to no splitting up of the element. An important difference in our results and his, however, is seen in the number found for the atomic weight. From the determination of the loss in weight of crystallised telluric acid ($H_2TeO_4 \cdot 2H_2O$), Prof. Marckwald comes to the conclusion that the atomic weight of tellurium is 126·85, compared with iodine 126·97. This result, if confirmed, would be of the greatest possible interest as removing one of what have been called "the two blots on the periodic system." The determinations, however, were made with a substance containing water of crystallisation. It has been pointed out by chemists distinguished in this most delicate branch of enquiry (Mallet, "Stas Memorial Lecture," *Journ. Chem. Soc.*, 1902, 204; Richards, *Zeit. Phys. Chem.*, xlvi.) that there is always great danger in using such substances for atomic weight determinations. Mr. Bennett and I, in the paper referred to above, mentioned that twenty-six determinations of the atomic weight of tellurium were done by us by finding the ratio of $H_2TeO_4 \cdot 2H_2O : TeO_2$. The acid had been very carefully purified, and crystallised as quickly as possible in order to obtain the crystals as small as possible. The acid was placed in a porcelain boat; this was placed in a thin Jena glass tube which served to prevent loss by the small volatilisation of the dioxide, both boat and tube being weighed together against a similar counterpoise. During the heating a slow current of dried air was drawn through the tube. The operation was carried on at as low a temperature as possible, and was complete usually in twelve hours. The fine crystals of the acid were dried in different ways: in air at the ordinary temperature, *in vacuo*, and in air over calcium chloride, over sulphuric acid, and over phosphorus pentoxide. The results obtained varied between 126·8 and 128·2 (O = 16). Treated in the same way the same acid gave the same result, but varying the treatment by more complete drying or by powdering gave widely varying numbers. Some of the fine crystals dried over sulphuric acid, which gave an atomic weight of 127·2, were powdered to an impalpable dust in an agate mortar. This then gave after standing in a desiccator over sulphuric acid for twenty-four hours an atomic weight of 127·6. It was thought that some of the water might have been driven off by the heat produced in grinding. Some of the original crystals were therefore ground under a saturated solution of the same acid, drained on a platinum plate pierced with extremely small holes, powdered again when moist, and again dried. The atomic weight obtained from them was 126·9. It seemed to us necessary to abandon the method not only on account of the doubt attaching to the constancy of the water of crystallisation, but also on account of the possibility of water being included in the crystal. In large crystals of the acid there is often seen a phenomenon which points to this inclusion. When first prepared the crystals are wonderfully bright and clear. On standing for a few hours in air, moist or dry, there frequently appears an opacity in the interior of the crystal. This probably indicates the inclusion of a saturated solution inside the crystal.

Again, telluric acid crystals show very marked crackling on heating, and this, as in the analogous cases of potassium chlorate and sodium chloride, is probably due to included water. What holds for the large crystals probably holds for the very small ones, though, of course, in a minor degree. Lastly, experiments were done by Mr. Bennett and myself which render it almost certain that the water in crystallised telluric acid is not constant; in these the residues of tellurium dioxide in two determinations, performed by heating the crystallised acid, which gave atomic weights of 126·8 and 128·0, were used for further atomic weight determinations by the sulphur method. The numbers obtained were practically identical, 127·64 and 127·62. It is to be hoped that Prof. Marckwald will apply some other method of atomic weight determination to his material, with the view of finding out if the above objections apply to the determinations which he has made.

With regard to the experiments on silver telluride ores described by Mr. Bettel (Chemical News, xcvii., 169), I fear that the interesting phenomenon which he discovered cannot be ascribed to the presence of a missing element. On reading his paper it occurred to me that the difference which he noticed in the cupellation of the silver buttons might be due to the way in which the tellurium was combined with the silver. I happened to have a specimen of silver tellurate which had been prepared from telluric acid which had been purified in the most careful way by (1) fractionally crystallising telluric acid, (2) converting into the dioxide, (3) reduction to the element, (4) conversion into the hydride, and (5) oxidation to the acid. The silver was prepared for atomic weight work by Stas's method. This silver tellurate was reduced to telluride by heating in very pure hydrogen. The telluride was cupelled with lead in the ordinary way, and immediately the "brightening" of the bead took place, the bead spread out, wetting the surface of the cupel to a nearly complete circle of 2 cm. in diameter. The description which Mr. Bettel gives of his experiment coincides in every respect with the above, and there is little doubt that the phenomena were due to the same cause. His experiment of adding tellurium to silver and cupelling was then repeated, the

tellurium being of the highest degree of purity. Again, his result, that the spreading only took place to the extent of 2 mm. round the bead, was confirmed. As it was possible that in the latter case most of the tellurium was volatilised before it entered into combination with the silver, some highly purified tellurium was heated on pure silver foil to low redness in a slow current of hydrogen. The resulting telluride was then cupelled with lead, and the spreading again took place. Lastly, some tellurium dioxide of the highest degree of purity was mixed with molecular silver and sugar charcoal and heated to low redness in a cupel. The bead of telluride was then cupelled with lead, and again the spreading took place. Some of the film was detached from the cupel, and was found to contain a considerable proportion of tellurium, and on heating the rest to the highest temperature of the furnace, fumes of tellurium dioxide were seen in the muffle, and at the end of an hour a bead of silver was obtained which did not spread at all, and which on testing was found to contain only traces of tellurium.

Hence the experiment of Mr. Bettel, interesting though it is in itself, can be repeated with tellurium which has been carefully purified, and the explanation of it seems to be simply that silver telluride has a lower surface tension than pure silver. I am afraid I know little of silver telluride ores, but if they are similar to gold telluride ores there is a possible explanation of the fact that Mr. Bettel's result was found in only one ore among the many tried. Ores of gold containing tellurium contain it in the deeper levels as telluride of gold, while in the ores obtained nearer the surface the gold is free and the tellurium is partly free and partly as the dioxide. An ore from the deeper levels might therefore show the phenomenon of spreading on cupellation, while that from nearer the surface might contain so little of the tellurium in combination with the silver as to fail in giving this result.

Christ Church, Oxford.

THE CENTENARY OF DAVY'S DISCOVERY OF THE METALS OF THE ALKALIS.*

By Prof. T. E. THORPE, C.B., Ph.D., LL.D., D.Sc., F.R.S.

(Concluded from p. 196).

SIR JAMES DEWAR has been so good as to have prepared for me a photographic reproduction of a water-colour drawing of the laboratory of the Royal Institution as it existed in Davy's time, showing the actual spot where the isolation of the metals of the alkalis was first effected.

The publication of Davy's discovery created an extraordinary sensation throughout the civilised world, a sensation not less profound, and certainly more general from its very nature, than that which attended his lecture of the previous year. But at the very moment of his triumph, it seemed that the noise of the universal acclaim with which it was received was not to reach him. I have already made reference to the condition of mental excitement under which the discovery was made and prosecuted. Almost immediately after the delivery of his lecture he collapsed, struck down by an illness which nearly proved fatal, and for weeks his life hung on a thread. He had been in a low feverish condition for some time previously, and a great dread had fallen upon him that he should die before he had completed his discoveries. It was in this condition of body and mind that he had applied himself to the task of putting together an account of his results. Four days after this was given to the world he took to his bed, and he remained there for nine weeks. Such a blow following hard on the heels of such a triumph aroused the liveliest sympathy. The doors of the Royal Institution were beset by anxious inquirers, and written reports of his condition at various periods of the day had to be posted in the hall. The strength of the feeling may be gleaned, too, from the sentences with which the Rev. Dr. Dibdin, who had been hurriedly engaged to take his place in the theatre, began the lecture introductory to the Session of 1808.

"The Managers of this institution have requested me to impart to you that intelligence, which no one who is alive to the best feelings of human nature can hear without the mixed emotion of sorrow and delight.

"Mr. Davy, whose frequent and powerful Addresses from this place, supported by his ingenious experiments, have been so long and so well known to you, has, for the last five weeks, been struggling between life and death. The effects of these experiments recently made in illustration of his late splendid discovery, added to consequent bodily weakness, brought on a fever so violent as to threaten the extinction of life. Over him it might emphatically be said in the language of our immortal Milton, that—

'. . . . . Death his dart
Shook, but delayed to strike.'

"If it had pleased Providence to deprive the world of all further benefit from his original talents and intense application, there has certainly been sufficient already effected by him to entitle him to be classed among the brightest scientific luminaries of his country."

After having, "at the particular request of the Managers," given an outline of Davy's investigations, Dr. Dibdin proceeded to say:—

"These may justly be placed among the most brilliant and valuable discoveries which have ever been made in chemistry, for a great chasm in the chemical system has been filled up; a blaze of light has been diffused over that part which before was utterly dark; and new views have been opened, so numerous and interesting, that the more any man who is versed in chemistry reflects on them, the more he finds to admire and heighten his expectation of future important results.

"Mr. Davy's name, in consequence of these discoveries, will be always recorded in the annals of science amongst those of the most illustrious philosophers of his time. His country, with reason, will be proud of him, and it is no small honour to the Royal Institution that these great discoveries have been made within its walls—in that laboratory, and by those instruments which, from the zeal of promoting useful knowledge, have, with so much propriety, been placed at the disposal and for the use of its most excellent professor of chemistry."

And now, in the few minutes that remain to me, let me indicate what has been the outcome of this great and fundamental discovery. How far has the expectation of future important results been realised? Have sodium and potassium at all justified the hope that they would facilitate the means of procuring the comforts and conveniences of life?

I have not the time, even if I had the intention, to attempt to follow the many changes in the metallurgy of the metals of the alkalis of the past century. Let me at once proceed to show how the matter stands at the end of a hundred years.

The general properties and chemical activities of potassium and sodium are so very similar that as a matter of commercial production that metal which can be most economically obtained is necessarily the one most largely manufactured, and of the two that metal is sodium. To-day, sodium is made by thousands of tons, and by a process which in principle is identical with that by which it was first made by Davy, *i.e.*, by the electrolysis of fused caustic soda. It is very significant that after a series of revolutions in its manufacture, sodium, having been produced from time to time on a manufacturing scale by a variety of metallurgical methods involving purely thermal processes of reduction and distillation, entirely dissociated from electricity, we should have now got back to the very principle of the process which first brought the metal to

* A Discourse delivered before the Royal Institution, January 17, 1908.

light. And that this has been industrially possible is entirely owing to another of Davy's discoveries—possibly indeed the greatest of them all—Michael Faraday. As we all gratefully acknowledge, it is to the genius and labours of Faraday—Davy's successor in this place—that the astonishing development of the application of electrical energy which characterises this age has taken its rise.

The modern method of production of sodium is based, therefore, as regards principles upon the conjoint labours of Davy and Faraday.

These principles took their present form of application at the hands of a remarkably talented American—Mr. Hamilton Y. Castner—whose too early death, in the full vigour of his intellectual powers, was an incalculable loss to metallurgical chemistry. It is by Castner's process that all the sodium of to-day is manufactured.

In the Castner process melted caustic soda produced by the electrolysis of a solution of common salt by a method also devised by Castner, is brought into an iron vessel shaped like a large cauldron, mounted in brickwork, and provided with an extension adapted to receive the negative electrode. Suspended directly above the cathode is an iron vessel attached to a lid; to its lower edge is secured iron-wire gauze, which, when the receptacle is in position, completely surrounds the cathode. The positive electrode is connected with the lid of the vessel, which is provided with openings for the escape of the gases resulting from the electrolysis, and is suitably insulated.

As the electrolysis proceeds the alkali metal, being much lighter than the molten caustic, rises from the negative electrode and passes into the receiver, the gases escaping around the edges of the cover. The molten metal collects on the surface of the caustic, and is removed by means of a large perforated spoon, the perforations enabling the melted caustic to flow out, while the metal remains in the spoon. As the several vessels are thus skimmed in succession the fused sodium is collected into an iron vessel, whence it is poured into moulds in which it congeals, forming blocks of the size and shape of an ordinary building brick. These, after being trimmed to remove adherent oxide, are immersed in paraffin oil, and are then packed into large iron drums holding about 6 or 7 cwt., capable of being closed air-tight, and protected in transit by an outer casing of wood.

The due regulation of the volume and intensity of the current is a matter of the greatest importance in order to obtain the most economical yield of the metal. No very high temperature is needed; indeed, the temperature of the fused caustic soda should not be much higher than that of its melting-point. By suitably regulating the current, the soda, in fact, may be maintained at the proper temperature and in the proper degree of fluidity without extraneous heat. Fresh melted caustic soda is added to the vessel from time to time to replace the metal removed, and in this manner the process is made continuous.

The Castner process is now worked in England at Wallsend-on-Tyne, and at Weston Point, in Cheshire; at Rheinfelden, in Germany; at Clavaux, in France; also in Switzerland, and at Niagara, in America. The present yearly output amounts to about 5000 tons, but the plant already laid down is capable of producing at least twice this quantity.

The greater quantity of the sodium made in England is sent to Glasgow, where it is converted into sodium cyanide by the Cassel Cyanide Company for use in the extraction of gold. As gold is, I suppose, generally considered the principal material factor in procuring the comforts and conveniences of life, Davy's great discovery may be thus said to have secured the primary object which the projectors of the Royal Institution had in view. Other important uses of sodium are in the manufacture of peroxide for bleaching purposes, of artificial indigo, and of a number of other synthetic dye stuffs and of drugs like antipyrin.

It need hardly be said that this extraordinary development of the manufacture has not been without its influence on the price of sodium. A quarter of a century ago it was a comparatively rare metal, and a stick of it was regarded as a chemical curiosity, to be handled with circumspection and care. Even as late as 1890 its selling price was as high as 8s. per lb. To-day it is 8d. Sodium now takes rank, therefore, with zinc, tin, copper, or aluminium as a common, ordinary metal of commerce.

I am indebted to the directors of the Castner-Kellner Company, and in particular to my friends Sir Henry Roscoe and Mr. Beilby, for affording me the opportunity, in connection with this lecture, of actually witnessing the modern process of manufacturing sodium as it is carried out at Wallsend; and I am further indebted to Mr. Beilby for the loan of the lantern slides and specimens with which I have sought to illustrate that process.

And in concluding may I be permitted to recall here the feelings to which that visit to Wallsend gave rise. There, grouped together on the very spot where ended the old wall—the visible symbol of the power and might of a civilisation long since passed away—were some of the characteristic signs of another civilisation ampler and more beneficent. Before me, stretching down to the river, was the factory where a score of workers, clad in helmets and gauntlets and swathed like so many Knights Templar, travel-stained and war-worn, their visages lit up by the yellow soda flames, and their ears half-deafened with the sound of exploding hydrogen—a veritable inferno—were repeating on a Gargantuan scale the little experiment first made a century ago in the cellars of this building; turning out, day and night, hundredweights of the plastic metal in place of the little pin-heads which then burst upon the astonished and delighted gaze of Davy. Behind me was the magnificent power-house—one of the most magnificent of its kind in the world—furnishing not only the electrical energy which transformed the soda into sodium, but diffusing this energy for a multitude of other purposes over an entire district—a noble temple to the genius and prescience of Faraday. Surely one might here say, if you desire to see the monuments of these men, look around! And to my right, and close at hand, was the huge building slip just vacated by the *Mauretania*, herself a symbol of the supremacy of an empire, far mightier, more world-wide, and more potent for good than that which massed its legions behind the old wall.

Iron and Steel Institute.—*Annual Meeting*, 1908.—The Annual Meeting of the Institute will be held at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 14 and 15, 1908, commencing each day at 10.30 a.m. Thursday, May 14: General Meeting of Members. The Bessemer Gold Medal for 1908 will be presented to Mr. Benjamin Talbot (Middlesbrough). At 7 p.m., Annual Dinner of the Institute in the Grand Hall of the Hotel Cecil. Friday, May 15: General Meeting of Members. The awards of the Andrew Carnegie Gold Medal and Research Scholarships for 1908 will be announced. *Autumn Meeting*.—The Council has accepted a cordial invitation to hold the Autumn Meeting of the Institute in Middlesbrough on September 29, and following days. *Visit to Canada*.—The Canadian Mining Institute is arranging for an excursion in September, 1908, to the mineral areas of Eastern Canada, including the silver-cobalt ore region, the nickel mines, and the iron ore mines of Ontario, the asbestos and chromite regions of the Province of Quebec, and possibly the coal and iron areas of Nova Scotia. It is expected that the excursion will extend over a period of three weeks. The Canadian Mining Institute has extended to the members of the Iron and Steel Institute a cordial invitation to take part in this excursion, and any members wishing to avail themselves of this kind invitation are requested to communicate with Mr. H. Mortimer Lamb, Secretary of the Canadian Mining Institute, 413, Dorchester Street West, Montreal, Quebec.

EXPLOSIVE COMBUSTION, WITH SPECIAL REFERENCE TO THAT OF HYDROCARBONS.*

By Professor WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S.

(Concluded from p. 198).

Having thus, I hope, explained the main issues involved in the controversy, I shall now proceed to perform a series of experiments on the explosive combustion of acetylene, ethylene, and ethane, some of which are crucial as regards the rival theories under discussion.

Experiment II.

I have here three cylindrical bulbs of stout borosilicate glass (capacity = about 60 cc.), fitted with firing wires, hermetically sealed, and containing respectively equimolecular mixtures of each of the three hydrocarbons with oxygen, that is to say, mixtures corresponding to $C_2H_2+O_2$, $C_2H_4+O_2$, and $C_2H_6+O_2$, respectively.

Now, according to the theory of the preferential combustion of carbon, these mixtures should, on explosion, yield nothing but carbonic oxide and hydrogen, without any separation of carbon, or formation of steam, as follows:—

	p_2/p_1.
(*a*) $C_2H_2+O_2=2CO+H_2$	1·5
(*b*) $C_2H_4+O_2=2CO+2H_2$	2·0
(*c*) $C_2H_6+O_2=2CO+3H_2$	2·5

(The symbols p_1 and p_2 used in this and subsequent tables denote the initial and final pressures of the *cold* original mixture and gaseous products, dry, at constant volume and at the same temperature).

On firing the mixtures, it is at once evident that something very like this does happen in the cases of (*a*) and (*b*). There is absolutely no deposition of carbon, and no appreciable condensation of steam in the cold products. Far otherwise is it, however, in the case of the bulb containing the mixture $C_2H_6+O_2$. A lurid flame fills the vessel, accompanied by a black cloud of carbon particles, and a close inspection of the cold bulb will reveal a considerable condensation of water. The pressure ratio p_2/p_1 is approximately 1·5, and an analysis of the gaseous products would prove the presence of about 10 per cent of methane. The bulb will now be opened, rinsed out with water, and the formation of aldehydic products demonstrated by means of Schiff's reagent. It is clear that these results are wholly inconsistent with the theory of the preferential burning of carbon.

As it is obviously impracticable for me to complete the experiment by analysing the gaseous products before you, I will draw your attention to the following tabulated results of three similar experiments carried out some time ago. (Table I.).

Did time permit, I could easily demonstrate to you by other similar experiments, that the *outward* difference here revealed between the burning of ethylene and that of ethane extends to all the other gaseous olefines and paraffins; that is to say, whereas mixtures of olefines and oxygen corresponding to $C_nH_{2n}+n/2\ O_2$ on explosion yield mainly carbonic oxide and hydrogen, without separation of carbon, mixtures of paraffin and oxygen corresponding to $C_nH_{2n+2}+n/2\ O_2$ yield carbon, oxides of carbon, methane, hydrogen, and steam, all in considerable quantities. Are we then to conclude that there is some peculiarity about the constitution or combustion of an olefine which induces a preferential burning of its carbon, whilst the corresponding paraffin is burnt in an entirely different way? The following experiment will show that such a view cannot for a moment be entertained.

Experiment III.

I will now fire a bulb containing a mixture of 60 per cent of ethylene and 40 per cent of oxygen (*i.e.*, $3C_2H_4+2O_2$). As might be expected, the flame is accompanied by a large deposition of carbon, but what is of greater importance still is the fact that a considerable amount of water is also formed. The full significance of this experiment may be gathered from the following data.

Original mixture: $C_2H_4 = 59{\cdot}65$ per cent. $p_1 = 562$ mm. $p_2/p_1 = 1{\cdot}45$; $O_2 = 40{\cdot}35$,, $p_2 = 816$,,

Gaseous products: $CO_2 = 2{\cdot}5$, $CO = 37{\cdot}2$, $C_2H_2+C_2H_4 = 6{\cdot}4$, $CH_4 = 6{\cdot}5$, $H_2 = 47{\cdot}4$ per cent.

	C	H	O
Units in original mixture ..	670	670	227
Units in gaseous products..	482	572	172
Difference	188	98	55

I think it will be now admitted that such an experiment as this completely destroys the foundations of the theory of the preferential burning of carbon. As I have already stated, the original experimental basis of the theory was the behaviour of an equimolecular mixture of ethylene and oxygen, yet here is proof that on closer examination the behaviour of ethylene is inconsistent with the theory. I would therefore say to those who may be inclined to cavil at my views as to the mechanism of combustion, that whatever may be the final issue of the controversy, this fact, amongst others, must be explained, namely, that whereas a mixture of an olefine and oxygen corresponding to $C_nH_{2n}+n/2\ O_2$, yields mainly carbonic oxide and hydrogen on explosion, in harmony with the equation $C_nH_{2n}+n/2O_2=nCO+nH_2$, a diminution of the oxygen below this limit at once gives rise to steam formation.

Experiment IV.

The next experiment is designed to illustrate the infinitely greater affinity of acetylene and ethylene as compared with that of hydrogen for oxygen at the high temperatures of flames. I have here two bulbs containing mixtures of each of these hydrocarbons with hydrogen and oxygen corresponding to $C_2H_2+2H_2+O_2$ and $C_2H_4+H_2+O_2$ respectively, and I will ask you to contrast the behaviour of these with that of the equimolecular mixture of ethane and oxygen, $C_2H_6+O_2$, which was exploded a few minutes ago. It should be noted that whilst all three mixtures contain the same relative proportions of carbon, hydrogen, and oxygen, they differ in respect of the proportions between the combined carbon and hydrogen. Asking you to bear in mind how the equimolecular mixture of ethane and oxygen on explosion gave rise to a black cloud of carbon and a considerable formation of water, I will now fire the other two mixtures. You will observe that in neither case has there been any deposition of carbon, and an inspection of the cold bulbs will show that little or no steam formation has occurred. In fact, the hydrocarbon has been burnt to carbonic oxide and hydrogen, leaving the hydrogen absolutely untouched by the oxygen, as the following detailed results show (Table II.).

These experiments have an important bearing on the chemistry of flames. Hydrogen is usually considered as one of the most combustible of gases, but here we see it pushed to one side by the all-powerful hydrocarbon, as though it were so much inert nitrogen. This at once raises another question which has lately been occupying my attention. Ever since Davy's experiments on flame, the combustibility of hydrogen has been considered to be superior to that of methane; this, however, cannot be true in regard to slow combustion, since it can be easily proved that between 300° and 400° C. methane is oxidised at a far faster rate than hydrogen. Nevertheless, I have recently observed facts which incline me to think that possibly it may be true in regard to flames. If further investigation confirms this opinion, it will be necessary to enquire into the cause of the peculiar relative inertness and stability of methane as compared with other gaseous

* Discourse delivered before the Royal Institution, February 28, 1908.

TABLE I.—*Results of Experiments on Inflammation in Sealed Glass Bulbs.*

Original mixture	$C_2H_2+O_2$.	$C_2H_4+O_2$.	$C_2H_6+O_2$.
p_1	352 mm.	545 mm.	746 mm.
p_2	508 „	1053 „	1148 „
p_2/p_1	1·44	1·93	1·54
Composition of gaseous products (per cent)—			
CO_2	0·75	0·30	4·20
CO	67·10	50·00	33·55
$C_2H_2+C_2H_4$	Nil	Nil	2·75
CH_4	1·55	1·70	10·85
H_2	30·60	48·00	48·60

	C.	H.	O.	C.	H.	O.	C.	H.	O.
Units in original mixture	352	176	176	545	545	272	746	1119	376
Units in gaseous products	352	171	175	547	541	267	621	854	241
Difference	Practically nil			Practically nil			125	265	135

TABLE II.—*Experiments on Inflammation in Sealed Glass Bulbs.*

Original mixture	$C_2H_4+H_2+O_2$.	$C_2H_2+2H_2+O_2$.
p_1	503 mm.	534 mm.
p_2	750 „	653 „
p_2/p_1	1·49	1·22
Composition of gaseous products (per cent)—		
CO_2	0·35	0·2
CO	39·60	39·8
$C_2H_2+C_2H_4$	1·25	Nil
CH_4	3·65	0·2
H_2	55·15	59·8

	C.	H.	O.	C.	H.	O.
Original mixture	341	505	168	267	400	133
Gaseous products	346	478	151	262	394	131
Difference	—	27	17	Negligible		

TABLE III.—*Inflammation of an Equimolecular Mixture of Ethane and Oxygen.*

	A. In long tube.		B. In large globe.	
p_1	701 mm.		685 mm.	
p_2	1018 „		1187 „	
p_2/p_1	1·45		1·73	
Composition of gaseous products (per cent)—				
CO_2	4·20		3·40	
CO	34·80		36·10	
C_2H_2	5·00	7·65	0·15	
C_2H_4	2·65			
CH_4	8·85		7·25	
H_2	44·50		53·05	

	C.	H.	O.	C.	H.	O.
Original mixture	694	1041	354	678	1017	346
Gaseous products	643	738	220	558	805	255
Difference	51	303	134	120	212	91
Difference (per cent)	7·6	29	37·8	18	20	27·5

TABLE IV.—*Results of Explosion of an Equimolecular Mixture of Ethane and Oxygen under High Pressures.*

	A. Detonation in lead coil.	B. Explosion in steel bomb.
p_1	1180 mm.	25·2 atmos.
p_2	2240 „	51·7 „
p_2/p_1	1·90	2·05
Composition of gaseous products (per cent)—		
CO_2	1·80	2·6
CO	39·10	37·2
C_2H_2	0·90	Nil
C_2H_4	0·50	1·40
CH_4	7·70	7·0
H_2	50·00	52·2

	C.	H.	O.	C.	H.	O.
Original mixture	1186	1779	587 mm.	25·35	38·0	12·55 atmos.
Gaseous products	1151	1507	488 „	24·50	34·6	11·05 „
Difference	35	272	99 „	0·85	3·4	1·5
Difference (per cent)	3	15	17	3·4	9	12·0

hydrocarbons when subjected to the action of oxygen at high temperatures.

It does not, I think, impose too great a strain on the imagination to picture the probable mechanism of combustion in hydrocarbon flames, and for this purpose ethylene and ethane may be taken as typical examples. It may be assumed that, with the possible exception of methane, the affinity of a hydrocarbon for oxygen is so great at high temperatures that the initial stage of its combustion takes precedence of all other chemical phenomena in flames. This is probably true of the propagation of flame through explosive mixtures of hydrocarbons and oxygen. In the special case of a stream of a hydrocarbon burning in air, partial decomposition may occur in the innermost regions of the flame, where the supply of oxygen is very limited, before combustion begins. But, in general, whenever the hydrocarbon and oxygen are brought together at high temperatures, their mutual affinities will prove superior to any disruptive forces which would otherwise break down the hydrocarbon. It is probably not so much the original hydrocarbon as its hydroxylated molecule which decomposes in flames; the

sudden increase in the internal energy of the hydrocarbon molecule, consequent upon its initial association with oxygen, would render the resulting hydroxylated molecule extremely unstable, and, in default of its immediate further oxidation, it would speedily decompose. The explosive combustion of ethylene may, therefore, be represented by the following scheme:—

$$H_2\overset{0}{C}{:}\overset{}{C}H_2 \rightarrow HO.\overset{1}{C}H{:}CH_2 \rightarrow HO.\overset{2}{C}H{:}CH.OH$$

$$\left\{\begin{matrix} \overbrace{C_2H_2+H_2O} \\ 2C+H_2+H_2O \end{matrix}\right\} \qquad 2CH_2O = \overbrace{2CO+2H_2}$$

In a sufficient supply of oxygen the transition from the original hydrocarbon to the *dihydroxy* state is probably so rapid that no breaking down of the ethylenic structure occurs in passing through the initial *monohydroxy* stage. Indeed, it is conceivable that under the extreme conditions of detonation the passage from 0 to 2 may be effected in a single molecular impact. The *dihydroxy* derivative would at once break down into carbon monoxide and hydrogen, *via* formaldehyde.

But when the oxygen supply is reduced below the equimolecular proportion, it is evident that the initial *monohydroxy* derivative cannot all be oxidised to the *dihydroxy* stage; some of it would, therefore, decompose, partly into acetylene and steam, and partly also into carbon, hydrogen, and steam, together with some methane.

In a similar manner the combustion of ethane would involve the rapid passage through *ethyl alcohol* to *acetaldehyde*, and *steam*, with subsequent decomposition of the aldehyde into carbon, hydrogen, methane, and carbonic oxide, with the proviso that a reduction of the oxygen supply below the equimolecular proportion would bring about in some measure the decomposition of the alcohol into ethylene and steam, &c., at Stage 1.

$$H_3\overset{0}{C}.CH_3 \rightarrow CH_3.\overset{1}{C}H_2OH \rightarrow CH_3.\overset{2}{C}H(OH)_2$$

$$\left\{\begin{matrix} \overbrace{C_2H_4+H_2O} \\ 2C+2H_2+H_2O \end{matrix}\right\} \qquad \overbrace{CH_3.CHO+H_2O}$$

$$\left\{\begin{matrix} \overbrace{CH_4+CO} \\ C+2H_2+CO \end{matrix}\right\}$$

But the cases of ethane and ethylene are typical of all other hydrocarbons, so that it may be said that, in general, the mechanism of explosive combustion involves, (1) the initial formation and subsequent decomposition of hydroxylated (or "oxygenated") molecules; (2) in a sufficient supply of oxygen, the independent oxidation of the decomposition products; (3) in an insufficient oxygen supply, the subsequent breaking down of unsaturated hydrocarbons, interactions between carbon and steam, or between oxides of carbon, hydrogen, and steam, the final system depending on the amount of available oxygen, the temperature of the flame, and the rate of cooling.

Experiment V.

The influence of different rates of cooling of the flame on the final system may be illustrated by firing an equimolecular mixture of ethane and oxygen in two glass vessels, having approximately the same volume but widely different surface areas. For this purpose I have selected (1) a tube about 1 metre long and 2 cm. internal diameter, and (2) a globe of 8·5 cm. internal diameter. Both these vessels have the same volume (about 300 cc.), but the surface area of the tube is very nearly three times that of the globe. It is therefore to be expected that, in consequence of the more rapid cooling of the flame, there will be a greater accumulation of the primary combustion products in the case of the tube experiment. On comparing the results of the two explosions, it is at once evident that more water and less carbon have been produced in the case of the tube; moreover, the pressure ratio p_2/p_1, is 1·45 as compared with about 1·75 in the globe experiment, and an examination of the products would show that the lower ratio is accounted for by the much greater survival of acetylene, ethylene, and aldehydic products in the tube experiment. These facts, which are set forth in Table III., are in complete harmony with the hydroxylation theory.

Experiment VI.

The experiments I have so far shown you, refer more particularly to the initial period of "*inflammation*" in explosive combustion; that is to say, to the conditions ordinarily prevailing in hydrocarbon flames. The question may be asked whether or not the views I have advanced are applicable to the extreme conditions of "*detonation*" or of explosions under high initial pressures. The question may be put in the following form:—Is there any experimental evidence of discontinuity between "*inflammation*" and "*detonation*" as regards the nature and sequence of the chemical changes involved? or, Is the hydrocarbon attacked by oxygen in an entirely different way in explosive combustion at high pressures, or in the explosion wave, to what it is in ordinary flames? This question can, I think, best be answered by a consideration of the behaviour of an equimolecular mixture of ethane and oxygen under these extreme conditions.

It is difficult to set up detonation in this mixture; the gases must be fired at an initial pressure of about one and a-half atmosphere in a stout leaden coil of about one inch internal diameter. Even then, it is necessary to start the explosion wave in a special firing piece containing electrolytic gas under pressure. I therefore regret that, owing to the special arrangements requisite for success, it is not possible to make the experiment to-night. I will, however, give you the results obtained on detonating the mixture in my laboratory, but before doing so, I will carry out an experiment on the explosion of the gases at an initial pressure of fifteen atmospheres.

The cylindrical steel bomb on the table is part of an apparatus recently installed in the Fuel and Metallurgical Laboratories of the University of Leeds for investigations on gaseous explosions under high pressures. The bomb is about a foot long with an external diameter of four inches, and the central cylindrical explosion chamber is eight inches long by one inch in diameter. It has been tested by hydraulic pressure up to 2000 atmospheres, and has been repeatedly used for experiments with mixtures of hydrocarbons and oxygen at initial pressures of as much as forty atmospheres. The bomb is now connected, through a valve at the top, with a standard Bourdon gauge, and contains an equimolecular mixture of ethane and oxygen at a pressure of 15·8 atmospheres. The valve will now be closed, and the mixture fired by means of an electrical arrangement in the special firing piece.

All that is audible of the explosion is a sharp click, and on opening the valve connecting with the gauge again, the final pressure of the cold products of explosion is recorded. After applying the necessary correction for the "dead space" in the gauge connections, but the final "corrected" pressure is as nearly as possible 30·8 atmospheres, corresponding to a ratio $p_2/p_1 = 1·93$. I would now direct your attention to the tabulated results of a similar bomb experiment carried out a few weeks ago at Leeds at an initial pressure of twenty-five atmospheres, and also at the same time to those of another experiment in which the gases were detonated in a lead coil at an initial pressure of one and a-half atmosphere (see Table IV.).

In both these experiments carbon was deposited, and it is evident also that steam was formed. The ratio p_2/p_1 was as nearly as possible 2·0 instead of the 2·5 required by the theory of the preferential combustion of carbon. Moreover, a notable feature of the results is the presence of as much as 7 per cent of methane among the products of the experiment at twenty-five atmospheres; the fact that so much methane survived when all other hydrocarbons were battered to pieces during the explosion (no traces of either acetylene or ethylene being found in

the products) is a remarkable testimony to its relatively great stability at the highest temperatures of explosion flames. There is no evidence in these experiments of any real discontinuity between the chemical phenomena of ordinary "*inflammation*" and those of "*detonation*." The higher temperatures and more violent conditions in "*detonation*" are responsible for the more complete breaking down of unsaturated hydrocarbons, and a greater "unburning" of steam by carbon, but there is probably no difference as regards the mode in which the hydrocarbon is attacked by the oxygen in the two cases.

I therefore believe that, so far as our present knowledge goes, the views I have put forward afford a simple and consistent interpretation of hydrocarbon combustion, whether it be the slow flameless kind discovered by Davy, or the more complex phenomena of ordinary flames so wonderfully expounded by him, or finally the extreme conditions characteristic of the explosion wave.

I desire to acknowledge the devoted help rendered to me in the conduct of these investigations by the following research students of the Manchester University :—Messrs. R. V. Wheeler, W. E. Stockings, G. W. Andrew, Julien Drugman, and H. Henstock.

VOLUMETRIC METHOD FOR THE DETERMINATION OF ZINC.*

By WM. HERBERT KEEN.

(Concluded from p. 202).

To Determine Zinc in Ores.

DECOMPOSE 1 grm. of the sample in a beaker with hydrochloric acid, or if necessary with aqua regia. Evaporate to dryness, and if nitric acid has been added re-dissolve in hydrochloric acid and evaporate again. Dissolve in 15 cc. of hydrochloric acid (1·20), dilute with water, filter, and wash. Burn off the filter (unless it contains lead) in a platinum crucible, and treat with hydrofluoric and sulphuric acids—exactly as in a silica determination. Dissolve the residue in hydrochloric acid, and add to the solution. Usually this treatment of the residue is not necessary, as it rarely contains more than a few hundredths of a per cent of zinc. If lead sulphate is present in this residue, use a perforated crucible with an asbestos felt for a filter. Remove the filtrate after washing the residue thoroughly, and dissolve out the lead sulphate with a strongly ammoniacal solution of ammonium citrate. Wash with hot water, and then transfer the remaining residue, together with the felt, to an ordinary platinum crucible and treat with hydrofluoric acid as before, finally adding the hydrochloric acid solution of the remaining residue to the filtrate. (Advantage may be taken of the above steps to determine the lead in the same portion—the only changes necessary being to evaporate with sulphuric acid instead of hydrochloric, and to weigh the perforated crucible before and after treatment with the ammonium citrate, calling the difference lead sulphate). Neutralise the filtrate with ammonia, and again acidify, adding about 3 cc. of acid in excess for every 200 cc. of solution. Pass hydrogen sulphide through the solution to remove the copper group, and, having filtered out the precipitate thus obtained, heat until the free hydrogen sulphide has boiled off, and then add an excess of bromine water, and evaporate to about 50 cc. Precipitate the iron with ammonia, using a large excess, and washing with water containing ammonia. If the precipitate amounts to more than a few tenths of a per cent it should be dissolved and re-precipitated, and in case of large amounts of iron a third precipitation is sometimes necessary. Acidify the filtrate with hydrochloric acid, adding 3 cc. in excess. The solution is now ready for titration, unless manganese is present, if its volume does not exceed 150 to 200 cc. If it is of larger bulk than this, it should be evaporated until of approximately this volume, before titration. In the case of very large amounts of iron the sulphide of zinc should be separated from it just as described below when nickel is present, or, if preferred, the ether separation may be used.

When Manganese is present in the Ore.—If the iron is small in amount, add to the solution after evaporation, but before removing the iron, 5 grms. or more of potassium or sodium bromide. Make strongly ammoniacal, and stir for an hour by means of some such device as that used for the solution of steels in the determination of carbon. If no appliance of this sort can be had, the solution should be allowed to stand over-night at room temperature. The manganese and iron are completely precipitated, and should be filtered off, and washed with water containing ammonia. The filtrate should then be acidified as above and titrated. If the iron is present in large enough quantities to require re-precipitation, it should be removed before treatment with the bromide; but if both the manganese and iron are precipitated together, as above, and it is desired to re-precipitate them, they should be dissolved in a mixture of hydrochloric and sulphurous acids, the solution boiled to expel the sulphurous fumes, and then oxidised with bromine water. The bromine should be boiled off as before, and the precipitation then repeated with the alkali bromide and ammonia. The amount of bromide may be varied without any effect on the titration. If it is desired to determine the manganese, it may be dissolved in sulphurous acid alone, and after solution is complete, nitric acid added, the nitrous fumes boiled out, and the determination completed by the bismuthate method.

Of course the manganese may be readily avoided by precipitating the zinc as sulphide from a slightly acid solution, and this is to be advised in the case of large amounts of manganese—also if any nickel is in evidence. The presence of nickel will be made known by a blue colour of the ammoniacal filtrate from the iron. If it is necessary to precipitate the sulphide of zinc to avoid these metals, the best plan is to evaporate the hydrochloric acid as first obtained to a small bulk in order to expel most of the free acid, dilute with a little water, and neutralise with sodium carbonate solution, using methyl orange as an indicator. The neutral point should be carefully obtained and then *ten drops* of hydrochloric acid added. Wash down the sides of the beaker, dilute to 200 cc., and pass hydrogen sulphide through the *cold* solution for an hour. Let the solution stand for several hours, or, if convenient, over night before filtering. Zinc sulphide precipitated in this way should filter out like so much sand. Put the paper containing the precipitate into a beaker and digest until dissolved in 10 cc. of hydrochloric acid diluted with water. Pass hydrogen sulphide for a few minutes to be sure that all the copper is precipitated, and then filter and wash thoroughly with hot water. Evaporate the filtrate after adding a slight excess of bromine water to oxidise any iron that may have been occluded by the zinc, and when it is reduced to a small volume add an excess of ammonia and boil. Filter, if necessary, and neutralise the filtrate with hydrochloric acid, adding 3 cc. in excess. Dilute to 150 cc. and titrate. This method is excellent if the conditions are just right, but my idea has been to avoid a precipitation of the zinc, if possible, and thus get rid of what may be a troublesome filtration. Accordingly, I have endeavoured, except in cases where nickel is present, to precipitate from the zinc all metals interfering with the titration.

Brasses.—Remove the tin, copper, and lead in the usual way—by solution in nitric acid, filtration of the metastannic acid, and deposition of the two latter metals by electrolysis. If it is certain that the copper is entirely removed, evaporate to dryness the nitric acid solution, which now contains only the zinc and perhaps a small amount of iron. Dissolve the residue in 10 cc. of strong hydrochloric acid and, after dilution, precipitate the iron with ammonia, being careful to boil long enough to insure a complete precipitation, as iron comes down very slowly when present in such small quantities. Filter and wash with dilute ammonia water and then with hot water. Neutralise

* *Journal of the American Chemical Society*, xxx., No. 2.

the filtrate with hydrochloric acid, add an excess of 3 cc., dilute to 150 cc., and titrate with the standard ferrocyanide solution. In the case of a manganese bronze, the only modification would be the treatment with alkali bromide, as described above under ores.

It is sometimes easier, in the case of brasses, to make the filtrate from the electrolysis ammoniacal and add colourless ammonium sulphide. Digest at a temperature near the boiling-point for about an hour, allow to settle and filter, keeping as much of the precipitate in the beaker as possible. When the liquid has run through the funnel, replace the filtrate beaker by the one containing the precipitate and pour dilute hydrochloric acid over the filter, allowing it to run through on to the main bulk of the precipitate. Wash the filter once or twice and heat the solution until the zinc is dissolved. Pass a current of hydrogen sulphide for a few minutes and filter out any small traces of copper that may be precipitated as sulphide. Oxidise the filtrate with bromine water and evaporate to a small volume, finally precipitating the small amount of iron and finishing as before.

Aluminium Alloys containing Zinc.—Aluminium does not affect the ferrocyanide, and so the natural idea would be to dissolve in hydrochloric acid and proceed directly with the titration as soon as solution was complete. But iron is almost always present in such alloys to a considerable amount, and hence the necessity for a more roundabout method. Dissolve 1 grm. in either nitric or hydrochloric acid. Add a few crystals of citric acid, make ammoniacal, and heat to boiling. Remove from the source of heat and add a little colourless ammonium sulphide. Allow to settle and then filter, being careful to wash out the last traces of citric acid with a wash water containing a little ammonium sulphide. The precipitate will consist of sulphide of zinc, iron, and copper metals. Treat it exactly as described for brasses under similar conditions. If desired, the metal may be dissolved in hydrochloric acid and the zinc precipitated as sulphide from a slightly acid solution just as when it is required to separate it from nickel.

In general, any one working intelligently, realising the final conditions, and knowing something of the material in hand, will find no difficulty in following out the plan of this method.

MISCELLANEOUS.

Institute of Chemistry.—*April Examinations*, 1908.—Of twelve candidates who presented themselves for the Intermediate Examination, the following nine passed: F. S. Aumonier, T. Blackadder, B.Sc. (St. Andrews), R. H. Findlater, G. A. Freak, B.Sc. (Lond.), C. Harris, J. Kenyon, B.Sc. (Lond.), W. N. Morley, O. J. Patrick, and A. R. Smith, B.Sc. (Manc.) In the Final Examination for the Associateship, of seven candidates who presented themselves in the Branch of Mineral Chemistry, the following four passed: W. Colet Birch, B.A. (Cantab.), J. Gibbon, E. S. Poole, B.Sc. (Lond.), and W. E. F. Powney. Three candidates presented themselves in Organic Chemistry, and passed: G. H. Frank, B.Sc. (Leeds), F. W. Linch, and W. W. Reed, B.Sc. (Wales). Of six candidates in the Chemistry of Food and Drugs, &c., four passed: L. Clement, B.A., (Cantab.), J. C. Cowap, B.Sc. (Vict.), J. W. Haddon, B.Sc (Vict.), and D. R. Wood. Four candidates presented themselves for examination for the Fellowship, and one passed in Metallurgical Chemistry: T. H. Byrom.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Manufacture of Sodium Nitrite," by G. T. Morgan. "Some Simple and Mixed Esters of Cellulose—The Alkaline Decomposition of Nitro-derivatives of Cellulose and other Carbohydrates," by W. Smith, jun. "The Mechanism of Filtration," by E. Hatschek. "Metanil Yellow—Its Use as a Selective Indicator," by E. Linder. "Conversion of Oleic Acid into Stearic Acid," by J. Lewkowitsch.

TUESDAY, 5th.—Royal Institution, 3. "The Development of the Modern Turbine and its Application," by Gerald Stoney, M.Inst.C.E., &c.

WEDNESDAY, 6th.—Royal Society of Arts, 8. "The Gramophone, and the Mechanical Recording and Reproduction of Musical Sounds," by Lovell N. Reddie.
—— Society of Public Analysts, 8. "Examination of Oil of Turpentine and Turpentine Substitutes," by J. H. Coste. "Estimation of Ferrocyanide in Crude Commercial Products," by H. G. Colman. "Studies in Steam Distillation III., The Fatty Acids," by H. D. Richmond. "New Method for Milk Testing, and some Remarks on the Sydney Supply," by W. M. Doherty.

THURSDAY, 7th.—Royal Institution, 3. (The Tyndall Lectures). "Mendelian Heredity," by William Bateson, F.R.S., &c.
—— Chemical, 8.30. "Interaction of Diazonium Salts with Mono- and Di-hydric Phenols and with Naphthols," by K. J. P. Orton, and R. W. Everatt. "Condensation of Benzoin with Methyl Alcohol," by J. C. Irvine and D. McNicoll. "Mutual Solubility of *a*-Methylpiperidin and Water," by O. Flaschner and B. MacEwen. "Melting-points of the Anilides, *p*-Toluidides, and *a*-Naphthylamides of the Normal Fatty Acids," by P. W. Robertson. "Refraction and Dispersion of Triazo-compounds" and "Dissociation Constants of Triazoacetic and *a*-Triazopropionic Acids," by J. C. Philip. "Absorption Spectrum of Camphor," by W. N. Hartley. "Viscosity of Solutions," by C. E. Fawsitt. "Action of Fused Potassium Hydroxide and of Hydrogen Peroxide on Cholesterol," by R. H. Pickard, and J. Yates. "Fermentation of Mannose and Fructose by Yeast Juice," by A. Harden and W. J. Young. "Volumetric Estimation of Silver," by W. R. Lang and J. O. Woodhouse. "Constituents of Olive Leaves," and "Constituents of Olive Bark," by F. B. Power and F. Tutin.

FRIDAY, 8th.—Royal Institution, 9. "Ice and its Natural History," by J. Y. Buchanan, F.R.S., &c.
—— Physical, 8. "A Modified Theory of Gravitation," by C. V. Burton. "An Examination of the Formulæ for the Grading of Cables," by C. S. Whitehead. "Illustrations of Geometrical Optics," by R. M. Archer.

SATURDAY, 9th.—Royal Institution, 3. "Chile and the Chilians," by C. F. Scott Elliot, M.A., &c.

THE CHEMICAL NEWS.

VOL. XCVII., No. 2528.

THE DECOMPOSITION OF DOLOMITE.

By NICHOLAS KNIGHT.

THE dolomites of Iowa and other sections of the country, belonging to the Niagara period of the Upper Silurian, in the course of centuries apparently undergo decomposition. The rock loses its massive structure and becomes crumbly and mealy in appearance. In the vicinity of Mount Vernon, Iowa, the top layer to the depth of 3 or 4 inches seems to be quite thoroughly disintegrated and powdery. The same phenomenon is observed in lower strata where a layer projects, by which it is especially exposed to the elements. A similar disintegration is observed in many other localities.

It seemed reasonable to suppose that some constituent or constituents of the rock are more soluble than the others, or more easily acted upon by atmospheric agencies. The analysis of a more or less disintegrated air-dried specimen resulted as follows :—

SiO_2	0·56 per cent
Fe_2O_3 and Al_2O_3	0·74 ,,
$CaCO_3$	48·43 ,,
$MgCO_3$	50·56 ,,
	100·09

The analysis of a typical massive specimen gave :—

SiO_2	0·83 per cent
Fe_2O_3 and Al_2O_3	0·59 ,,
$CaCO_3$	53·62 ,,
$MgCO_3$	44·96 ,,
	100·00

It is thus seen that about 5 per cent of the calcium carbonate has been removed, and the magnesium carbonate is relatively stable. Other portions of the rock would doubtless show greater disintegration.

Immediately above the disintegrated layer referred to are found portions of what appears like a ferruginous clay. In all likelihood it formerly existed as a distinct layer, but was largely removed by the ice-sheet. It has accumulated in various cavities and depressions in the rock. This formation is quite widely extended. In North-East Iowa it is several feet in thickness, and in South-Western Wisconsin, on broad uplands, where it has been but little disturbed by the ice-sheet, it has a thickness of 13 feet.

An analysis of the ferruginous clay resulted as follows :—

SiO_2	16·68 per cent
Fe_2O_3	60·87 ,,
Al_2O_3	6·18 ,,
CaO	0·22 ,,
MgO	0·03 ,,
H_2O	17·14 ,,
	101·12

This clay probably resulted from the dolomite by the slow solution of the calcium and magnesium carbonates. The typical specimen of the rock referred to above contained 0·25 per cent Al_2O_3 and 0·34 per cent Fe_2O_3; therefore the alumina seems to have been removed much more rapidly than the ferric oxide.

If this deposit resulted from the decomposition of dolomite it must have been very slow in forming, and the accumulation of as great a quantity as 13 feet must have required a very long time.

Our thanks are due to Mr. Merle S. West for making the analyses described in the foregoing.

Cornell College, April 2, 1908.

A METHOD FOR THE SEPARATION OF IRON FROM INDIUM.

By F. C. MATHERS.

ONE of the most difficult steps in the purification of indium is its separation from iron. Winkler (*Journ. Prakt. Chem.*, 1865, xciv., 1) obtained a separation by the fractional precipitation of the sulphide, the indium sulphide being less soluble than the iron sulphide. A more satisfactory method was devised by Bayer (Bayer, *Liebig's Annalen*, 1871, clviii., 372), who treated a solution of the mixed chlorides with sodium sulphite. Basic indium sulphite is precipitated from this solution upon boiling. The precipitate, after filtration, was dissolved in a solution of sulphurous acid, and basic indium sulphite was again precipitated by boiling. This solution and re-precipitation was repeated several times to completely purify the indium. The Bayer method was tested in this laboratory, but gave unsatisfactory results. Weselsky (*Journ. Prakt. Chem.*, 1865, xciv., 443) treated the chlorides of indium and iron with sulphur dioxide or sodium thiosulphate, and then with barium carbonate, which precipitated indium hydroxide, together with traces of iron and zinc. Meyer (*Liebig's Annalen*, 1869, cl., 137) treated the material that contained indium and iron with sodium carbonate until neutral and then with a solution of potassium cyanide until the precipitate that first formed was re-dissolved. The solution thus formed was diluted with ten volumes of water and was boiled. This decomposed the potassium indium cyanide and indium hydroxide was precipitated, while the iron remained in solution as potassium ferri- or ferro-cyanide. This method was found, upon trial, to give fair results. The indium, however, is not completely precipitated by boiling, considerable amounts of it being found in the filtrate. The precipitate is very gelatinous, difficult to wash, and often passes through the filter-paper before the washing is completed. For these reasons the method is not satisfactory. Some quantitative results obtained in this laboratory with the Weselsky method follow :—

Indium oxide present (grm.)	0·0320	0·0543
Indium oxide precipitated by dilution and boiling (grm.)	—	0·0528 or 96·8 per cent
Indium oxide precipitated from the filtrate with ammonium hydroxide (grm.)	0·0022 or 6·8 per cent	0·0014 or 2·5 per cent

Dennis and Geer (*Journ. Am. Chem. Soc.*, 1904, xxvi., 437) have proposed the removal of the iron by extracting the ferric sulphocyanate with ether. This method has been applied to the removal of iron from nickel, cobalt, copper, aluminium, &c. Indium sulphocyanate, however, is quite soluble in ether, and for this reason indium is always present with the iron in the ether extract. The labour involved in recovering the indium thus dissolved constitutes a serious drawback in this method, which is otherwise very satisfactory and yields an indium that is free from iron.

Several other methods have been suggested for the separation of iron and indium, but those cited above seem to have been the ones most generally used and to have been the most satisfactory.

The method here proposed for the removal of iron from indium is the precipitation of iron from nitroso-β-naphthol. This reagent (Ilinski and Knorre, *Ber.*, 1885, xviii., 2728; Knorre, *Ber.*, 1887, xx., 283) quantitatively precipitates cobalt, copper, and iron, but does not precipitate aluminium, lead, zinc, or nickel. Experiment showed that indium also was not precipitated, and this led to the development of the following method of separation:—

A solution of the indium chloride or sulphate containing a small quantity of iron was evaporated to a volume of 20 to 25 cc., was neutralised with ammonium hydroxide, and then an equal volume of 50 per cent acetic acid was added. The iron in these solutions was precipitated with nitroso-β-naphthol dissolved in 50 per cent acetic acid. The solution may be either hot or cold when precipitated, but it should stand several hours before filtering, and should be cold when filtered. The residue is washed with 50 per cent acetic acid and finally with water. Before using this method the bulk of the iron must be removed by some other method. Since the precipitate of iron with nitroso-β-naphthol is very bulky, 0·05 grm. of iron is about the maximum quantity that can easily be handled on a 12 mm. filter-paper. The indium precipitated by electrolysis from a solution containing indium sulphate and quite large amounts of ferric sulphate and strongly acidulated with sulphuric acid, contains only small amounts of iron. This metal can then easily be freed from the iron that it still contains by precipitating the iron with nitroso-β-naphthol. Colorimetric analysis of the indium, after the precipitation of the iron by this method, showed that the content of iron was very low. This small amount of iron (Stokes and Cain, *Journ. Am. Chem. Soc.*, 1907, xxix., 409) could easily have been introduced into the solution during evaporation by the dust from the air. Quantitative determinations of the iron remaining in the indium gave the following results:—

Indium oxide taken (grm.)	0·3148	0·1738	0·2184	0·3061	0·2142
Ferric oxide added (grm.)	0·0328	0·0262	0·0197	0·0262	0·0262
Nitroso-β-naphthol used (grm.)	5·0	4·0	3·0	2·5	2·5
Ferric oxide still present in the indium oxide (grm.)	Less than 0·00005			Less than 0·0001	Very faint red

Some indium remains in the residue with the iron and a second precipitation will not remove all of it. The indium in these residues can easily be detected with the spectroscope. The total quantity of indium that is lost in these iron residues is, however, quite small, as is shown by the following data:—

Indium oxide taken (grm.)	0·3061	0·1520	0·2142
Ferric oxide added (grm.)	0·0262	0·0262	0·0262
Ferric oxide obtained from first precipitation (grm.)	0·0286	0·0283	0·0281
Second precipitation (grm.)	0·0273	0·0273	0·0266
Indium oxide in ferric oxide in first precipitation (grm.)	0·0024	0·0021	0·0019
Second precipitation (grm.)	0·0011	0·0011	0·0004

—*Journal of the American Chemical Society*, xxx., No. 2.

New Type of Compounds of Sulphur with certain Iodides.—V. Auger.—When sulphur and iodoform are dissolved in the smallest possible quantity of warm carbon disulphide, and the solution is cooled, pale yellow crystals separate out. They have the formula $HCI_3.3S_8$. This method of preparing molecular compounds of sulphur and iodides can be applied to other iodides, both organic and inorganic, and the products appear to have the general formula $RI_n.nS_8$. The author has prepared the following compounds:—$HCI_3.3S_8$, $CI_2CI_2.4S_8$, $AsI_3.3S_8$, $SbI_3.3S_8$. —*Comptes Rendus*, cxlvi., No. 9.

THE ESTIMATION OF IRON BY POTASSIUM PERMANGANATE AFTER REDUCTION WITH TITANOUS SULPHATE.

By H. D. NEWTON.

Knecht (*Ber.*, xxxvi., 166) was the first to point out and recommend the use of titanium sesquioxide and its salts in volumetric operations where a rapid and powerful reducing agent is required. Somewhat later the same author in collaboration with E. Hibbert (*Ber.*, xl., 3819) published a method for the direct titration of ferric chloride by a standard solution of titanous chloride, using potassium sulphocyanate as an indicator, the reaction between the two salts taking place according to the following equation: — $FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4$. According to these authors, the above method yields excellent results, and rapidly. The only precautions necessary are that the solution of titanous chloride, being naturally very sensitive to the action of atmospheric oxygen, must, after being boiled in presence of marble to expel occluded oxygen, be kept under a constant pressure of hydrogen. It has been found, however, that even with such precautions the standard of the solution gradually changes, and must be checked from time to time against known amounts of ferric iron.

The present investigation was undertaken for the purpose of adapting the well known and accurate method of titration with standard potassium permanganate to the determination of ferrous salts, after reduction has been effected by a titanous salt according to the excellent and rapid method of Knecht.

It has been shown in a former paper that bismuth oxide completely oxidises titanous sulphate while having no appreciable effect on salts of ferrous iron (*Am. Journ. Sci.*, xxiii., 365; Chemical News, xcvi., p. 148). So the plan of this work has been to reduce the iron by titanous sulphate, oxidise the excess of titanous sulphate by bismuth oxide, and titrate the remaining ferrous salt by permanganate.

A solution of titanous sulphate of convenient strength was made up by mixing 20 grms. of commercial titanic acid, in two portions, with three times its own weight of a mixture of sodium and potassium carbonates, and fusing in a platinum crucible until all the titanic acid was converted into the soluble alkali titanates. The melt obtained in this manner, after being finely ground, placed in a platinum dish, and treated with hot concentrated sulphuric acid (which soon effected solution) was cooled, diluted a little, and filtered. To these concentrated solutions of titanium sulphate, zinc was added until reduction was complete, and while there was some zinc left in the flask the solution was quickly filtered through a platinum cone into about 2 litres of freshly distilled water contained in a small reservoir, the latter being set up and connected with a burette and hydrogen generator as described by Knecht and Hibbert (*loc. cit.*).

A test solution of ferric sulphate was prepared by treating ferrous ammonium sulphate with oxalic acid, drying, and igniting the resulting ferrous oxalate, dissolving the ferric oxide thus formed with concentrated hydrochloric acid, and converting the ferric chloride to sulphate by digesting with concentrated sulphuric acid. After diluting and filtering, the solution was made up to known volume and standardised by drawing from a burette into 50 cc. flasks several portions, reducing each by a definite amount of zinc of known iron content, cooling, pouring into a litre of cold distilled water, and immediately titrating with tenth normal potassium permanganate.

In the following table are recorded results obtained by effecting the reduction of carefully measured amounts of the ferric sulphate solution by addition of an excess of titanous sulphate in the cold, destroying this excess by treating with a little bismuth oxide, filtering from the excess of bismuth oxide, and reduced bismuth into about a litre of cooled distilled water, and titrating with permanganate.

$Fe_2(SO_4)_3$.	$KMnO_4$.	Fe_2O_3 taken.	Fe_2O_3 found.	Error.
Cc.	Cc.	Grm.	Grm.	Grm.
20	13·46	0·1063	0·1064	+0·0001
20	13·42	0·1063	0·1060	−0·0003
20	13·44	0·1063	0·1062	−0·0001
20	13·44	0·1063	0·1062	−0·0001
20	13·41	0·1063	0·1060	−0·0003
30	20·18	0·1594	0·1594	—
30	20·20	0·1594	0·1596	+0·0002
30	20·20	0·1594	0·1596	+0·0002
30	20·22	0·1594	0·1598	+0·0004
30	20·19	0·1594	0·1595	+0·0001
40	26·92	0·2127	0·2127	—
40	26·90	0·2127	0·2125	−0·0002
40	26·90	0·2127	0·2125	−0·0002
40	26·93	0·2127	0·2128	+0·0001
40	26·90	0·2127	0·2125	−0·0002

In later experiments it was found that the bismuth oxide failed to oxidise the sesquioxide of titanium when there was an appreciable amount of hydrochloric acid present in solution. Therefore it is advisable if the original solution is made with hydrochloric acid, to evaporate to dryness, and convert the chloride to sulphate by use of concentrated sulphuric acid. Upon addition of the sulphuric acid a white pasty mass of basic ferric sulphate is formed which rapidly goes into solution on diluting with water and warming. As titanous sulphate prepared in the above manner always contains some iron, it is necessary to make a correction for this, by treating with bismuth oxide an amount of the solution equal to that used, filtering, and running in potassium permanganate to colour. This correction should not amount to more than 0·1 cc. when working with 0·3 grm. of ferric oxide.

If these simple precautions be taken, ferric iron may be determined with rapidity and exactness by reduction with titanous sulphate, and subsequent titration with potassium permanganate.—*American Journal of Science*, xxv., p. 343.

THE INTERACTION OF ALUMINIUM POWDER AND CARBON.*

By FRANK E. WESTON, B.Sc., and H. RUSSELL ELLIS, B.Sc.

In attempting to remove the grease with which aluminium powder is coated by gently heating, it was noticed that a black deposit was formed on the surface of the powder, accompanied by an evolution of heat with incandescence; as the temperature of heating was not above 400° C., it was thought probable that the aluminium powder had attacked the vapour produced from the grease, with the production of a carbide of aluminium differing from that formed by Moissan in the electric furnace at a very high temperature. (A gas with odour of acetylene was evolved in treating a portion with water). Very little information on the direct union of aluminium and carbon, without the use of the electric furnace, is available, and even that which has been published is vague, and in some cases contradictory. Moissan states ("The Electric Furnace," 1904, p. 235, in a footnote):—"According to Mallet aluminium does not combine with carbon; on the other hand, Franck, by calcining a mixture of aluminium and lampblack, obtained a metallic substance yielding hydrogen contaminated with acetylene when treated with hydrochloric acid" (see also *Bull. Soc. Chim.*, 1894, [3], xi., p. 439). Mallet's statement need not be considered in view of the fact that fine aluminium powder was not used or procurable, and for a similar reason the amount of carbide produced by Franck was small.

Franck (*Chem. Zeitung*, 1898, p. 236) prepared a small quantity of aluminium carbide by heating aluminium powder in carbon monoxide or carbon dioxide, and confirmed the experiments of Guntz and Moissan (*Comptes Rendus*, 1897, cxxiv., No. 4). He also made aluminium react with lampblack, producing a body which evolved a large amount of methane with water.

Fritz Fichter (*Zeit. Anorg. Chem.*, 1907, liv., p. 322), using a mixture of aluminium powder and soot, prepared an impure aluminium nitride as follows:—A mixture of aluminium powder with 4 to 5 per cent of soot is made and heated to a high temperature; it is then exposed to the air, when a vigorous action takes place, producing a fairly large yield of aluminium nitride.

Kusnetzkoff (*Ber.*, 1907, xl., p. 2871) showed that aluminium at temperatures near its melting-point decomposes CH_4, C_2H_6, C_2H_4, and C_2H_2 completely into their elements. The H and part of the C are obtained in the free state, whilst the remainder of the carbon forms aluminium carbide.

Matignon (*Comptes Rendus*, 1907, cxlv., No. 17) states Berthelot has shown that a large disengagement of heat takes place when aluminium and carbon react; and, therefore, since the reaction is exothermic, combination ought to take place without the aid of an electric furnace. Matignon showed that the two elements would combine when heated in a Perrot furnace, forming an olive-green or yellow product. He used lampblack, and obtained an intimate mixture by working the two together with terebenthene, the proportion of lampblack to aluminium being 24 to 70 or 140; Al_4C_3 requires 24 of carbon to 72 of aluminium. When the large excess of Al was used the action could be started by igniting the mixture in one place, when it spread throughout the mass. The product gave on treating with water a gas consisting of 96·36 per cent CH_4 and 3·36 per cent H. As will be shown later by the authors, the product of reaction must have contained nitride.

In a letter to the CHEMICAL NEWS, November 29, 1907, the authors call attention to the fact that a mixture of aluminium powder and wood charcoal could be made to react with a fuse of Mg and BaO_2, similar to the ordinary thermite reaction. The authors now present in this paper the results of their investigations on the interaction of aluminium powder with wood charcoal, sugar charcoal, and graphite respectively. With each kind of carbon it was found possible to prepare a mixture with aluminium powder which, when started with a fuse of Mg powder and BaO_2, would react with vivid incandescence throughout the mass, similarly to the ordinary thermite reaction, the action being most pronounced in the case of wood charcoal. Mixtures which would not react with a fuse were found to do so when placed in a muffle furnace and heated to temperatures varying from 400° C. to 1100° C. In some cases it was found that in heating the mixture in a closed Hessian crucible to dull redness, and then withdrawing the crucible and opening to the air, vigorous action took place throughout the mass, starting at the surface and proceeding downwards. In all cases the product of the reaction was found to contain the following: Aluminium carbide, aluminium nitride, aluminium oxide, carbon, and aluminium. The percentage of Al_2O_3 produced varied from 10 to 55, not only in the different mixtures, but in different parts of the same mixture. All the products gave with water mixtures of CH_4 and H, the former produced by the action of water on the aluminium carbide, Al_4C_3, viz., $Al_4C_3+12HO=4Al(OH)_3+3CH_4$, whilst the H was produced by the action of free Al in water in the presence of the NH_3 liberated by the action of water on the aluminium nitride (see later). Since CH_4 was the only hydrocarbon obtained either by the action of water or hydrochloric acid, the authors conclude that the only carbide formed in the reactions mentioned is the one described by Moissan, viz., Al_4C_3. (This result confirms that of W. H. Patterson, CHEMICAL NEWS, December 20, 1907, who prepared aluminium carbide in the electric furnace at different temperatures, and could only obtain the carbide Al_4C_3).

The authors are of opinion that in all the reactions between aluminium and carbon mentioned above, the air

* A Paper read before the Faraday Society, April 28, 1908.

plays a most important part; the first action being the oxidation of the carbon to CO and CO_2,* thus producing sufficient heat to cause the oxidation of the Al powder to Al_2O_3, and this latter reaction raising the temperature sufficiently high to cause combination between the aluminium and the carbon, as well as the aluminium and nitrogen, the nitrogen coming from both the atmosphere and the occluded gases in the carbon. That the reason assigned is most probable follows from the following experimental facts:—

1. The reaction was most vigorous in the case of wood charcoal. All the mixtures of Al and wood charcoal were extremely porous, and hence contained plenty of air; also the volume of the carbon was greater proportionately to the aluminium in these mixtures than in the others; moreover, the wood charcoal contained ten times its own volume of occluded gases consisting of O and N.

2. Mixtures of aluminium and carbon which reacted with a fuse, when exhausted with a Töpler pump and heated to a full red heat, underwent very slight change (see analysis, *prox.*).

3. Mixtures of Al and C (all kinds) when heated in a current of air, reacted before temperature had risen to a visible red heat, and continued throughout the mass. The products always contained carbide, nitride, and oxide, the two latter predominating under these conditions.

Experimental.

Series I.—*Aluminium and Wood Charcoal.*

The aluminium powder used was the finest obtainable from the British Aluminium Company. It was freed from its adherent coating of grease by extraction with ether and dried in a steam oven. The wood charcoal used was first heated for an hour in a closed tin at a temperature of about 1000° C.; allowed to cool, powdered, and sieved. After passing through a 40,000-mesh sieve, it was again separated into a fine and coarse portion by means of a Goreham-Griffin theorometer to which a special receiver was fitted to collect the fine powder; this fine powder was used in the experiments. On igniting a weighed portion of the wood charcoal in a muffle, a brown residue was obtained which was 3 per cent of the charcoal taken.

Three sets of mixtures were made up, having compositions represented by the following:—(1) 4Al to 3 C; (2) 4 Al to 6 C; (3) 8 Al to 3 C.

Mixture containing 4 Al *to* 3 C:—

1. The mixture was placed in a Hessian crucible and a fuse of Mg powder and BaO_2 powder placed on top; into this a piece of Mg ribbon was put and lighted. The reaction commenced slowly at first, but then proceeded with increasing vigour and incandescence throughout the mass. It was found that the reaction took place best when the fuse was spread all over the surface, thus showing that a good heat supply must be available in order to start the action.

2. The mixture was placed in a porcelain basin and gently heated over a Bunsen burner. In five minutes a slight glow appeared at the bottom of the basin and slowly spread throughout the mass, and on reaching the upper surface bright incandescence took place, due to the burning of the Al in air. On cooling and examining the contents of the basin, a white layer one-sixteenth inch thick completely covered the top, whilst below was found a greyish black solid mass; no Al was visible.

3. The mixture, in a Hessian crucible, was placed in the front part of the muffle furnace and heated to about 400° C. After a few minutes a glow appeared on the top, when the crucible was withdrawn; the reaction spread throughout the mass slowly.

4. The mixture was placed in a Hessian crucible, covered with a piece of asbestos cardboard, and then tightly packed with a layer, three-quarter inch thick, of finely powdered MgO. Two crucibles were prepared and placed at the back of the muffle, which was at a temperature of between 1000° and 1100° C. One was left there two hours; the other was withdrawn at the end of five minutes and immediately opened; the contents instantly became incandescent.

Mixture containing 4 Al *to* 6 C.—This mixture could not be made to react with a fuse. The mixture was placed in a Hessian crucible and covered as before and heated half-an-hour at a temperature of about 1000° C. On cooling the resulting mass was found to be soft and easily removable; at the top was found a very thin layer of Al_2O_3.

Mixture containing 8 Al + 3 C.—This mixture would not react in the cold with a fuse, but on heating in a crucible over a Bunsen the reaction took place easily. The mixture, placed in a Hessian crucible and covered as before, was heated for fifteen minutes at about 1000° C. After five minutes CO appeared at a crack near the bottom of the crucible and burnt, and the crucible could be seen getting visibly hotter; CO also burnt on the top of the crucible. On cooling and opening the contents of the crucible were quite hard and crystalline, and at the top and near the crack a very thin layer of Al_2O_3 was found.

The products obtained in all the above experiments were more or less greyish-black in colour, and the core contained in all cases distinct yellowish crystals.

In no case were the contents of the crucibles the least disturbed, showing that very little gaseous products had been produced, but that combination between the carbon and aluminium had taken place.

On treating the powdered residue with water no action took place for some five to ten minutes; after this a gas was slowly evolved, but at a gradually increasing rate, and in the cases where only a small quantity of water was used a very violent evolution of gas took place after a short time and the flask became very hot. Using a large excess of water, no heating took place, and the gas was steadily and very slowly evolved for several weeks (in one case six weeks, another twelve, &c.). The solutions smelt strongly of NH_3, especially after a day or two, and the gas had a slight odour of acetylene and burnt readily with a slight whitish flame. The gas was fully analysed, and contained less than 0·2 per cent of acetylene or other unsaturated hydrocarbons (see analyses). When generating flask was placed in hot water the action was immediately vigorous. The solid products, therefore, contained carbide and nitride as well as aluminium, &c. After several attempts at analysing the solid the following process was adopted, which, although not of a high degree of accuracy, is sufficiently accurate to show the difference between the constitution of the products obtained in the various reactions.

Method of Analysis of the Crude Product of Reaction.

1. *Estimation of Free Aluminium.*—0·1 to 0·3 grm. of the substance, after crushing and sieving through 40,000 sieve, was placed in ice-cold conc. HCl, kept well cooled in ice and salt, and thoroughly and continuously shaken for twenty minutes (see Moissan, "Electric Furnace"). The evolution of gas was fairly rapid at first, but at end of ten minutes was almost over. The solution was diluted with ice-cold water, filtered at the pump, washed with ice-cold water, and the dissolved Al in the filtrate estimated in the usual manner with NH_4OH. This treatment dissolved free Al, but left undissolved the whole of the carbide, nitride, and alumina. Comparative tests were made.

2. *Estimation of Free* C, Al_2O_3, Al_4C_3, *and* AlN.—This involved two distinct processes, viz.:—

A. About 2 grms. of substance—ground, &c., as in 1—are boiled in a conical flask for two to three hours with equal vols. of conc. HCl and water (100 cc.). The prolonged boiling is necessary in order to dissolve that carbide and nitride which are protected with a

* Pring (*Journ. Chem. Soc.*, October, 1905, p. 1532), in preparing aluminium carbide in the electric furnace, considers it is formed by action of Al on CO and CO_2 from the furnace gases.

layer of Al_2O_3. H and CH_4 escape rapidly at first and then slowly for a time. At end of time stated the solution is diluted and filtered at the pump through a tared filter-paper and residue well washed—washing collected with original filtration. The residue, which is black, is dried and weighed to constant weight. This residue consists of C, H_2O_3, and traces of SiO_2 (found to be very small and hence neglected); it was placed in muffle and burnt till quite white and to constant weight. This process burns off the C. It was observed early in the work that when the boiling with the HCl was not prolonged the residue gained weight on ignition, showing the presence of unacted upon carbide and nitride, viz., $Al_4C_3(144) \rightarrow 2Al_2O_3(204)$ and $2AlN(82) \rightarrow Al_2O_3(102)$. The filtrate contained $AlCl_3$ (and traces of $FeCl_3$) derived from action of HCl in the free Al, the Al_4C_3, the AlN, as well as some of the Al_2O_3 (see Note). It was evaporated to dryness in a water-bath, re-dissolved in water, and again evaporated to dryness with NH_4OH, and then ignited in the muffle in a tared basin; the Al_2O_2 thus obtained was weighed. The residue obtained was always found to be quite white, though it contained traces of Fe_2O_3 which were neglected in the estimation.

B. *Estimation of the* AlN.—The principle used was the decomposition of the nitride by HCl and estimating volumetrically the amount of NH_3 produced. A weighed quantity of the powdered substance was heated in a flask with HCl, as in 2 A, for two to three hours; the flask B was then fitted up as shown in a diagram; excess of strong KOH solution was then run in through the funnel (D), and the evolved NH_3 collected in standard H_2SO_4 in C. It will be noticed that NH_3 free air is aspirated through the apparatus during the whole time of the distillation; this ensured a regular and steady ebullition in the flask A; a few drops of phenol-phthalein solution was always placed in B before fixing up in order to indicate when excess of KOH had been added. A contains dilute H_2SO_4. Flasks B and C were easily removed, and replaced without disturbing remainder of apparatus. Blank experiments were carried out with the apparatus as well as tests with known strengths of NH_4OH solution in order to test its accuracy.

Contents of Flask B ..	1.	100 cc. concentrated KOH
	2.	50 ,, ,,
	3.	5 cc. N/10 NH_4OH and excess KOH
	4.	5 ,, ,, ,,
Contents of Flask C ..	1.	10 cc. N. H_2SO_4
	2.	20 ,, ,,
	3.	5 ,, ,,
	4.	10 ,, ,,
Acid found in C after distillation ..	1.	10 ,, ,,
	2.	20 ,, ,,
	3.	45 cc. N/10 H_2SO_4.
	4.	95 ,, ,,

Method of Calculating Composition of Product.

1. By direct estimation is obtained weight of Al, C, and AlK.
2. By direct estimation is obtained weight of Al_2O_3 produced from Al, AlN and Al_4C_3, and Al_2O_3.
3. Let X be weight of substance taken and
   Let X^1 be weight of (Al + C + AlN) found.
   Then $X - X^1$ is weight of Al_4C_3 and Al_2O_3 in original substance.
   Let x be weight of Al_2O_3 found by experiment produced from Al, AlN, Al_4C_3, and Al_2O_3,
   And y be calculated weight of Al_2O_3 produced from X^1 parts of (Al + C + AlN);
   Then $x - y$ is the weight of Al_2O_3 produced from $(X - X^1)$ parts of (Al_4C_3 and Al_2O_3).
   When Al_4C_3 (144) is converted into $\rightarrow 2Al_2O_3$ (204), an increase of 60 parts by weight corresponds to 144 Al_4C_3.

Hence an increase of $[(X - X^1) \backsim (xy)]$ parts by weight corresponds to $\frac{144[X - X^1) \backsim (x - y)]}{60}$ parts of Al_4C_3 (say = Z), and hence also weight of $Al_2O_3 = (X - X^1) - Z$.

Note on the Solubility of Al_2O_3 *in* HCl.

Statements as to the solubility of Al_2O_3 in HCl differ considerably. As in our method of analysis we wished for confirmatory evidence as to the solubility of Al_2O_3 under the conditions there carried out, the following tests were performed:—

Test 1.—Anhydrous Al_2Cl_6 was heated in the muffle furnace at a temperature of 1000°—1100° C. for five hours, thus converting it into Al_2O_3. A weighed quantity of this Al_2O_3 was boiled for three hours with conc. HCl, allowed to stand three hours, filtered, and residue well washed, &c. The Al in filtrate was estimated by NH_4OH in usual manner:—

Weight of Al_2O_3 used	2·4085 grms.
Weight of insol. portion in HCl..	0·6900 ,,
Weight of soluble	1·7026 ,,
Total..	2·3926 ,,

Test 2.—A layer of Al powder (purified) about one-eighth inch deep was spread over a porcelain basin and inserted into the hottest part of the muffle, which was left open. The Al commenced to burn and was brought to the front of the muffle, and here continued to burn with intense light and heat. The residue was greyish-white, not pure white, whilst a fairly large amount of black substance was present. This was boiled for three hours with 2N . HCl to remove any nitride (see analysis of nitride in Al powder burnt in air) and free Al, and after drying a weighed amount was then boiled with conc. HCl for three hours.

Weight of Al_2O_3 used	1·9300 grms.
Weight of Al_2O_3 insoluble	1·3845 ,,

Pionchon (*Comptes Rendus*, cxvii., 328, 330) showed that grey powder was probably Al_6O_7 or $Al_2O_3.3Al_2O_3$. Duboin (*Comptes Rendus*, cxxxii., No. 13) showed that grey powder not a mixture of Al_2O_3 and Al became in mixing Al_2O_3 and 4 Al, and on heating a vigorous action takes place.

Test 3.—A portion of the slag from a Goldschmidt's reduction of Fe_2O_3, after grinding to pass a 40,000-mesh sieve, was boiled with conc. HCl for six hours and nine hours respectively.

Weight of slag used	4·3800 grms.
Weight of insol. matter after six hours .	2·2632 ,,
Weight of insol. matter after nine hours	1·9010 ,,

The filtrate in each case contained Al and Fe.

Conclusion.—It is evident that strongly heated Al_2O_3 is slowly attacked by conc. HCl, and hence in the method of determining constitution of products obtained from Al_4C some of the Al_2O_3 went into solution on boiling with the HCl, as was found by the calculation of results.

The content of Al_4C_3 in the product could have been estimated by determining the volume of CH_4 evolved by the action of water in HCl, but this method was not adopted for two reasons. First, the action of water was extremely slow (1 grm. of the well-powdered substance slowly produced gas for a week and then the action was incomplete); secondly, even on using dilute HCl, the evolution of gas was slow and protracted owing to the protecting layer of Al_2O_3 present; hence the method adopted was the one described.

Analysis of the Gas Evolved by Action of Water and Hydrochloric Acid.

No attempt was made to determine the quantity of gas evolved from known amounts of the solid for the reasons just given, but the gas evolved from different samples

Sample.		Analysis. Free C. Per cent.	Free Al. Per cent.	AlN. Per cent.	Al_4C. Per cent.	Al_2O_3. Per cent.
A. 4Al+3C:—						
1. Made in open crucible	Top layer	3·3	2·9	22·65	42·09	29·06
	Bottom layer	4·8	2·8	22·83	53·34	16·23
2. Made in closed crucible and heated two hours	Top layer	8·09	1·07	11·84	23·46	55·54
	Bottom layer	7·96	1·40	16·87	36·11	37·66
B. 8Al+3C: Middle portion, containing blue and yellow crystals		2·29	0·5	40·37	9·12	47·72
C. 4Al+6C: Lower layer		20·1	0·25	3·67	65·91	11·07

and different portions of the same crucible were carefully examined, with a view to throwing light upon the nature of the carbides present. The samples were placed in small Bohemian flasks (300 cc.), having a side tube in the neck, and connected to a Winchester quart bottle filled with water, which acted as an aspirator gas-holder; the flask was filled with distilled water, and a well-fitting cork inserted into the neck, care being taken to exclude air. The apparatus was then put by and allowed to remain for intervals of time extending from one day to sixteen weeks.

Hempel's technical gas apparatus was used for estimating the constituents of the gas evolved, all the solvents and the containing water in the measuring and pressure burettes being well shaken with the various samples before making observations. Each sample was tested for CO_2, CO, O, and unsaturated hydrocarbons, but in no case was a ıy of these gases found. The saturated hydrocarbons and hydrogen were then determined by taking a known volume of the gas, mixing it with a known excess of air, and exploding over water in a Hempel's explosive pipette, measuring diminution in volume absorbing CO_2 produced, and measuring its volume, passing residual gas into alkaline pyrogallic acid, and measuring the volume of O thus absorbed. In order to check this work some half-dozen samples of the gas were likewise analysed in Dr. Bone's apparatus for exact gas analysis over Hg, and the results so obtained did not differ by 1 per cent from the results obtained with Hempel's apparatus. From the diminution in volume after explosion of the volume of CO_2 formed and the volume of O used in explosion, it was deduced that the explosive gas was a mixture of CH_4 and H. In all experiments a gas residue was obtained, which could only be put down as N, and for some time it was a matter of speculation as to the source of this N. Explosions with pure O were carried out, and still the same percentage of residue (N) was obtained. It was, however, noticed that the percentage of N was greater in those samples which had been standing for some time; in fact, those gases which were analysed within twenty-four hours of their starting contained less than 2 per cent, whereas one that had stood three months contained 8 per cent. It was then thought that the N came from the dissolved air in the water used. An active sample of powdered material was therefore treated with water in the apparatus described and the gas analysed at end of known intervals of time in Dr. Bone's apparatus, with the following results:—

At end of twenty hours..	CH_4 = 43·8	H = 52·0	N = 4·2
At end of three days ..	CH_4 = 43·0	H = 51·0	N = 6·0
At end of seven days ..	CH_4 = 42·5	H = 50·3	N = 7·2
At end of fourteen days .	CH_4 = 42·4	H = 50·1	N = 7·5

It will thus be seen that the explanation suggested is the correct one. (That the residual gas was N was confirmed by (*a*) sparking with O over KOH solution, (*b*) spectroscopic investigation).

At first the presence of H in the evolved gases was inexplicable, but when the large amounts of nitride were noticed the explanation was evident. The nitride is slowly decomposed by the water producing NH_3, viz., $AlN + 3H_2O = Al(OH)_3 + NH_3$. This NH_3 in the presence of water is acted upon by the finely divided Al, similarly to the action of NaOH in Al, with the evolution of H. (About 6 grains of purified Al was placed in distilled water in the generating flask, &c., and at the end of two months not more than 1 cc. of gas had been evolved—this probably came from traces of Fe). To test this hypothesis some of the purified Al powder was placed in the gas-generating apparatus and treated with NH_4OH solution; gas was slowly evolved, and in twelve hours over 200 cc. had been collected, which proved to be nearly pure H (about 2 per cent of N was present from the same cause as before).

Analyses of Gas.

The following analysis is typical of the method used throughout when using Hempel's apparatus:—

Volume of gas taken = 100 cc.
Volume after passing into KOH pipette = 100·0 cc. CO_2 = 0·0 cc.
Volume after passing into P pipette = 100·0 cc. O = 0·0 cc.
Volume after passing into Br pipette and then into KOH pipette = 100·0 cc. Unsaturated hydrocarbon = 0·0 cc.
Volume after passing into acid Cu_2 and Cl_2 pipette = 100·0 cc. CO = 0·0 cc.
Gas passed into P pipette and a sample of it taken for explosion:
Sample taken = 8·3 cc.
Volume sample and air = 99·8 cc.
Volume of air = 91·5 cc.
Volume after explosion = 85·0 cc.
Diminution in volume = 14·8 cc.
Volume after passing into KOH = 78·5 cc.
Volume of CO_2 = 6·5 cc.
Volume after passing into P = 73·8 cc.
Volume of O left = 4·7 cc.
Volume of CH_4 = volume of CO_2 = 6·5 cc.
Diminution due to CH_4 = 2 × 6·5 = 13·0 cc.
Hence volume of H = $\frac{2}{3}$ (14·8 − 13·0) = $\frac{2}{3}$ × 1·8 = 1·2 cc.
Hence volume of N = 8·3 − (6·5 + 1·2) = 0·6 cc.
Actual volume of O taken = $\frac{1}{5}$ × 91·5 = 18·3 cc. (approximate).
Volume of O used = (2 × 6·5) (+ $\frac{1}{2}$ × 1·2) = 13 × 0·6 = 13·6 cc.
Hence volume of O should = 4·9 cc.
Actual volume found = 4·7 cc.
Composition of gas = 78·3 per cent CH_4, 14·4 per cent H, 7·3 per cent N.
Other samples gave:—
1. Analysed twelve hours after commencement, 78·6 per cent CH_4, 19·1 per cent H, 2·3 per cent N.
2. Analysed three weeks after commencement, 75·0 per cent CH_4, 18·1 per cent H, 6·9 per cent N.

(To be continued).

Royal Institution.—On Tuesday next, May 12, at 3 o'clock, Professor F. T. Trouton begins a course of two lectures at the Royal Institution on (1) "Why Light is believed to be a Vibration," (2) "What it is which Vibrates"; and on Saturday, May 16, Mr. Laurence Binyon commences a course of two lectures on "Japanese Prints." The Friday Evening Discourse on May 15 will be delivered by Dr. H. T. Bulstrode on "The Past and Future of Tuberculosis"; and on May 22, by Professor Dr. J. C. Kapteyn, on "Recent Researches in the Structure of the Universe."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 26th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

DR. A. MCKENZIE and Dr. G. T. Morgan were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT announced that communications from Prof. W. J. Pope, Mr. John Allen, and Prof. Adrian J. Brown had been received, stating their unwillingness to accept nomination as Vice-President and as Ordinary Members of Council respectively.

The President presented the Report of the Council, on the progress of the Society during the past twelve months, and the Treasurer gave a statement as to the Society's income and expenditure during the year 1907.

The adoption of the Report of the Council, together with the Balance Sheet and statements of Accounts for the year ended December 31, 1907, was proposed by Prof. A. LIVERSIDGE, seconded by Prof. E. DIVERS, and carried unanimously.

A vote of thanks to the Auditors, which was proposed by Dr. ALEXANDER SCOTT, seconded by Mr. OTTO HEHNER, was acknowledged by Dr. H. FORSTER MORLEY.

Report of the Council.

As in recent years, the Council have the satisfaction of stating that the prosperity of the Society continues, both the number of papers read and the number of Fellows on the list showing a considerable increase.

On December 31st, 1906, the number of Fellows was 2860. During 1907, 137 Fellows were elected, and 5 reinstated, making a gross total of 3002. The Society has lost 30 Fellows by death; 30 have resigned; 1 election and 1 reinstatement have become void; 1 newly-elected Fellow has withdrawn, and the names of 43 Fellows have been removed from the list for non-payment of Annual Subscriptions.

The total number of Fellows, therefore, at December 31st, 1907, was 2896, showing an increase of 36 over the number for the previous year.

The names of the deceased Fellows, with the dates of their election, are:—A. C. Aitkin (1901), T. Andrews (1870), P. T. Austen (1877), A. Bottle (1873), W. Bowen (1903), E. Chapman (1868), E. D. Chester (1882), J. Clark (1876), George Davey (1893), A. Dupré (1860), J. Gale (1866), Sir D. Gamble, Bart. (1851), S. Hall (1876), L. F. V. Harcourt (1863), B. J. Harrington (1897), J. Ince (1867), F. Keeling (1883), C. O'Sullivan (1876), F. J. M. Page (1871), A. C. Palmer (1906), S. Parfitt (1906), Sir W. H. Perkin (1856), H. D. Perkins (1905), B. C. Polkinghorne (1899), W. Pritchard (1870), R. R. Swann (1905), J. F. Walker (1865), R. Warington (1863), H. A. Wetzel (1883), H. E. Wright (1900).

The number of those Fellows who were elected prior to 1860 has been still further diminished by the death of Sir David Gamble, Bart., who was elected on March 17th, 1851, and Sir William H. Perkin, who was elected on December 15th, 1856.

The number of Honorary and Foreign Members at the close of 1906 was 33. No elections have taken place during 1907, but the Society has to mourn the loss of Prof. Marcellin Berthelot, elected March 1st 1860, deceased March 18th; Prof. Dr. Dmitri Ivanovitsch Mendeleeff, elected February 1st, 1883, deceased February 2nd; Prof. Dr. Nicolai Menschutkin, elected January 20th, 1898, deceased February 5th; and Prof. Henri Moissan, elected January 20th, 1898, deceased February 20th. The number of Honorary and Foreign Members, therefore, at December 31st, 1907, was 29.

During the year 1907, 268 scientific communications have been made to the Society, 203 of which have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of *Transactions* for 1907 contains 2089 pages, of which 2021 are occupied by 205 memoirs, the remaining 68 pages being devoted to the Faraday Lecture, the Obituary Notices, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 186 memoirs, which occupy 1890 pages.

The *Journal* for 1907 contains also 4686 abstracts of papers published mainly in foreign journals, which extend to 2100 pages, whilst the abstracts for 1906 numbered 4541, and occupied 1912 pages.

The abstracts for 1907 may be classified as follows:—

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	1104	1831
PART II.		
General and Physical Chemistry ..		725
Inorganic Chemistry		622
Mineralogical Chemistry		117
Physiological Chemistry		545
Chemistry of Vegetable Physiology and Agriculture		244
Analytical Chemistry		602
	996	2855
Total in Parts I. and II. ..	2100	4686

In the hope of diminishing the confusion which had arisen in the nomenclature of the proteins, consideration of the subject was undertaken by the Publication Committee, in conjunction with representatives of the Physiological Society; the Joint Committee concluded their deliberations early in 1907, and their recommendations appear in the *Proceedings* for that year.

Recognising the importance, from a public standpoint, of the Presidential Address delivered by Prof. Meldola, F.R.S., in March, 1907, the Council have felt it desirable that his remarks on that occasion should attract the attention of a wider circle than is reached by the Society's *Transactions*; accordingly 5000 copies of the Address have been circulated among the members of various public bodies, including both Houses of Parliament, and the Council hope that this unusual step will have the effect of bringing the subject of Prof. Meldola's discourse into suitable prominence.

During the past year, the Society has had to mourn the loss of Sir William Perkin, which took place on July 14th, 1907, just twelve months after the International Celebration which marked the Fiftieth Anniversary of the Foundation of the Coal-tar Colour Industry. This is not the place in which to deal with the splendid achievements of the late Past-President, or the qualities which endeared him to the Fellows, who will remember with melchanoly satisfaction that he lived to participate in the widely-supported public appreciation of the preceding year, and in the subsequent commemoration celebrated in the United States. The marble bust of Sir William Perkin has now been placed in the meeting room, and a large photograph of the portrait painted by Mr. A. S. Cope, A.R.A., is also the property of the Society, having been presented by Sir William a few months before his death.

In view of the losses incurred during recent years through the death of several Honorary and Foreign Members, thereby reducing the number of survivors to 29, the Council recommended for election the following distinguished chemists:—Prof. A. E. J. Gautier, Prof. Albin Haller, Prof. J. W. Hittorf, Prof. J. A. Le Bel, Prof. H. L. Le Chatelier, Prof. T. W. Richards, and Prof. Otto

Wallach. This recommendation was duly ratified by the Society at the meeting on Thursday, February 6th, 1908.

An agreeable feature of the past year has been the Jubilee Celebration of the Société Chimique de France, and on that occasion an Address of congratulation was presented by Sir William Ramsay, F.R.S., on behalf of the Society, which was represented also by Prof. H. E. Armstrong, F.R.S., and Dr. Horace Brown, F.R.S.; a commemorative medal has been received from the French institution and added to the Society's collection. A somewhat similar event took place in September, when the Geological Society celebrated their Centenary, the President being again delegated to offer the felicitations of the Chemical Society. A copy of the recently compiled History of the Geological Society has been since presented to the Library.

Prof. J. Bretland Farmer, F.R.S., accepted the invitation of the Council to deliver a discourse before the Society, and his lecture, entitled, "Some Borderline Problems in Botany," was greatly appreciated by the Fellows.

Late in 1906, Geheimrat Prof. Emil Fischer, F.R.S., an Honorary and Foreign Member since 1892, was nominated Faraday Lecturer, and gave his Address, in German, on October 18th, 1907, in the theatre of the Royal Institution, kindly lent by the managers for the occasion; at the termination of the lecture, entitled "Synthetical Chemistry in its Relation to Biology," the Faraday Medal was presented to Prof. Fischer by the President.

In common with all corporate bodies engaged in scientific pursuits, the Chemical Society has keenly deplored the death of Lord Kelvin, who, although not on the roll of Fellows, has been the guest of the Society on many occasions. At the request of the Council, the President transmitted to Lady Kelvin a resolution of sympathy, and the Society was represented at the funeral ceremony in Westminster Abbey.

Prof. W. Wislicenus, of Tübingen, having initated a memorial to the late Prof. Lothar Meyer, the Treasurer was authorised to contribute from the funds of the Society, and the Council venture to hope that the memorial may be supported by individual Fellows.

The ventilation of the meeting room and council chamber has occupied the attention of the House Committee, who have recommended the installation of electric fans; since their Report was received and adopted by the Council, a Fellow who desires to remain anonymous, has most kindly undertaken to defray the cost of this highly necessary improvement.

In addition to an engraving of Daniell and Faraday, for which the Society is indebted to Prof. Meldola, F.R.S., numerous articles of historical interest and value have come into the possession of the Society in virtue of a bequest by the late Prof. Warington.

The number of books borrowed from the Library during 1907 was 1317, as against 1126 in the previous year. The additions to the Library comprise 138 books, of which 79 were presented, 401 volumes of periodicals (representing 243 journals), and 40 pamphlets, as against 121 books, 385 volumes of periodicals (representing 229 journals), and 32 pamphlets last year.

The experiment of opening the Library during Thursday evenings other than those on which the Society meets has been discontinued, so few Fellows having used the Library on those occasions.

In May, 1907, a special leaflet was issued with the *Journal* indicating the parts required to complete certain sets of periodicals in the Library, in the hope that Fellows happening to possess copies of the desired numbers would present them to the Society. In response to that circular, donations were received from numerous Fellows, and this favourable response has encouraged the Council to hope that further contributions of a similar character may be added to the Library.

As was announced at the last Annual Meeting, the Society received from the Worshipful Company of Goldsmiths a munificent donation of £1000 for the Research Fund. This fund has been still further increased by the handsome sum of £2704 3s. 8d., which was handed over to the Treasurer in July by the Perkin Memorial Fund Committee. These two sums, as now invested, have augmented the annual income of the Research Fund by £126 5s., and will enable the Research Fund Commitee in the present year to recommend the Council to make grants to the amount of £340 to £350. Of this sum, about £34 is more or less especially to be devoted to the encouragement of research in inorganic and metallurgical chemistry, and about £92 for investigations relating to problems connected with the coal-tar and allied industries.

In spite of several items of a somewhat exceptional nature, the Treasurer is glad to be able to report that he has a substantial surplus to carry forward as the result of the year's finance. The income of the Society from all sources for 1907 is £7260 4s. 10d. as against £7121 8s. 11d. in 1906, and the expenditure is £6750 8s. 5d., instead of £6379 15s. 9d., so that, whilst our expenditure has increased by £370 12s. 8d., our income has only grown by £138 15s. 11d. This still leaves a surplus of £509 16s. 5d. on the year's working.

The increase in income may be put down almost entirely to the increase in Annual Subscriptions, for the increase of £100 in the Life Compositions is more than neutralised by the drop of £104 in Admission Fees.

The *Journal* and *Annual Reports* have cost respectively £182 19s. 8d. and £24 8s. 5d. more than last year, but a saving of £23 18s. has been effected on the *Proceedings* and the List of Fellows. The reprinting of certain numbers of the *Proceedings* which were "out of print" has put it within the power of Fellows to complete their sets of *Proceedings*, and the increase in the sale has already more than repaid the cost of the reprints.

A certain amount of redecoration beyond the annual cleaning, the balance of the Dinner account, and the printing and distribution of 5000 copies of last year's Presidential Address are the chief items which have raised the "administrative expenses" so much above those of last year.

In July the Treasurer was able to purchase £1200 North British Railway 3 per cent Debenture Stock; a glance at the balance-sheet will show that the value of the invested capital of the Society was on December 31st, 1907, £18.362 9s. 9d., and that of the Research Fund £10,016 11s. 10d.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Dr. Frank Clowes, seconded by Dr. W. E. Adeney, and unanimously adopted. Prof. J. Emerson Reynolds responded.

The President then delivered his Address entitled "The Electron as an Element."

Prof. Raphael Meldola proposed a vote of thanks to the President for his Address and for his services in the Chair during the past year, coupled with the request that he would allow the Address to be printed in the *Transactions* of the Society. Dr. Rudolph Messel seconded the motion, which was put to the Meeting and carried with acclamation.

The Report of the Scrutators was presented to the President, who declared the following to have been elected as Officers and Council for the ensuing year:—

President—Sir William Ramsay, K.C.B., F.R.S.

Vice-Presidents who have filled the office of President—H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; A. G. Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents—J. Campbell Brown, D.Sc., LL.D., J. J. Dobbie, M.A., D.Sc., F.R.S.; F. Stanley Kipping, D.Sc., Ph.D., F.R.S.; Rudolph Messel, Ph.D.; Sir

Alexander Pedler, C.I.E., F.R.S.; W. H. Perkin, Ph.D., F.R.S.

Treasurer—Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries—M. O. Forster, D.Sc., Ph.D., F.R.S.; A.W. Crossley, D.Sc., Ph.D.

Foreign Secretary—Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council—Julian L. Baker; George T. Beilby, F.R.S.; Alfred C. Chapman; Julius B. Cohen, Ph.D., B.Sc.; J. T. Hewitt, M.A., D.Sc., Ph.D.; W. R. E. Hodgkinson, Ph.D.; H. A. D. Jowett, D.Sc.; H. R. Le Sueur, D.Sc.; F. E. Matthews, Ph.D.; A. G. Perkin, F.R.S.; W. J. Sell, Sc.D., F.R.S.; John Wade, D.Sc.

PHYSICAL SOCIETY.

Ordinary Meeting, April 10th, 1908.

Dr. Charles Chree, F.R.S., President, in the Chair.

Miss E. N. Ladler and Mr. S. D. Chalmers were elected Fellows of the Society.

A paper by Prof. W. H. Bragg and Mr. Madsen, entitled "*An Experimental Investigation of the Nature of γ-Rays*," was read by the Secretary. (See Chemical News, xcvii., p. 162).

A paper by Miss D. D. Butcher, entitled "*Experiments on Artificial Fulgurites*," was read by Mr. S. Skinner.

Fulgurites are tubes formed by lightning striking sand or rock and fusing it. The fact that the tubes formed are of two sorts—strong, rocky, thick-walled tubes, and smooth cylindrical tubes with glassy walls—was pointed out by Dr. Fiedler in 1817, and he suggested the possibility that one sort was formed by positive and the other by negative electricity. This idea seemed to be supported by the fact that the cross-section of a thick tube shows a radial structure bearing a marked resemblance to the Lichtenberg figures made by a spark from a positively charged conductor. It was with the view of testing this hypothesis that attempts were made to form fulgurites artificially. The first part of the paper deals with natural fulgurites, and the second with the production of artificial fulgurites. The results of the experiments may be summarised as follows:—

1. The tubes are formed by fusion of the powder which surrounds the column of air in which the spark passes. The length and thickness of the tube depend on the energy of the spark and also on the character of the spark, *i.e.*, whether it is unidirectional or oscillatory. This latter is shown by the fact that the same quantity of energy stored in the Leyden jars does not form a tube when the discharge is abrupt and oscillatory, but forms one if the discharge is rendered less oscillatory by the intervention of a wet string resistance, although a large portion of the energy in the latter arrangement is absorbed in overcoming the resistance of the string.

2. There is no appreciable difference in the two ends of a tube provided that the two electrodes are alike. When one electrode is a point and the other a flat plate, any branching that may occur will be towards the plate whichever electrode is made positive.

In nature, the flat plate would be represented by the moist lower strata of the soil. Therefore we cannot say from the character of the tube whether the lightning discharge was from a positive or negative cloud.

3. The difference between thick and thin tubes is due probably to a difference in the sharpness of the flash and the resulting explosive effect. When the explosive effect is great and the quantity of material melted is small, the result will be a large-bored thin-walled tube. Whether this remains circular or becomes pressed together and distorted, depends merely on whether the fused matter has time to cool before the outward pressure of the blowing has been overcome by the inward pressure on the surrounding sand or not. In Nature, the damp sand or soil probably acts as the damp string in these experiments, and consequently causes many lightning discharges to be unidirectional. In the experimental tubes the outward pressure was so great and the quantity of fused material so small, that the walls were broken through and left as a mere network.

Mr. Alexander Russell congratulated the authoress on her interesting paper. Although he had never found a fulgurite he had noticed several phenomena which seemed connected with their formation. Several years ago during a thunder-shower on the sea, he noticed several flashes striking its surface. Where they struck puffs of steam apparently shot upwards. The appearance was not unlike the splash made by a gannet when diving. It was probably caused by the evaporation of the water in the path of the discharge. Now, a striking peculiarity about fulgurites is that they have a hollow core. The material originally filling it has probably been vapourised. It is therefore highly probable that when a lightning flash strikes sand, a puff of smoke will be shot out from the end of the fulgurite. When testing insulating materials with high voltages, a puff of smoke from the perforation is often the first indication of the breakdown. Electricians frequently notice that when a fuse consisting of a thin wire embedded in sand "blows," a tube of siliceous material is formed. When there is considerable power involved, the tube is raised to a very high temperature and, like the glower of a Nernst lamp, it allows quite a considerable current to pass through it. It would be of interest if the authoress would investigate the conducting power of fulgurites when heated. The difference between thick-walled and thin-walled fulgurites appears to be only one of degree. If we assume that the energy to be got rid of is the same in the two cases, then, when a lightning discharge has a long path to traverse before reaching a good conducting stratum, the fulgurite would in general be thin-walled, but when the path is short it would be thick-walled. It is obvious that a very appreciable amount of energy must have been expended in making some of the fulgurites, parts of which were exhibited.

Dr. C. H. Lees asked if fulgurites, when found, were hollow or filled with sand, &c.

The Chairman asked if there were any changes in the magnetic properties of a material when it was formed into a fulgurite.

Mr. Skinner expressed his interest in the remarks of Mr. Russell on the electrical conductivity of fulgurites, and pointed out that if the sand contained salt the fulgurites would probably be conducting. The suggestion that there might be changes in the magnetic properties was interesting and might be tested by experiment.

A paper entitled "*Short Spark Phenomena*" was read by Mr. W. Duddell.

The paper deals with two effects which the author has observed in connection with some measurements of the current in the secondary circuit of an induction coil. The apparatus in use consisted of a twelve-inch Newton induction-coil which was supplied from the 200-volt direct-current mains. A large resistance was placed in series with the primary of the coil to limit the current, and the current was interrupted by means of a mercury-jet interrupter. The secondary circuit contained a galvanometer to measure the mean current, and a thermo-ammeter to measure the root mean squared current. When there was no spark-gap in the secondary circuit and the coil was in action, the mean current, as read by the galvanometer, was zero, and the root mean squared current about 3·8 milliampères. If, now, a microscopic spark-gap, say, between two aluminium points, was introduced into the secondary circuit, two curious effects took place. Firstly, the R.M.S. current enormously increased in value, and secondly, a very large deflection was produced on the galvanometer in the direction corresponding to that due to making the primary circuit. The introduction of a spark-

gap one-tenth mm. long caused the R.M.S. current to rise to 38·5 milliampères, and this continued to increase with increasing length of spark-gap until it reached a maximum with a gap about 1·4 mm. The author thinks that this effect is due to very high frequency oscillations set up in the wires connected to the secondary circuit of the coil when a spark-gap is introduced. He has observed the effect with brass, iron, zinc, and aluminium electrodes, but the latter metal is the best to use. The large deflection in the negative direction observed on the galvanometer was investigated by recording the wave-forms of the P.D. and the current by means of an oscillograph. The author showed a series of curves which he had obtained and gave an explanation of the phenomenon. The effects were shown experimentally at the meeting.

Mr. ALEXANDER RUSSELL thanked Mr. Duddell for his valuable paper and for the exceedingly interesting and very successful demonstration of short-spark phenomena. The author's complete analysis of the phenomena he has discovered would be a great help in elucidating the difficult theory of the action of the induction-coil and would throw light on many still unexplained effects. He believed that the change of sign of the direct current component in the secondary circuit of an induction-coil was first discovered by Mr. Duddell, and the Physical Society was to be congratulated on having been the first Society to which this phenomenon was clearly described and demonstrated. He considered that the rise in the value of the effective current when the air-gap was widened was a resonance phenomenon. The capacity *between the electrodes* was in series with the inductance of the secondary, and hence, as the author pointed out, Kelvin oscillatory discharges were continually taking place. The shape of the curve showing the connection between the effective current and the distance between the electrodes was strong evidence in support of this view. The explanation of the direct current component when the electrodes are at considerable distances apart, may be made by remembering that the wave pulses of E.M.F. round the secondary at "make" and "break" are of very different shapes although their integral values are the same. The maximum value of the induced E.M.F. at break is much greater and the consequent rush of electricity is more "impulsive" than at make. Hence, when the electrodes are sufficiently far apart the air-gap is only broken down by the break E.M.F., and so we get a unidirectional pulsating current of triangular shape. When the electrodes are closer together we get an alternating current, the shape of the positive and negative waves being quite different owing to the differently shaped waves of E.M.F. at make and break. When they are very close together, the author's oscillograms show that we get a pulsating unidirectional current in the direction due to the "make" E.M.F. The reason for this strange phenomenon is by no means obvious.

Mr. S. SKINNER expressed his interest in the paper, and referred to the experiments on the electrolysis of steam carried out by J. J. Thomson by a modification of Perrot's method. He found that with short sparks the hydrogen appeared at the positive electrode instead of at the negative as in ordinary electrolysis. Perhaps this phenomenon was due to the same causes as the effects shown by the author.

Dr. R. S. WILLOWS asked if the maximum current obtained was connected in any way with the minimum sparkling voltage.

Prof. CASSIE pointed out that the minimum sparking voltage occurred at distances very much less than those used in Mr. Duddell's experiments.

Mr. C. C. PATTERSON asked if the author had tried experiments with spark-gaps of different capacities.

Mr. A. CAMPBELL asked if it was possible that the rectifying action of the spark-gap might be similar to that of an ordinary aluminium electrolytic rectifier.

Mr. DUDDELL said he did not think the effect was in any way connected with the minimum sparking voltage. He had tried varying the materials of the electrodes and using electrodes of various capacities, and the effect was the same.

ROYAL INSTITUTION.

Annual Meeting, May 1st, 1908.

Sir JAMES CRICHTON-BROWNE, Treasurer and Vice-President, in the Chair.

THE Annual Report of the Committee of Visitors for the year 1907, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the Report on the Davy-Faraday Research Laboratory of the Royal Institution, which accompanied it, was also read.

Forty-one new Members were elected in 1907. Sixty-three Lectures and nineteen evening Discourses were delivered in 1907. The books and pamphlets presented amounted to about 203 volumes, making with 693 volumes (including periodicals bound) purchased by the Managers, a total of 896 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committee of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year :—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Sir William Crookes.

Managers—Sir Thomas Barlow, Bart., Sir George Darwin, The Rt. Hon. The Earl of Halsbury, W. A. B. Burdett-Coutts, Charles Hawksley, Dr. Donald William Charles Hood, Dr. Rudolph Messel, Henry Francis Makins, George Matthey, Dr. Ludwig Mond, The Rt. Hon. Sir John Fletcher Moulton, Alexander Siemens, The Rt. Hon. Sir James Stirling, The Rt. Hon. The Earl of Rosse, and Sir William H. White.

Visitors—Arthur N. Butt, Dugald Clerk, Charles A. Ballance, John B. Broun Morison, Edward Dent, John Cameron Graham, Dr. James Dundas Grant, Charles Edward Groves, Sir Henry Harben, Major E. H. Hills, John List, Robert Mond, Francis Lys Smith, James Swinburne, and Lieut.-Colonel Sir Frederick Nathan.

CORRESPONDENCE.

THE PERIODIC LAW.

To the Editor of the Chemical News.

SIR,—I have noticed recently the difficulty experienced by more than one writer in fitting new elements into the tables which represent existing classifications. The obvious effort in every table is to conform to the Period 8, and the difficulty in doing so is well illustrated in Group VIII. of the table which is due to the genius of Mendeleeff. There does not appear to me to be any very weighty reason why the tables should be limited to eight groups, and if there is no such reason then the effort to make all elements fit into eight neatly ruled-off compartments seems to be misplaced.

It is not, however, my object to dwell on well-known difficulties, but to point out a direction for work that may lead round them.

1. Inorganic evolution, as developed, for instance, by Sir Norman Lockyer in his well-known work of that name, will, I think, be admitted as a possibility by most people. If it is so admitted, we must consider the heavier atoms as being built up either of the lighter, or of groups of corpuscles still more elemen-

tary than the lightest atoms known. In either case there should then be a simple numerical relation extending throughout the whole atomic series. We should then expect to be able to tabulate the elements in accordance with the form of the series which shows this relation.

2. Periodicity is unquestionable, and the reason of it should be traceable to the recurrence of particular intra-atomic grouping, or of the same group which, whilst preserving its own individuality, might be attached to a larger group. In either case, each recurrence should be a well-marked feature in the series, and should be plainly shown in the scheme of tabulation.
3. Considered as a series, perhaps the most remarkable correlative attribute of the elements is their specific gravity. The specific gravity atomic weight curve must be a graphic expression of the internal peculiarities which determine atomic individuality, and should therefore not be lost sight of in formulating a scheme of tabulation.

If we allow that there is any weight in arguments Nos. 1, 2, and 3, then our tabulation should primarily take the form of a definite series to satisfy No. 1. To satisfy No. 2 the numbers which represent the elements should be broken up into parts, in such a way that the recurrence of parts shall have the same periodicity as elemental properties. This is plain when we remember that in any table, no matter what its properties, an element is represented solely as a number. To satisfy No. 3 the form of the series must show a plain relation to the specific gravity curve.

If now we consider the peculiar position of the members of Group VIII. in Mendeleeff's table with respect to the vacant spaces in the zero group, and also consider the position occupied by the elements of the latter group in the specific gravity curve, I think we can form a very good idea of the general form of the atomic series.

We may write the following series as representing the general form that will satisfy requirement No. 1:—

TABLE I.

							3	4
							7	8
					11	12	15	16
	19	20	23	24	27	28	31	32
&c.	—	—	55	56	59	60	63	64
				&c.	—	—	127	128
					&c.	—	—	256

Wherein the number in the last column is severally added to itself and all previous smaller numbers to give the next step in the series. This arrangement does not, however, satisfy Nos. 2 and 3. A little analysis of the above figures will enable us to make the disposition shown in Table II., taking for the purpose of illustration the zero group as a basis. It may be mentioned in passing that the halogen group or the lithium group gives more easily defensible results, but require at the same time more explanation. To emphasise the relation I show the parts that give us a close approximation to the even-number elements, omitting the others.

It will be noticed that this arrangement outlines a definite series of numbers that closely approximate the atomic weights of the elements. The steps in the series follow exactly the undulations in the specific gravity curve, but the periodic recurrence of parts with properties is not exact, fractions are not accounted for, and there are other minor irregularities and divergences which require explanation.

If it is conceivable that the atoms are made up of definite groups, it appears to be also reasonable, and I think necessary, to suppose that free corpuscles may be attached to the atoms or sub-groups. Sir William Ramsay has pointed out to me that these must affect the weight, and

TABLE II.

Primary Parts.	Secondary Parts.																			
He 4	Be 4	C 8	O 12	Ne 16																
Ne 20	Mg 4	Si 8	S 12	Ar 16																
Ar 36	Ca 4	Sc 8	Ti 12	Cr 16	Fe 20	Ni 24	Zn 28	— 32	Ge 36	Se 40	Kr 44									
Kr 80	Sr 8	Zr 12	Mo 16	Ru 20	— 24	Ag 28	Cd 32	Vc 36	Sb 40	Te 44	Xe 48									
Xe 128	Ba 8	Ce 12	Nd 16	Sm 20	Eu 24	Gd 28	Tb 32	Er 36	— 40	Tm 44	— 48	— 52	W 56	— 60	Ir 64	Au 68	Hg 72	Tl 76	Bi 80	? 84
? 212	Rd 12		Th 20		U 28		? Act 36		&c.		&c.									

To get a close approximation to the atomic weight of any element, add its secondary part to the primary of its series.

might possibly account for fractions and other divergences from a main fundamental series, if one exists.

I will not go into this question here as it requires a lengthy analysis, and also as the introduction of a third small part will not affect the general form of tabulation which is advocated.

I think that the figures already given will show that, whilst the fitting of the elements to existing classifications may be productive of very interesting and useful results, the converse operation—fitting the classification to the elements—is likely to be quite as fruitful, and for many reasons would appear to be more logical.—I am, &c.,

W. Denham Verschoyle.

NOTICES OF BOOKS.

The Chemistry of the Diazo-cbmpounds. By John Cannell Cain, D.Sc. (Manchester and Tübingen). London: Edward Arnold. 1908.

In this book a complete account is given of our present knowledge of the diazo-compounds and their most important derivatives. In the first part the preparation and reactions of the compounds are described, the historical order of discovery being adopted, while the theory of their constitution is reserved for the later part of the book. Here, again, the order is historical, and a full discussion of the controversy between Hantzsch and Bamberger on the structure of the diazo-compounds is included. Students interested in organic chemistry will be glad to receive this particularly clear analysis of a question upon which it is difficult to decide from the study of the original papers owing to the great mass of detail with which they are necessarily encumbered. In an appendix the author suggests a new theory relating to the constitution of the diazo-compounds which he thinks may possess a quinonoid structure. This theory undoubtedly throws light upon some of the reactions of the compounds, which are difficult to explain otherwise; for example, the readiness with which the whole of the diazo-nitrogen is eliminated, whereas in all other cases singly-linked nitrogen appears to be bound firmly to the benzene nucleus. As far as can be seen from the outline no tenable objection can be advanced against the author's theory, and thus the book, both as a compilation and as an original contribution to organic chemistry, constitutes a valuable monograph.

La Psychologie Inconnue. Introduction et Contribution à l'Etude Expérimentale des Sciences Psychiques. ("Unknown Psychology. An Introduction and Contribution to the Experimental Study of Psychic Science"). By Emile Boirac. Paris: Félix Alcan. 1908.

This work contains a collection of the articles dealing with experimental psychology which the author has written for various periodicals. The papers are welded together into a continuous whole, and thus the book constitutes a general survey of the whole of this branch of science. The author divides the subject under three heads:—Hypnotic phenomena, magnetic phenomena, and psychic phenomena. He endeavours to examine into the evidence for the various experiences which have been reported, and to refute the main arguments of his adversaries. The views of the schools of Paris and Nancy are specially discussed. The anthor states his opinions very clearly, and attacks the subject in a thoroughly scientific spirit, proceeding from the investigation of the simplest phenomena to the study of those which are more complicated, and thus laying a firm foundation for the development of the science upon well attested lines. Magnetism is specially considered, the author believing that it is accountable for definite and characteristic phenomena.

Quarterly Journal of the Institute of Commercial Research in the Tropics. Vol. III., No. 6. Liverpool: The Offices of the Institute. London: Williams and Norgate. 1908.

It is impossible to over-estimate the value of the work which is being done by the Liverpool Institute of Commercial Research in the Tropics, and each number of the Quarterly Reports issued bears witness to the zeal and activity of the scientific staff. The most important papers in this volume are those by D. Spence, Ph.D., on the distribution of the protein in Para-rubber and on the analysis of the latex from *Ficus Vogelii*. In addition, the possibilities of the oil palm in cultivation is discussed by Dr. Drabble in an article in which practical suggestions are made relating to the most suitable varieties for planting, and the use of white mangrove for tanning is another subject which is of considerable commercial importance. Every one of the seventeen papers which are contained in the journal is full of valuable material for all who are interested in the development of the tropics, and a most encouraging account is given of the Liverpool Tropical Products Exhibition which was held last autumn.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 10, March 9, 1908.

Neutral Carbonates of Alkalis and Alkaline Earths.—M. de Forcrand.—The author has investigated the decomposition by heat of the neutral carbonates of the alkaline earths and alkalis, and has compared the results with the corresponding thermo-chemical data. As a general result he has found that the temperature of dissociation of the carbonates of calcium, lithium, strontium, and barium is always lower than that deduced from thermo-chemical data, the difference increasing from calcium to barium. Probably the heat of formation of calcium carbonate, for instance, is lower at a high than at the ordinary temperature.

Combustion without a Flame, and Ignition of Gases at the End of a Strip of Metal.—Jean Meunier.—The author has studied the combustion of gases in a spirit lamp in which the flame is spread by a metallic disc which serves to mix the spirit and air, and a rod of metal runs up the central cylinder. When the perforated disc gets red-hot the flame dies down. The flameless combustion of gases and vapours is localised at the surface of the disc, and the combustible gases are collected round the disc. When a lighted match is brought near the rod of metal the flame at its extremity is attracted by the flame of the match. This seems to show that gases have a certain cohesion, and will rise along a rod of metal without mixing with neighbouring gases, as if they were protected by a solid envelope.

MEETINGS FOR THE WEEK.

Tuesday, 12th.—Royal Institution, 3. "Why Light is believed to be a Vibration," by Prof. F. T. Trouton, F.R.S., &c.

Wednesday, 13th.—Royal Society of Arts, 8. "The Underground Water Supplies of the Thames Basin," by Clayton Beadle.

Thursday, 14th.—Royal Institution, 3. (The Tyndall Lectures). "Mendelian Heredity," by William Bateson, F.R.S., &c.

Friday, 15th.—Royal Institution, 9. "The Past and Future of Tuberculosis," by H. T. Bulstrode, M.D., D.P.H.

Saturday, 16th.—Royal Institution, 3. "Japanese Prints," by Laurence Binyon.

THE CHEMICAL NEWS.

VOL. XCVII., No. 2529.

ON THE ATOMIC WEIGHT OF RADIUM.*

By T. E. THORPE, C.B., LL.D., F.R.S.

ALTHOUGH there has been a considerable amount of discussion, based upon spectroscopic considerations and on its supposed mode of genesis, respecting the place of radium in the system of the elements, and inferentially, therefore, concerning its atomic weight, we are indebted for the only direct experimental determinations of this value hitherto made known to the discoverer of the element, Mdme. Curie. Her first observations, published in 1902, were made on about 90 mgrms. of the chloride, and furnished the value 225 as the mean of three fairly concordant experiments (*Ann. de Chim. et de Phys.*, 1903, xxx.).

In the autumn of last year Mdme. Curie communicated to the French Academy the results of a second series of estimations. These were made upon much larger quantities of the carefully purified chloride (about 4 decigrms.), and afforded the value 226·2 as the mean of three closely concordant determinations (Ag = 107·8, Cl = 35·4) (*Comptes Rendus*, 1907, cxlv., 422; "La Radium," October, 1907).

In 1906, at the instance of Sir William Huggins, then President of the Society, and by the aid of the kind interest shown by H.R.H. the Prince of Wales, the Austrian Government placed about 500 kilogrms. of pitchblende residues from the mine at Joachimsthal at the disposal of the Royal Society. These residues were sent to be worked up by M. Armet de Lisle at his factory at Nogent-sur-Marne, by the method employed by him in the case of the material which served M. and Mdme. Curie for their researches. The funds for both these purposes were defrayed from a grant made by the Goldsmiths' Company to the Royal Society in 1904 for the purpose of the investigation of radium.

The residues, as received by M. Armet de Lisle, were stated to have a radio-activity of about two and a-half times that of uranium.

The process of extraction employed by M. Armet de Lisle resulted in the production of about 413 grms. of practically anhydrous barium chloride, containing radium chloride suffic ent to give the salt a radio-activity 560 times that of uranium.

This salt was received by the Royal Society in the autumn of 1906, and was handed to me in January, 1907, with the request that I would extract the radium chloride from it, and undertake, if possible, a re-determination of the atomic weight of the element. This in view of the discussion, already referred to, which was then taking place, as to the relation of radium to certain other elements, seemed at the time the most profitable use to which the radium salt, when extracted, could be put. When received by me the barium-radium chloride was distinctly cream-coloured, and the bottle in which it was contained was coloured violet.

The method of extraction was substantially the same as that originally adopted by Mdme. Curie, and described in her thesis (*loc. cit.*), namely, systematic fractional crystallation, first from water and then from increasingly strong hydrochloric acid, until finally the acid used was the strongest that could be obtained by distillation. All the solvents employed were carefully purified, the acid being distilled in a platinum retort, and preserved in a platinum bottle. The crystallisations were made first in porcelain, subsequently in Jena glass, and finally, as the radio-active matter became more and more concentrated, in vessels of fused rock-crystal. Every precaution was taken to guard against loss and accidents, and to ensure the recovery of the radium should such occur. It is satisfactory to be able to state that the whole scheme of extraction, involving some 9400 re-crystallisations, was carried through without a mishap.

I have to thank Mdme. Curie for her courtesy in affording me information concerning certain details of her method of isolating the radium salt. At the outset of our exchange of letters she informed me, of what at the time I was unaware, that she was then actually engaged on the same problem, and she has since, as already stated, published the results of her determinations. She was good enough, however, to express the hope that I would continue the work which I had been requested to undertake, in view of the desirability of gaining all possible knowledge as to the true atomic weight of the element.

During the autumn of 1907, whilst still engaged in the isolation of the radium chloride from the material furnished by M. Armet de Lisle, I received a further small supply of radium from the Royal Society. It was bought in Cambridge, and was of German origin, and had been purchased through the instrumentality of Prof. Liveing. It purported to be radium bromide, but on removing it from the metallic capsule in which it had been stored since 1903, it was found to be wholly insoluble in water. On treatment with pure dilute hydrobromic acid it readily passed into solution. The salt obtained by evaporation was sent to Prof. Rutherford, who had kindly undertaken to make any measurements of radio-activity which I needed. He estimated the amount of radium present as equivalent to 33 mgrms. of radium bromide.

This salt was eventually converted into chloride, and was purified by repeated crystallisation from strong hydrochloric acid.

Traces of lead cling persistently to the radium chloride thus separated by means of hydrochloric acid. Mdme. Curie was so kind as to draw my special attention to this fact, and accordingly care was taken to remove this metal. When practically the whole of the radio-active matter had been concentrated into a few grms. of the material, this was dissolved in water acidulated with hydrochloric acid, and treated with sulphuretted hydrogen out of contact with air. A small precipitate of lead sulphide was formed. The liquid was further treated with sulphuretted hydrogen, the lead sulphide removed by filtration, the filtrate evaporated to dryness, the residue treated with strong hydrochloric acid, and the process of fractionation resumed. That the precipitate was lead sulphide was confirmed by its conversion into the yellow iodide.

Determination of Atomic Weight.

This was effected by ascertaining the amount of silver chloride yielded by a weighed quantity of the anhydrous radium chloride—the principle of the method already employed by Mdme. Curie.

Since it was very improbable that the amount of the radium salt at my disposal would amount to as much as a decigrm., it was absolutely necessary so to arrange the process of carrying out the estimations as to minimise, to the greatest possible extent, the errors due to manipulation. Accordingly a method was devised whereby the whole of the operations of drying and weighing the radium chloride, precipitating, washing, drying, and weighing the silver chloride, might be performed in one and the same vessel, thus obviating the necessity of transferring the silver salt, and of separating it by any of the ordinary processes of filtration.

The vessel in which these operations were made consisted of a thin glass tube with a conical base furnished with a hollow well-ground stopper. It had a capacity of about 15 cc., and was as light as was consistent with the requisite strength, and could be suspended from the balance-arm by fine platinum wire. In all the weighings a precisely similar bottle of almost identical weight and

* Bakerian Lecture for 1907. Delivered before the Royal Society, June 20, 1907.

capacity, suspended in like manner, was employed as a tare. The weighings were made on a very sensitive assay balance, with 4-inch arms, carrying a maximum load of 12 grms., and provided with light stirrup pans. I am indebted to Mr. Oertling for the loan of it. It was a beautifully finished instrument of great delicacy, and remarkably constant in its indications (Fig. 1).

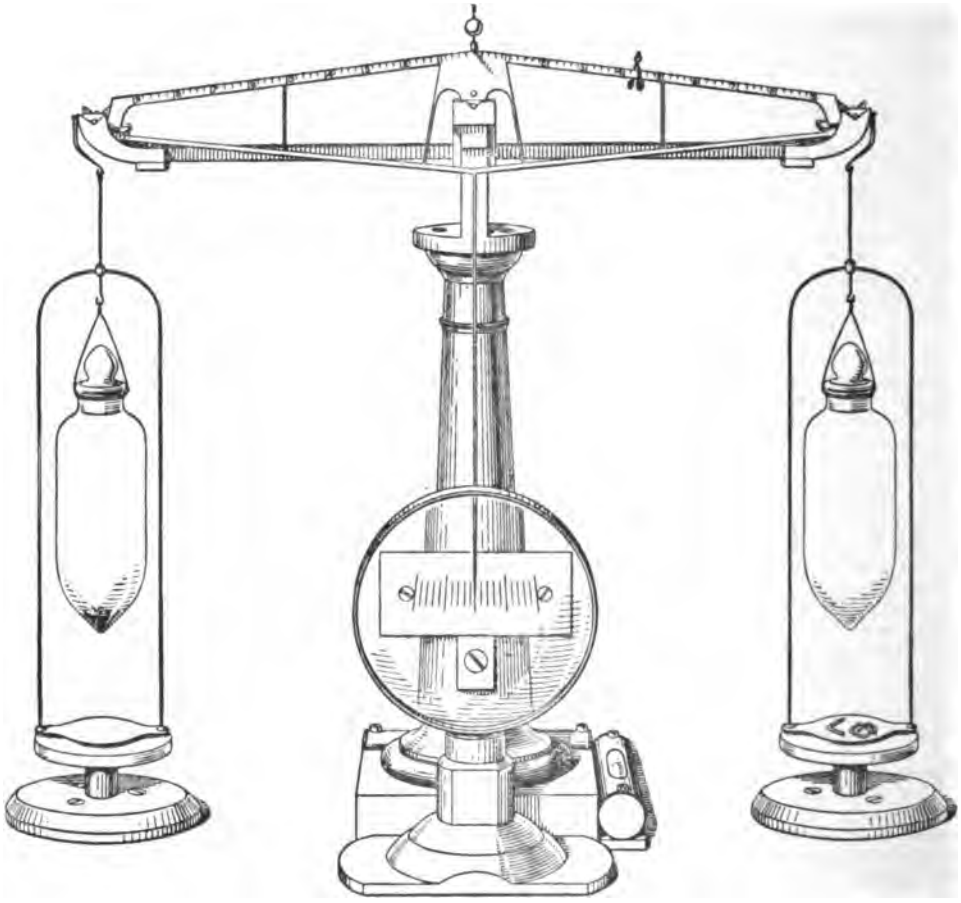


FIG. 1.

The weights were also of Oertling's make, and were compared before use with a standard set belonging to the Government Laboratory.

A room was specially set apart and arranged for the determinative work. It was a small apartment on one of the upper floors of the Government Laboratory, and had a wooden block floor arranged "herring-bone" fashion. The walls of the building were subject to a very slight tremor, due to a small steam-engine in the basement. The balance table therefore was not bolted to the walls, as is the usual practice, but was placed directly on the floor, which, by reason of its mode of construction, was less susceptible to tremor than the walls. The legs of the table stood on packets of filter-paper, as did also the levelling screws of the balance case. Under these conditions the balance was found to be quite free from tremor, and the levels remained absolutely constant throughout the entire course of the work.

The weighings were made by the method of vibrations, the zero-point being determined before and after each determination.

The course of the operations was as follows:—The small glass vessel and its tare were first heated to about 150° in an air-bath for an hour, and allowed to stand over-night in a desiccator containing phosphoric oxide. They were then weighed one against the other in the manner described. The chloride, previously dried at 140° to 150°, was next transferred by means of a platinum spatula from the rock-crystal basin in which it was contained, to the glass vessel, and this and its tare were again heated to 150° for about an hour in the air-bath, and after standing over-night in the desiccator containing phosphoric oxide, were again weighed. The chloride was then dissolved in 2 cc. of distilled water, the solution acidulated with two drops of dilute nitric acid (1 : 4), warmed, and mixed with a slight excess of silver nitrate solution of known strength added drop by drop, with constant shaking, from a narrow burette capable of being read to 1/50 cc. When clear, the liquid was again tested with the silver nitrate solution in order to ascertain that the precipitation was complete, and after standing for about eighteen hours in a warm place when the silver chloride had wholly subsided into the bottom of the conical portion of the vessel, the clear supernatant solution was drawn off by means of a capillary glass tube.

This was conveniently effected in the manner illustrated by Fig. 2. The vessel (*a*) containing the silver chloride was placed on a small elevating table (*b*), the height of which could be adjusted by means of the rack and pinion arrangement seen at (*c*), so that the end of the drawn-out capillary syphon (*d*), made of thermometer tubing, could be brought to within a mm. or two of the deposit of silver chloride. By gentle aspiration at (*e*) the action of the syphon was started, and by far the greater quantity of the

clear liquid could be drawn over into the flask (*f*) without the slightest risk of disturbing the precipitate.

The table was then lowered, and the end of the syphon as well as the internal sides of the vessel washed by a fine stream of hot distilled water. After clarification, the wash-water, which was about 4 or 5 cc. in bulk, was drawn over as before, and the process repeated. After each addition of hot water the vessel containing the silver chloride was

As the precipitated silver haloid was always thus washed six times in succession, it may be assumed that it was practically freed from all soluble matter.

Care was of course taken to protect the silver chloride from the action of light, and to the extent that was practicable all the operations were carried out in a photographic dark room which adjoined the small laboratory set aside for the work. No matter what precautions were taken to

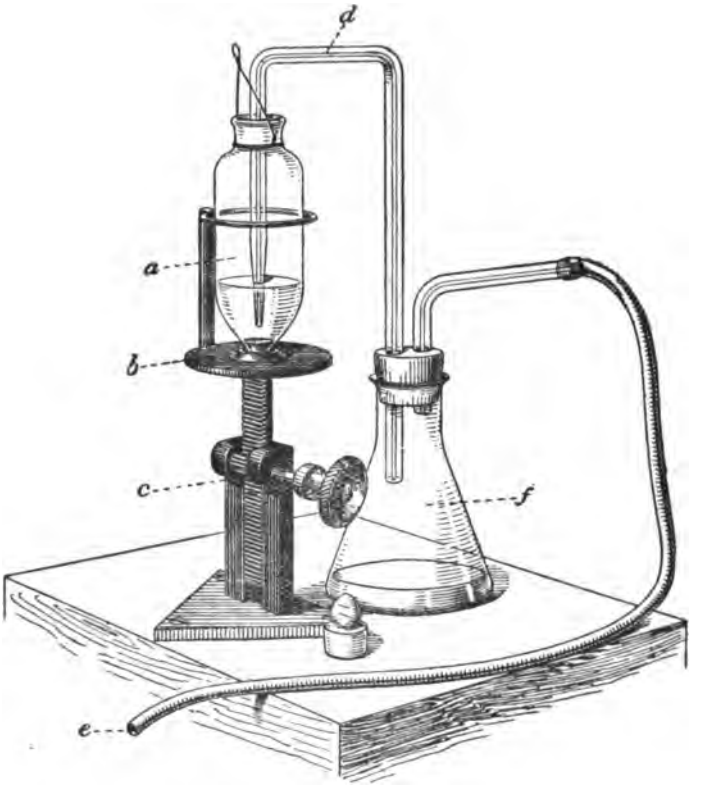


FIG. 2.

well shaken, and the precipitate broken up by means of a fine platinum wire, so as to bring the washing water in thorough contact with it. As is well known, silver chloride which has become granular by standing shows little or no tendency to occlude soluble matter, and is readily washed. Both the end of the syphon and the platinum wire were always washed by a stream of hot water, and were carefully examined by a lens, but in no case was any silver chloride found to have become attached. The liquid drawn over was invariably perfectly clear.

Assuming that we have 100 mgrms. of soluble matter in the 4 cc. of the clear supernatant liquid, and that we draw over 3·5 cc. at each successive operation as above described, it is readily calculable that the amount of matter in solution, even after the third operation, is probably too small to be appreciated by the balance.

The following table shows how rapidly the soluble matter is removed by systematic washing in the manner described :—

	Mgrms.
Original solution contains	100
After first decantation, residual liquid ..	12·5
,, first washing ,, ,, ..	1·56
,, second ,, ,, ,, ..	0·19
,, third ,, ,, ,, ..	0·02
,, fourth ,, ,, ,, ..	0·003
,, fifth ,, ,, ,, ..	0·0004

exclude ordinary white light, the silver chloride invariably became violet in contact with radium solutions.

The washed silver chloride was first dried at 100°, and then heated in the air-bath to 160° for about a couple of hours, and, after standing in the desiccator over phosphoric oxide for about eighteen hours, weighed in the manner described.

In order to test the practicability of the method and to acquire experience of its working, as well as to gain some idea of its accuracy before actually making use of it in the case of the radium salt, a series of determinations of atomic weight was made with barium chloride, purified by systematic re-crystallisation from water, according to the method already indicated, the same apparatus, reagents, and solutions being employed as were to be used subsequently in the radium determinations.

The results were as follows :—

Ag = 107·93. Cl = 35·45.

Barium chloride. Mgrms.	Silver chloride. Mgrms.	Atomic weight Ba.
114·7	157·8	137·5
172·1	236·8	137·5
57·1	78·8	136·9
62·6	86·1	137·6
68·1	93·7	137·5

As the corrections for displaced air for the silver chloride and for the barium chloride only amount to 0·00007 and 0·0002 per grm. respectively, they are of course wholly negligible in the case of quantities so small as were actually employed. The value for barium adopted by the International Committee on Atomic Weights, 1907-8, is 137·4

These determinations were made on independent amounts of material. As the quantity of radium salt I could hope to obtain would almost certainly not suffice to enable me to make similar independent determinations, it was desirable to prove that the element, which would exist in the solution in association with nitric acid after the precipitation of the chlorine as silver chloride, could be recovered and re-converted into chloride, and that the operations necessary to effect this would not influence the value of the atomic weight in a subsequent determination.

The first step was to remove the excess of silver in solution. This might be effected by means of hydrochloric acid. A difficulty at once presented itself. Silver chloride is not wholly insoluble in solutions of hydrochloric acid and of the chlorides of the alkaline earths, and presumably, therefore, in solutions of radium chloride. It was consequently necessary so to apportion the hydrochloric acid as to effect the precipitation of the silver without leaving any considerable excess of hydrochloric acid in solution. As the amount of the silver originally used, as well as that in the weighed silver chloride, were known, it was easy to calculate the amount remaining in solution, and so determine the quantity of hydrochloric acid required to precipitate it. This amount of hydrochloric acid, contained in a dilute solution of known strength, was then cautiously added, drop by drop, with constant shaking, and when the liquid was sufficiently clear it was tested, to ascertain that the precipitation was complete, by the addition of a single drop of the hydrochloric acid solution.

After standing until perfectly clear, the supernatant liquid was drawn off by the capillary syphon, the silver chloride thoroughly washed in the manner already described, and the solution transferred to a silica basin, and evaporated to dryness over a water-bath heated with an alcohol lamp to avoid any possible action of the oxides of sulphur produced by the combustion of London coal-gas.

The dried residue was then repeatedly evaporated with small quantities of pure hydrochloric acid, and so re-converted into the chloride.

Two determinations of the atomic weight of barium, made in the manner described on barium chloride thus recovered, gave the following results :—

Barium chloride.	Silver chloride.	Atomic weight Ba.
Mgrms.	Mgrms.	
139·5	191·4	138·1
78·8	108·3	137·7

In the hope that I might be able to employ the bromide of radium in the determination of the atomic weight of this element, I also made a similar preliminary series of determinations of the atomic weight of barium by means of barium bromide prepared from the pure chloride, and repeatedly re-crystallised from alcohol.

The results were as follows :—

Ag = 107·93. Br = 79·96.

Barium bromide.	Silver bromide.	Atomic weight Ba.
Mgrms.	Mgrms.	
89·9	113·6	137·5
96·0	121·4	137·3
111·0	140·3	137·4

Two determinations were made on the recovered barium bromide, with the following results :—

Barium bromide.	Silver bromide.	Atomic weight Ba.
Mgrms.	Mgrms.	
91·0	114·9	137·7
80·8	102·1	137·5

It will be seen from these numbers that a very close approximation to the true atomic weight of barium can be obtained by the method described, the maximum error being about half a unit, or less than 0·5 per cent. Considering that the atomic weight of radium is probably nearly double that of barium, the same fortuitous errors would affect its value to about a unit.

There is, however, one circumstance which, whilst not without influence in raising the value of barium, when determined on the recovered chloride, hardly affects the value of radium. In the case of radium, the effect of any minute quantity of retained silver haloid in the recovered salt, provided it is weighed with the precipitated silver chloride, is practically negligible, since radium chloride gives approximately its own weight of silver chloride.

As the work of isolating and purifying the radium chloride proceeded, determinations of the amount of chlorine were made as described from time to time, and as soon as approximately constant values were obtained it was assumed that any barium or other impurity present was too small in amount to affect the results when regard was had to the unavoidable experimental errors. The resulting chloride was then repeatedly and carefully re-crystallised from pure strong hydrochloric acid, the "tails," which were comparatively rich in radium, being specially set apart.

The purified salt finally extracted from the material supplied by M. Armet de Lisle weighed, when anhydrous, 64 mgrms.

I regard this salt as substantially radium chloride. I am not, however, in a position to say that it was absolutely free from barium. At the same time, I have reason to believe that the amount still present was probably too small to materially influence the result, considering the limited quantity of the salt I had to work with, and the consequent relatively large experimental errors.

With the aid of Sir William Huggins, who kindly made the spectroscopic trials for me, I was able to carry out Mdme. Curie's test of comparing the relative intensity of the lines of barium and radium in the spark spectrum of the separated radium chloride. Mdme. Curie compared the relative strengths of lines 4554·2 of Ba and 4533·3 of Rd. Although these have the advantage of being close together, they are of dissimilar intensity. Sir William Huggins advised that a more stringent test would be to take the line 5536·2 of Ba of intensity 10, and compare it with the Rd lines 5813·8 and 5560·8, which are also of intensity 10. On actually making the trials, which were repeated several times, the green Ba line 5536·2, although visible, was seen to be relatively very feeble—less intense, indeed, than that afforded by the most dilute solution of barium chloride that we were able to employ.

With this material, therefore, I attempted to make the determination of atomic weight. Accordingly, the greater portion was transferred to the vessel already described, and the amount of chlorine in the anhydrous salt determined with all possible care. The result was :—

Radium chloride.	Silver chloride.	Atomic weight Rd.
Mgrms.	Mgrms.	
62·7	60·4	226·8

The radium was recovered from the solution, re-converted into chloride, added to what remained of the original quantity, and the amount of chlorine again determined in the anhydrous salt. The second result was :—

Radium chloride.	Silver chloride.	Atomic weight Rd.
Mgrms.	Mgrms.	
63·9	61·8	225·7

The purified chloride obtained from the Cambridge material amounted to 24 mgrms. A chlorine determination on a portion gave a number exceeding 230 for the atomic weight. No more importance can be attached to this value, considering the very small amount employed, than as showing that the salt was of the same order of purity as that obtained from the French material.

It was accordingly added to the main bulk, and the whole was repeatedly crystallised from strong hydrochloric

acid, about 6 mgrms. being thus removed in the mother-liquors. The resulting chloride, after being dried at 150°, was again analysed with the following results :—

Radium chloride. Mgrm.	Silver chloride. Mgrm.	Atomic weight Rd.
78·4	75·3	227·7

The mean value is 226·7, or, to the nearest unit, 227. This, it will be observed, is in very close accord with Mdme. Curie's latest number.

I think, therefore, it is reasonably well established that the atomic weight of radium is now known to within a unit which, considering the relatively high number, is, under the present circumstances, as fair a degree of exactitude as could be anticipated.

There are, however, one or two facts connected with the behaviour of radium chloride which, as they may possibly affect the determination of its atomic weight, may here be mentioned. If a quantity of the salt be kept in perfectly dry air, it will be noticed that it very slowly increases in weight. The increase is very small, but it is plainly perceptible on a sufficiently delicate balance, and in the course of three or four days may amount to 0·3 per cent. On opening the vessel a marked smell of ozone is perceived, and on aspirating the air from above the chloride by means of a capillary tube passing into a freshly-prepared solution of potassium iodide and starch, iodine is found to be liberated, as seen from its action on the starch. Moreover, on dissolving radium chloride which has stood for some time in contact with the air in warm water, and acidulating the solution with dilute nitric acid, a smell recalling that of hypochlorous acid is perceived. The observed increase in weight may be due, therefore, to a portion of the air in the vessel becoming ozonised, or to a slight oxidation of the chloride, or to both these causes combined. Their joint effect would tend to increase the atomic weight of radium.

Another remarkable circumstance connected with radium chloride is its action on colourless rock-crystal, which is gradually turned a deep purplish black. Berthelot has already drawn attention to the action of radium on quartz. The silica vessels which I employed in connection with the foregoing work were thus strongly coloured in the course of a few months. Moreover, these vessels, as well as those of porcelain and glass, are slightly attacked by radium chloride, with the formation, apparently, of insoluble silicates. A similar observation has been made by Mdme. Curie. It occasionally happened that a sample of radium chloride, after standing for some considerable time in contact with glass, gave a faintly turbid solution, although when the salt was newly crystallised from hydrochloric acid its aqueous solution was perfectly clear.

I had hoped, as stated, to have obtained an additional series of values for the atomic weight of radium by the analysis of the bromide. As already mentioned, I reconverted the Cambridge material into this salt; but my experience with it leads me to infer that it is not sufficiently stable to afford trustworthy values for the atomic weight of the element. It appears to lose bromine, and eventually becomes insoluble in water. I hope to be able to study this change more minutely, as well as to throw some additional light on the action of radium salts on glass.

In conclusion, I desire to acknowledge my indebtedness to my assistant, Mr. Arthur G. Francis, B.Sc., for the assiduity, conscientiousness, and skill with which he has carried through what has proved to be the most irksome and tedious part of the work, namely, the isolation and purification of the radium chloride.

I am also indebted to Prof. Rutherford for the measurements of radio-activity which he made for me in the course of the fractionation of my material.

Royal Institution.—On Thursday next, May 21, at 3 o'clock, Dr. Alexander Scott will deliver the first of a course of three lectures at the Royal Institution on "The Chemistry of Photography."

THE INTERACTION OF ALUMINIUM POWDER AND CARBON.*

By FRANK E. WESTON, B.Sc., and H. RUSSELL ELLIS, B.Sc.

(Concluded from p. 222).

Series II.—*Aluminium Powder and Charcoal.*

The sugar carbon was made from white lump sugar by heating small portions at a time in a cylindrical tin and finally heating in the muffle to 1000°—1100° C. It was well crushed on cooling, powdered, and sifted through 40,000-mesh sieve; it was a bright, shiny powder, hard and difficult to crush, and it did not seem at all porous. The percentage of ash was none.

Mixtures 4 Al + 3 C.—The interaction was tried in four ways.

Method 1.—Mixture was placed in a Hessian crucible and embedded in sand, so that the crucible could be covered with a beaker and air excluded. The action was started with a fuse and spread slowly over the top, but on covering over with a beaker it ceased. This was found to be the case on repeating several times. The reaction proceeded when left uncovered. It thus appears that the reaction between the Al and C requires a high initial temperature, and this is supplied by the burning C and Al in contact with the air.

Method 2.—Some of the mixture was placed in a 5 × 8 inch test-tube and the top drawn out to a fine capillary tube. The mixture was then heated till red-hot, but no apparent change occurred, even after the whole of the mixture was red-hot. On looking the Al powder was quite visible and the mixture appeared unchanged. Only a very slight evolution of gas was obtained by allowing the mixture to stand over water all night. It is evident that sugar carbon in this state of fineness, and with air excluded, does not combine with Al at a red heat.

Method 3.—Some of the mixture was heated in an open porcelain crucible over a Bunsen burner. The mixture slowly burnt at the surface and finally became incandescent. The mixture was entirely changed, no Al being visible, and a gas was slowly evolved on treating some of it with water.

Method 4.—A sample was placed in a Hessian crucible and covered as in previous experiments. It was heated in the muffle for two hours at 1000°—1100° C. On removal and cooling the contents were found to be solid, no Al visible, und the core consisted of a mass of yellowish crystals.

The reaction between sugar carbon and aluminium powder is not nearly so striking as that between wood charcoal, due probably to (1) the superior hardness and compactness of the sugar charcoal; (2) the non-porosity of the carbon preventing the occlusion of air; (3) the powder not being in such a finely divided state; and (4) the absence of possible helpful impurities, *e.g.*, Fe_2O_3.

Mixtures 4 Al + 8 C.—This mixture could not be made to react in the cold, but on placing in the muffle reaction started, and on withdrawing and cooling a sample of carbide was obtained which reacted with water most vigorously. Samples were therefore made by heating mixture in closed crucible for half an hour. The resulting product was quite soft and black, with patches of yellow crystalline masses.

Mixtures of 8 Al + 3 C.—This mixture would not react in the cold, but did so easily in the muffle. Samples were therefore made as above. The resulting mass was found to be very hard and extremely difficult to remove.

* A Paper read before the Faraday Society, April 28, 1908.

Analyses.

Sample.	Percentages. Free C.	Free Al.	AlN.	Al_4C_3.	Al_2O_3.
A. 4Al+3C :—					
Top layer ..	9·04	1·00	13·93	24·78	52·25
Middle layer ..	9·57	1·75	18·05	34·39	36·24
Lower layer ..	9·25	1·75	40·59	20·05	28·36
B. 4Al+6C	25·05	1·00	15·04	27·74	31·22
C. 8Al+3C	6·08	3·62	24·68	46·18	19·44

Analyses of Gas.

Sample 1.—77·9 per cent CH_4, 18·0 per cent H, 4·1 per cent N.

Sample 2.—79·6 per cent CH_4, 17·5 per cent H, 2·9 per cent N.

Sample 3.—75·9 per cent CH_4, 18·3 per cent H, 5·8 per cent N.

Series III.—*Aluminium Powder and Graphite.*

Commercial graphite was used, which was found to be very impure and to readily react with Al powder in the cold. On igniting the commercial substance a brown ash was left which amounted to 50·1 per cent of substance taken.

Boiling for twelve hours with conc. HCl gave a product which still yielded 47·3 per cent of ash on ignition. The graphite obtained by treatment with conc. HCl was boiled for six hours with HF, and after this still yielded an ash of 15 per cent.

The partially purified graphite was now treated in an iron tray with fused NaOH for three hours, extracted with water, filtered, digested with conc. HCl, filtered, washed, and dried; after this treatment the ash was less than 1 per cent.

It was found that the original graphite could be purified by two successive fusions with NaOH. During the fusion H was evolved.

None of the mixtures of graphite and aluminium would react in the cold, but those in the proportion 4 Al to 3 C reacted with a fuse when heated to about 300° C. The action was brought about in each case by heating in the muffle, but the action was not so complete and vigorous as with the other forms of C.

The mixture 8 Al + 3 C gave a solid mass containing a yellow crystalline portion. (See Note to "Analysis"). This yellow crystalline formation was seen more or less in all the samples.

Analysis.

Sample.	Percentages. Free C.	Free Al.	AlN.	Al_4C_3.	Al_2O_3.
A. 4Al+3C (yellow crystals). ..	15·2	0·25	20·04	10·68	53·83 (Note)
B. 4Al+6C	26·78	0·5	17·52	33·69	21·51
C. 8Al+3C	7·95	2·3	42·16	36·58	11·11

Note.—Dr. Seligman (*Trans. Faraday Society*, vol. iii., p. 8) calls attention to the existence of yellow crystals in the mass produced when Al burns in air, and suggests that they are crystals of Al_2O_3; the authors find that the yellow crystalline portions of their products are always high in Al_2O_3.

Gas Analysis.

1. Sample taken one and a-half hours after starting :— 80·9 per cent CH_4, 16·9 per cent H, 2·2 per cent N.
2. Another sample one hour after :—77·1 per cent CH_4, 21·8 per cent H, 1·1 per cent N.

Series IV.

Some experiments were carried out to see the influence of the air and of N in the combination of Al and C under the conditions already described. The mixture of 4 Al + 3 C (wood C) were used.

1. *Heated in a Current of Air.*—Reaction proceeded before tube was visibly hot and proceeded vigorously. Product contained a very large amount of Al_2O_3 and 1·35 per cent of AlN.

2. *Heated in a Current of* N *in Glass.*—Mixture was heated to dull redness, no visible action was seen. The product contained large amount of free C + Al and 3·517 per cent AlN.

3. *Heated in Current of* N *in Berlin Porcelain Tube.*—The tube was heated to full red heat. Reaction had taken place to a greater extent than in 2. It contained 10·46 per cent AlN.

4. *Mixture Heated* in vacuo.—The mixture was placed in a piece of steel bicycle tubing and connected to a Töpler pump. A very slight leak occurred at the joint between the glass and the steel tube, and it is probably due to the small amount of air thus left (the pressure was less than 2 cm. during the heating) that action took place. The tube was heated in a small Fletcher furnace to a bright red heat for twenty minutes.

The product appeared almost unchanged, and where the powder had agglomerated portions were picked out, ground up, sieved, and analysed.

The analysis gave :—

Free C 23·44 per cent, Free Al 65·01 per cent, AlN 1·6 per cent, Al_2O_3 7·0 per cent, Al_4C_3 2·95 per cent.

The authors are of opinion that if air had been rigorously excluded very little action would have taken place. They hope to repeat this experiment again.

Note.—*Action of Magnesium and Carbon.*

Some experiments have been carried out on the direct combination of Mg and C, and evidence has been obtained, which the authors are now confirming, that a carbide of magnesium is produced under similar conditions to those described for Al and C.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 2nd, 1908.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

Messrs. H. Bassett, jun., H. T. Clarke, and C. Dickinson were formally admitted Fellows of the Society.

It was announced that the Council had appointed the following Committees for 1908-1909 :—

Finance Committee—Messrs. E. G. Hooper, G. T. Moody, T. E. Thorpe, W. A. Tilden, and the Officers.

House Committee—Messrs. W. R. Dunstan, J. E. Reynolds, W. J. Russell, J. M. Thomson, T. E. Thorpe, W. A. Tilden, and the Officers.

Library Committee—Messrs. E. C. C. Baly, B. H. Brough, F. D. Chattaway, B. Dyer, A. Harden, C. A. Keane, A. Lapworth, E. J. Mills, J. M. Thomson (Chairman), J. A. Voelcker, J. Wade, the Editor, and the Officers.

Publication Committee—Messrs. E. C. C. Baly, W. R. Dunstan, J. T. Hewitt, R. Meldola, G. T. Morgan, T. E. Thorpe, J. Wade, and the Officers.

Research Fund Committee—Messrs. G. T. Beilby, P. F. Frankland, A. D. Hall, G. Matthey, R. Meldola, R. Messel, W. H. Perkin, J. E. Reynolds, W. A. Tilden, Sir A. Pedler, and the Officers.

Certificates were read for the first time in favour of Messrs. Donald Francis Blyther, B.Sc., 77, Knights Road, Silvertown, E.; Henry Brougham Hutchinson, Ph.D., Ashby Villa, Devonshire Road, Harpenden; Stanley Allen Warrington Okell, 27, King's Road, Ealing, W.; John Day Speed, Mill House, Enfield Lock, Middlesex.

Certificates have been authorised by the Council for presentation for ballot under By-law I. (3) in favour of Messrs. Cyril Arden Hinds, 724, Russell Street, Bristol, Tenn.,

U.S.A.; William Seelhorst, Eastern Smelting Co., Ltd., Penang, Straits Settlements.

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

*72. "*Rate of Hydrolysis of Chloroacetates, Bromoacetates, and α-Chlorohydrin by Water and by Alkali, and the Influence of Neutral Salts on the Reaction Velocities.*" (Preliminary Note). By GEORGE SENTER.

In a former paper (*Trans.*, 1907, xci., 460), the results of an investigation of the rate of hydrolytic decomposition of certain chloroacetates by water and by alkali were given, and the effect of certain neutral salts on the rate of reaction was discussed. The rate of displacement of halogen by hydroxyl under different conditions has now been investigated for bromoacetic acid and sodium bromoacetate and for α-chlorohydrin, and the effect of certain neutral sodium salts on the reaction velocities has been examined.

Bromoacetic Acid.—The reaction represented by the equation $CH_2Br{\cdot}CO_2H + H_2O = HO{\cdot}CH_2{\cdot}CO_2H + HBr$ is unimolecular, and the value of $k = 1/t \log C_0/C_t$ is 0·0062 at 102°, as compared with $k = 0{\cdot}00048$ for chloroacetic acid under equivalent conditions. The reaction is slightly retarded by hydrogen bromide.

Sodium Bromoacetate.—The reaction—

$$CH_2Br{\cdot}CO_2Na + H_2O = HO{\cdot}CH_2{\cdot}CO_2H + NaBr$$

is unimolecular in dilute solution; the value of $k = 1/t \log C_0/C_t$ at 102° is 0·020. The hydrolysis of this salt by alkali, represented by the equation $CH_2Br{\cdot}CO_2Na + NaOH = HO{\cdot}CH_2{\cdot}CO_2Na + NaBr$, is bimolecular, and at 70·4° $k = \frac{1}{tC_0} \cdot \frac{C_t}{(C_0 - C_t)}$ has the value 0·0314 when referred to a N/10 solution.

Effect of Temperature.—The average velocity quotients for a rise of temperature of 10° between the limits of temperature given are as follows:—Chloroacetic acid and water (70—100°), 2·6; sodium chloroacetate and water (70—100°), 3·2; sodium chloroacetate and hydroxide (70—100°), 2·5; bromoacetic acid and water (70—100°), 2·4; sodium bromoacetate and water (70—100°), 2·9; sodium bromoacetate and hydroxide (30—70°), 2·75. The fact that the temperature-coefficients of the hydrolysis of sodium chloroacetate by water and by alkali are different, shows that the assumption often made, that the OH' ions in the latter case act in a catalytic manner, is not justified, and supports the views on the mechanism of the reactions advanced in the previous paper (*loc. cit.*).

α-Chlorohydrin.—The hydrolysis of α-chlorohydrin by water alone is extremely slow; the value of $k = 1/t \log C_0/C_t$ is 0·00010 at 101°. Hydrochloric acid retards the reaction slightly. In the presence of alkali the change is extremely rapid; the value of k for the bimolecular reaction represented by the equation—

$$HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl + NaOH = HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH + NaCl$$

is 0·052 at 0°, referred to a N/10 solution as unit.

Effect of Neutral Salts.—Neutral sodium salts slightly retard the hydrolysis of chloro- and bromo-acetates by water, they greatly accelerate the hydrolysis of these compounds by alkali, but have practically no effect on the rate of reaction between α-chlorohydrin and alkali. The accelerating effect of molar concentrations of different salts on 0·1 molar solutions of chloro- or bromo-acetates and alkali is represented in the table, the rate of the reaction in the absence of neutral salts being taken as unity.

Sodium Chloroacetate and Hydroxide at 70·4°.

Neutral salts.	Ratio of velocities.
None	1·0
$NaNO_3$	1·55
NaCl	1·55
$NaClO_3$	1·55
$\frac{1}{2}Na_2SO_4$	1·55
$CH_3{\cdot}CO_2Na$	1·58
$H{\cdot}CO_2Na$	3·3

Sodium Bromoacetate and Hydroxide at 70·4°.

Neutral salts.	Ratio of velocities.
None	1·0
$NaNO_3$	1·53
NaBr	1·53
$NaClO_3$	1·53
$H{\cdot}CO_2Na$	2·8

The effect of sodium nitrate on the reaction between sodium chloro-acetate and hydroxide is of the same magnitude, within the limits of experimental error, at 55° and 101°.

The above results confirm the views on neutral salt action advanced in the previous paper, that the effect in question is mainly due to the action of the salt on the reacting substances, and appear to be incompatible with the hypothesis advocated from time to time by different observers, most recently by Armstrong and his co-workers (*Proc. Roy. Soc.*, 1907, lxxix., A, 586), that neutral salt action is due to combination between salt and solvent, with consequent concentration of the solution.

DISCUSSION.

Mr. JEFFERS asked if Dr. Senter assumed that the pressure developed in the sealed tubes had no influence whatever on the velocity of hydrolysis. Pressure was known to have a large influence in the case of the hydrolysis of carbohydrates, and it seemed impossible to correlate the figure given for the velocity unless the pressure was known in all cases.

Dr. SENTER, in reply, pointed out that, according to the experiments of Röntgen (*Ann. Physik.*, 1891, xlv., 98; compare also Rothmund, *Zeit. Phys. Chem.*, 1896, xx., 170), the effect even of great changes of pressure on the rate of a reaction was very slight. In the case most fully investigated, a change of pressure from 1 to 500 atmospheres increased the rate of the reaction by 1 per cent. As in the present experiments the highest pressure in the sealed tubes was 2 atmospheres and the variations less than 1 atmosphere, it was obvious that the effect in question was quite negligible.

*73. "*The Constituents of Cyprus Origanum Oil. Isolation of a New Terpene 'Origanene.'*" By SAMUEL SHROWDER PICKLES.

The essential oil yielded by the principal origanum plant of Cyprus has been examined, and found to consist mainly of carvacrol (84 per cent). There are also present—(1) a hydrocarbon, $C_{10}H_{16}$, apparently a new terpene, for which the name *origanene* is proposed (2·5 per cent); (2) cymene, which, together with associated terpenes (b. p. 170—180°), constitutes 8·5 per cent; (3) terpene alcohols (3·5 per cent); and (4) high boiling residue (1·3 per cent) besides very small quantities of a second phenol which gives a purple coloration with ferric chloride, and a volatile acid, probably *iso*butyric acid.

The results of experiments on the constitution of the hydrocarbon "origanene" lead the author to conclude that the terpene is probably $\Delta^{1:3}$-p-*menthadiene*, $CMe\begin{matrix}\diagup CH{-}CH \diagdown \\ \diagdown CH_2{\cdot}CH_2 \diagup\end{matrix}C{\cdot}CHMe_2$.

*74. "*The Displacement of Halogen in l Phenylchloroacetic Acid by Hydroxy- and Methoxy-groups. A Contribution to the Chemistry of the Walden Inversion.*" By ALEX. MCKENZIE and GEORGE WILLIAM CLOUGH.

The authors have resolved *r*-phenylchloroacetic acid into its optically active components by means of morphine in methyl-alcoholic solution.

The action of water on *l*-phenylchloroacetic acid, the action of water on sodium *l*-phenylchloroacetate, the action of aqueous sodium hydroxide on sodium *l*-phenylchloroacetate, the action of water on silver *l*-phenylchloroacetate, the action of silver carbonate on *l*-phenylchloroacetic acid, and the action of methyl-alcoholic sodium methoxide on *l*-phenylchloroacetic acid have been examined with reference to the Walden inversion.

Discussion.

Dr. Smith, referring to the fact that *d*-chlorosuccinic acid is converted by sodium hydroxide into *l*-malic acid and by silver oxide into *d*-malic acid, stated that Walden assumes that the inversion, which must have occurred during one of these changes, takes place in the second reaction. In view of Dr. Senter's result, that sodium chloroacetate and sodium hydroxide react ionically, the converse would seem to be more probable, for during the reaction between sodium hydroxide and *d*-chlorosuccinic acid, which by analogy is ionic, there would be a greater possibility for change of configuration to occur than in the reaction between *d*-chlorosuccinic acid and silver oxide, which would be a case of simple substitution.

Dr. McKenzie stated that Walden regarded the change

$$d\text{-}CO_2H\cdot CH_2\cdot CHCl\cdot CO_2H \rightarrow l\text{-}CO_2H\cdot CH_2\cdot CH(OH)\cdot CO_2H$$

by means of potassium hydroxide as, in all probability, optically normal, because the rotation of the malic acid formed is of the same sign as that of the malic acid from which *d*-chlorosuccinic acid is formed by the action of phosphorus pentachloride.

Fischer had pointed out (*Ber.*, 1907, xl., 490) that the view that silver oxide acts abnormally, whilst potassium hydroxide acts normally, may appear somewhat strange to many chemists.

75. "*The Condensation of Epichlorohydrin with Phenols.*" By David Runciman Boyd and Ernest Robert Marle.

The authors find the statements of Cohn and Plohn (*Ber.*, 1907, xl., 2597) with regard to the products obtained by the action of epichlorohydrin on alkaline solutions of phenol and *p*-cresol to be incorrect. The crystalline compound (m. p. 81—82°) which is obtained from phenol and epichlorohydrin, and which is stated by Cohn and Plohn to be phenyl glycide ether, $C_6H_5\cdot O\cdot CH_2\cdot CH\langle{}^{CH_2}_{O}\rangle$, is really glyceryl diphenyl ether,—

$$C_6H_5\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot C_6H_5.$$

Phenyl glycide ether is an oil boiling at 133° under 23 mm. pressure.

Similarly, the crystalline compound (m. p. 88°) obtained from *p*-cresol and epichlorohydrin is the glyceryl di-*p*-tolyl ether, $C_7H_7\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot C_7H_7$, and not the *p*-tolyl glycide ether.

The authors have prepared *phenoxydichloropropane*, an oil boiling at 139—140° under 13 mm. pressure.

76. "*A New General Method of Preparing Diazonium Bromides.*" By Frederick Daniel Chattaway.

Primary aromatic hydrazines react quantitatively with the diazonium perbromides producing diazonium bromides, thus:—

$$2\ \begin{matrix}R\cdot N\cdot Br\\ |\\ Br\cdot N\cdot Br\end{matrix} + \begin{matrix}R\cdot N\cdot H\\ |\\ H\cdot N\cdot H\end{matrix} = 3\ \begin{matrix}R\cdot N\cdot Br\\ |\\ H\cdot N\cdot Br\end{matrix} + 3\ \begin{matrix}R\cdot N.Br\\ |||\\ N\end{matrix} + 3\ HBr$$

As the diazonium perbromides are so easily obtained in the solid state by adding bromine to aqueous solutions of diazonium salts, and as they can be kept in a dry atmosphere for a long time without alteration and are comparatively safe to handle, this reaction affords a very convenient method for preparing diazonium bromides in the solid state.

For this purpose it is only necessary to suspend the finely powdered perbromide in alcohol and, after cooling, to add the calculated quantity of the corresponding hydrazine also dissolved in alcohol and cooled. The solid diazonium bromide is at once formed, and, after adding an equal bulk of ether to complete the deposition, can be collected in a pure state.

The reaction is a general one, and takes place readily and quantitatively with all primary aromatic hydrazines and perbromides that have been studied.

77. "*The Absorption Spectrum of Triphenylmethane.*" By Alfred Godfrey Gordon Leonard.

In order to ascertain the cause of the difference between the absorption curve plotted by Hartley, in 1887, and that plotted by Baker, in 1907, the absorption spectrum of triphenylmethane was thoroughly re-examined.

All the specimens examined gave at first curves similar to that obtained in 1887, but, on purifying the samples by repeated recrystallisation from alcohol, the absorption curve became identical with that found by Baker. This curve is therefore the true absorption curve of triphenylmethane.

The difference is clearly shown to be caused by the presence of an impurity in the sample originally examined, and this impurity is always present when the triphenylmethane is prepared from benzene and chloroform by Friedel and Crafts' reaction (see following abstract).

78. "*The Nature of the Impurity found in Preparations of Triphenylmethane.*" By Walter Noel Hartley.

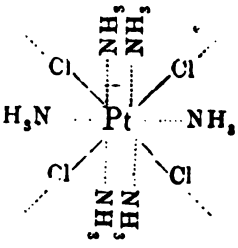
The experiments of Mr. A. G. G. Leonard have shown conclusively that in the preparation of triphenylmethane there are always two substances obtained, even when the materials are of the greatest purity and free from moisture.

The second substance must be a hydrocarbon; it is yellow, and apparently it undergoes oxidation, becoming still brighter in colour. From these and other considerations it appears to be identical with Gomberg's triphenylmethyl, and the final product with triphenylmethyl peroxide.

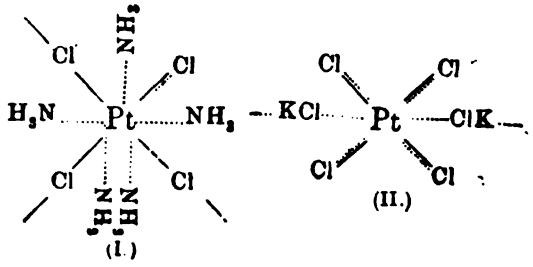
79. "*The Constitution of Co-ordinated Compounds.*" By Samuel Henry Clifford Briggs.

An attempt has been made to devise formulæ for co-ordinated compounds which will fulfil the requirements of the experimental results of Werner and his colleagues, and also give some idea of the manner in which the affinities of the atoms are disposed within the molecule.

The existence of the two compounds $(Pt6NH_3)Cl_4$ and $(PtCl_6)K_2$, in which the platinum atom is the basis of a complex cation and anion respectively, suggests the view that the platinum atom has both positive and negative affinities (compare Berzelius, Abegg, and others). Assuming that every element has two kinds of affinity, $(Pt6NH_3)Cl_4$, may be written:—



in which the saturation of the positive affinity of the platinum (situated at the centre of an octahedron) is expressed by a straight line, and the saturation of the



(I.) (II.)

negative affinity by a dotted line. On removing one molecule of ammonia and saturating the negative affinity

of the platinum thus liberated by the free positive affinity of one of the chlorine atoms, we obtain (I). Similarly, $(PtCl_6)K_2$ is represented by (II.).

These bonds are intended to represent the saturation of affinities only, and no assumptions are made with reference to the valencies of the atoms in question.

The formulæ were discussed from the point of view of the electrolytic dissociation of the compounds, and it is suggested that the non-ionisable chlorine atom in the compound $(Pt_5NH_3Cl)Cl_3$ is the one which has both the negative and positive affinities saturated as expressed in the formula given above.

In the salts with a complex anion, these formulæ suggest the possibility of isomerism due to differences in the points of attachment of the positive atoms. The cases of isomerism in compounds with an anionic complex, which are referred to by Werner (*Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*), can thus be satisfactorily explained.

80. "*A Combined Stopcock and Capillary Connecting Tube for Gas Burettes.*" By ARTHUR EDWIN HILL.

The familiar method of connecting a Hempel burette to the absorption pipette by means of a short piece of thick-walled glass capillary tubing bent twice at right angles and two short pieces of thick rubber tube is very unsatisfactory, as it is liable to give inaccurate results, and requires a great deal of attention.

Before commencing an absorption, the air, entrapped in the capillary tubes and rubber connexions, should be expelled; as this operation is rather troublesome, it is often not properly effected. Again, when absorption is complete in the pipette and the gas is returned to the measuring burette, the absorbent should be allowed to flow back as far as the capillary tube at the top of the burette, but, since this adjustment has to be made when the thread of absorbent is out of sight behind the rubber connexion, some of it often finds its way into the burette before the pinchcock can be closed.

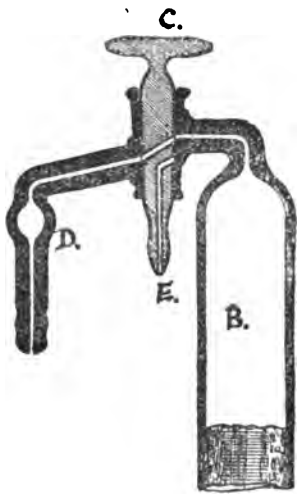
The combined stopcock and capillary connecting tube indicated in section in the figure is sealed to the top of the measuring burette B. The three-way stopcock C in addition to controlling the flow of gas from the burette, also affords a means of connecting the pipette with the outside air through the bottom outlet E when it is attached to the burette.

The burette is connected to the pipette by a short piece of thick rubber tube, which is slipped over and well wired to the end of the capillary connecting tube and to the capillary tube of the pipette.

To expel the air entrapped in the capillary tubes and rubber connexion, a piece of rubber tube is slipped over the bottom outlet E of the stopcock C, and the stopcock is turned to make connection between the pipette and the outside air; the air is then sucked out through the tube, and the absorbent fills the vacant space. The stopcock is closed by giving it a half turn, so that the handle is in a plane at right angles to that of the connecting tube. In order to connect the burette with the pipette, the stopcock is given another half turn in the same direction as before. The barrel of the stopcock is pierced in a way which makes it impossible to connect the burette with the outside air through the bottom outlet E, a source of accidental error being thereby eliminated.

When absorption is complete and the gas is returned to the burette, the absorbment is allowed to flow back as far as the stopcock C, which is quickly closed to prevent it from flowing any further. The bulb D facilitates this adjustment by retarding the advance of the absorbent before it reaches the stopcock; it also prevents the drops of absorbent, which often lodge in the rubber connexion, from passing over with the gas into the burette.

Before the pipette is disconnected from the burette, the stopcock is turned back to the position which will connect the pipette with the outside air, and the thread of absorbent is allowed to flow back into the pipette. They are then disconnected, and those parts of the capillary connecting tube and stopcock which have been in contact with the absorbent can be washed with water and subsequently dried in a current of warm air without in any way affecting the contents of the burette.



Subsequent absorptions are effected by a similar procedure.

(We are indebted to the author for permission to use the woodcut illustrating this paper).

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY.

(LONDON SECTION).

Ordinary Meeting, May 4th, 1908.

Dr. J. LEWKOWITSCH in the Chair.

"*The Manufacture of Sodium Nitrite.*" By GILBERT T. MORGAN.

The various processes for preparing sodium nitrite are reviewed, and an account is given of the manufacture of the salt by the lead and sulphur processes. Experiments are described bearing on the production of sodium nitrite from calcium nitrate.

"*On some Simple and Mixed Esters of Cellulose. The Alkaline Decomposition of Nitro-Derivatives of Cellulose and other Carbohydrates.*" By WATSON SMITH, jun.

The action of acid mixtures containing acetic anhydride and nitric acid with and without the addition of concentrated sulphuric acid as a dehydrating agent was investigated. Pure nitrocelluloses and aceto nitrocelluloses were in this way prepared.

Pure acetyl nitrate acts on cellulose with the production of nitrocelluloses containing a high percentage of nitrogen.

Acetyl nitrocelluloses were obtained by the action of acetic anhydride and sulphuric acid on nitrocellulose. These new bodies give well characterised compounds with phenylhydrazine.

The nitro-derivatives of cellulose, starch, glucose, and fructose were treated with alcoholic caustic soda. In each case products of partial denitration were isolated; thus from gun-cotton was obtained tetra-nitrocellulose, from which acetyl and phenylhydrazine derivatives were prepared. Aldehydic or ketonic acids were isolated from the final decomposition products, and were characterised by their forming well-crystallised compounds with aniline and phenylhydrazine. A close relationship is shown in this way to exist between cellulose, glucose, and levulose.

"*The Mechanism of Filtration.*" By E. Hatschek.

The structure of the solid deposit on the filtering surface is shown to be determined by the flow of the liquid into the latter, and to be independent of the pressure, which therefore does not affect the percentage of voids. The velocity of flow through a porous septum with varying pressure is discussed and illustrated by curves showing a maximum loss of head at a pressure characteristic for each septum. Various types of the latter are examined and classified according to their rigidity.

A number of the more important precipitates are shown in photo-micrographs, to illustrate crystalline, amorphous, and aggregated particles.

The effect of the method of precipitation on the nature of the precipitates is also shown, and the author urges the microscopic examination of such, and the systematic search for a method of precipitation giving the result best adapted for the subsequent process of filtration.

"*Metanil Yellow; Its Use as a Selective Indicator.*" By E. Linder.

The author finds that filter-paper dyed with metanil yellow is turned violet on exposure in the dry state to fumes of mineral acids, while no effect is produced upon the paper by sulphur dioxide, chlorine, sulphuretted hydrogen, or acetic acid.

The test-paper can therefore be applied selectively for the identification of mineral acid in gaseous mixtures.

The violet compounds so obtained are characterised by marked differences of stability in contact with atmospheric moisture, the compounds being unstable in proportion as the mineral acid is volatile. This property is made use of for differentiating between certain mineral acids.

The test-paper can also be applied for the detection of "mineral acid" in adulterated vinegar:—A drop of the liquid is placed on the test-paper, which is then re-dried at 80° to 90° C. If "mineral acid" is present, the paper assumes a violet tint, the depth of which is proportionate to the amount of "mineral acid."

"*Conversion of Oleic Acid into Candle Material.*" II. By J. Lewkowitsch, M.A., Ph.D.

In a continuation of a paper read eleven years ago on the same subject the author discussed the efforts made by a number of inventors to convert oleic acid into stearic acid by means of sulphuric and by the aid of the electric current. A new solution of the problem seemed to lie in the application of the classical work of Sabatier and Senderens, in 1902, to oleic acid, and since then a number of workers have endeavoured to carry into effect the reduction of oleic acid to stearic acid. The author has succeeded in converting oleic acid, in practically quantitative yield, to stearic acid, and showed samples of the product. Several patent specifications, also modifications of the original catalytic process of Sabatier, were referred to.

FARADAY SOCIETY.

Ordinary Meeting, April 28th, 1908.

Prof. A. K. Huntington, Vice-President, in the Chair.

The following nominations for the Officers and Council to be elected at the Annual General Meeting were announced:—

President—Sir Oliver Lodge, F.R.S.

Vice-Presidents—G. T. Beilby, F.R.S.; R. A. Hadfield; Geh. Reg.-Rat. Prof. W. Hittorf; Prof. A. K. Huntington; Lord Rayleigh, O.M., P.R.S.; Prof. A. Schuster, F.R.S.; Prof. J. J. Thomson, F.R.S.

Treasurer—F. Mollwo Perkin, Ph.D.

Council—Bertram Blount, F.I.C.; A. C. Claudet, M.I.M.M.; S. Z. de Ferranti, M.I.E.E.; F. W. Harbord, F.I.C.; R. S. Hutton, D.Sc.; T. M. Lowry, D.Sc.; H. F. K. Picard, M.I.M.M.; James Swinburne, F.R.S.; J. F. L. Vogel, M.I.E.E.; N. T. M. Wilsmore, D.Sc.

A paper by Prof. A. K. Huntington and C. H. Desch, D.Sc., Ph.D., on "*The Planimetric Analysis of Alloys, and the Structure of Phosphor-copper,*" was read by Prof. Huntington. Dr. T. M. Lowry occupied the Chair during the reading of the paper, which was illustrated by means of lantern-slides.

The authors discuss the conditions under which it is possible to estimate the relative proportions of the constituent metals of an alloy by means of a planimetric measurement of the areas of the solid phases exposed in a polished and etched micro-section. Details of the method are given, and its accuracy is shown by a series of measurements of analysed alloys. The method has been most fully studied in the case of phosphor-copper, of which a number of photo-micrographs are shown. In the case of alloys containing less than the eutectic proportion of phosphorus, however, the area of the copper crystals is found to be considerably greater than that calculated from the composition determined by analysis. The origin of the discrepancies was traced to the segregation of the eutectic, the copper crystals which separate at first drawing to themselves a portion of the copper of the surrounding eutectic. The crystals are therefore surrounded by a belt of copper phosphide. By measuring the area of this belt and thence calculating the amount of segregated copper, a correction may be applied to the area of the crystals, and a very satisfactory agreement with the analytical results is thus obtained.

Prof. W. W. Haldane Gee (communicated) suggested that the method might be used to compare the relative losses of the constituents of an alloy after prolonged etching with different reagents, or after electrolytic corrosion, and so throw light on the method of corrosion.

Dr. C. H. Desch stated, in reply to a question, that the method could not be of quite general applicability, it being useless, for example, in cases where the alloy was homogeneous. It was also necessary for the alloy to be in a state of physical equilibrium.

Prof. A. K. Huntington added that the method would probably be usefully extended to the case of the phosphor-tin alloys.

A paper on "*The Interaction of Aluminium Powder and Carbon,*" by Frank E. Weston, B.Sc., and H. Russell Ellis, B.Sc., was read in abstract by Mr. Weston. (See Chemical News, xcviii., p. 219).

Dr. F. Mollwo Perkin did not agree with the authors' view as to the cause of the reaction. There was no evidence that at 1100° CO could be reduced. Possibly the reaction was started by superficial oxidation of the aluminium.

Mr. Charles Weiss referred to the aluminium carbides found at the bottom of the furnaces in which aluminium is made. As a rule these carbides were entirely enclosed in a coating of alumina.

Mr. H. R. Ellis gave some further particulars regarding the nitride produced, probably by the action of nitrogen at a high temperature on the aluminium carbide. As crude aluminium carbide can be made by heating clay and carbon in the electric furnace, this method might be as economical a one for the fixation of atmospheric nitrogen as the combination of calcium carbide and nitrogen to form cyanamide.

Prof. A. K. Huntington suggested that perhaps the authors' reaction was a triple one, brought about by the presence of a gas (CO_2 or CO) between two solids which would not react alone. The gas, unlike the carbon, might be able to permeate the film of oxide surrounding the aluminium, getting at the actual metal, and so start the reaction.

A Note on "*Technical Chemistry in Russia*" was communicated by Prof. N. Piltschikoff.

The paper refers to copper-refining works at Moscow and St. Petersburg and the Laschinsky electrolytic method of copper recovery from its ore which is used at Boleslav. The special feature of the process is to prevent oxidation

of iron at the anodes, and consequent waste of current by coating these with lead. The Gorbov and Mitkievitch arc furnace for the fixation of atmospheric nitrogen is about to be worked on a technical scale. In this the current of air draws the arc (the voltage across which is 600—1500, direct or alternating) into a worm, in whose mouth is formed a "bunch of fire" through which all the air has to pass. The products of combustion are subsequently cooled in the further part of the worm. In an experimental 14-kw. furnace an output of 56 grms. HNO_3 per kw.-hour has been attained. The furnace is stated to be simpler and more economical than the Birkeland-Eyde furnace. Other processes mentioned are the late Prof. Kloboukoff's method of electric tanning, which prevents fermentation in the bath, and Dr. Danilevsky's process for depositing copper on leather. The purification of water by ozone is being experimented with at St. Petersburg, and at Moscow Prof. Sokotoff's powerful and economical ozoniser is being tried.

NOTICES OF BOOKS.

Thermochemistry. By JULIUS THOMSEN. Translated from the Danish by KATHARINE A. BURKE, B.Sc. (Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

THE original Danish edition of this work was an abridgment of the author's complete treatise on thermochemistry, entitled "Thermochemische Untersuchungen," which was published during the years 1882-1886. This treatise gives an account with full experimental details of all the investigations carried out by Prof. Thomsen, and is the most comprehensive work on the subject extant. In order to render the results of his investigations and the conclusions to be drawn from them more accessible, he published more recently the numerical and theoretical results without the minute descriptions of the experiments in a shorter book, of which this volume of the Text-books of Physical Chemistry is a translation. The illustrations of the apparatus used for typical determinations are sufficient to give a clear idea of the general experimental methods, while comparative tables of numerical results show the quantitative relations which have been determined. The value of the theoretical parts of the book is to some extent lessened, because Prof. Thomsen's work was published before the theory of ionisation had been introduced into chemistry, but the translator has added notes in many cases to point out the modern interpretation of the facts recorded. In Part I. of the book the thermochemistry of aqueous solutions is discussed; Part II. deals with the compounds of the non-metals among themselves; and Part III. with the compounds of the metals and non-metals. In the fourth part the heat phenomena of organic compounds are described, and it is shown that, as with inorganic substances, the chemical reactions of the carbon compounds are based upon the tendency of the atoms to attain a state of stable equilibrium.

Übersicht über die Deutschen Reichspatente betreffend Heilmittel und Desinfektionsmittel. ("Survey of the German Patents dealing with Remedies and Disinfectants"). By Dr. E. A. FRANZ DÜRING. Gräfenhainichen: C. Schulze and Co. 1908.

THIS book contains short abstracts of the specifications of recent patents dealing with disinfectants, &c., which have been taken out in Germany. Patents which have recently run out are also included, and the little book will be a useful addition to the library of the inventor or manufacturer of disinfectants. Its value would be greatly increased if an index were provided.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 11, March 16, 1908.

Hydrates of Arsenic Acid.—M. Auger.—The hydrate, $(AsO_4H_3)_2H_2O$, possesses an appreciable dissociation tension below 0°, and loses water even at −10°. At about 12° this loss of water ceases with the formation of the hydrate, $As_3H_{10}O_5$ or $As_2O_7H_4.AsO_3H$. Above 12° and up to 148° the composition of the hydrate obtained in a desiccating medium approximates closely to $As_3H_{10}O_5$. This is dehydrated completely between 180° and 440°, and above 440° it begins to lose oxygen.

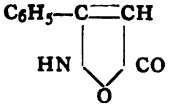
No. 12, March 23, 1908.

Absorption Spectra of Crystals of the Rare Earths Salts and their Modification in a Magnetic Field at the Melting-point and Boiling-point of Hydrogen.—Jean Becquerel and H. Kamerlingh Onnes.—The absorption bands of the crystals of the rare earth salts become narrower as the temperature is lowered, until at −190° the width of the bands is proportional to the square root of the absolute temperature. At lower temperatures most of the bands do not follow such a simple law. At the temperature of liquid air almost all the absorption bands of the compounds of the rare earths are much more intense than at the ordinary temperature. For every band there exists a temperature at which the absorption reaches a maximum. When the optical axis of a uniaxial crystal is oriented parallel to the magnetic field and to the beam of light, the distance apart of absorption bands of right and left vibrations remain invariable in the same magnetic field till −259°. The changes of frequence, under the action of magnetism, of oscillating systems are to a first approximation independent of the thermic movements, the intensity and width of the bands as well as of the paramagnetic properties of the substance. They seem to be the first cause of diamagnetism. This invariability of changes of frequence provides a confirmation of the hypothesis of positive electrons. With biaxial crystals the inertia of the oscillating systems varies with the direction of the movement.

Action of Chlorine on Dithymol.—H. Cousin.—When a current of chlorine is allowed to act on dithymol, $C_{20}H_{26}O_2$, in suspension in chloroform, dichlorodithymol is first formed, $C_{20}H_{24}Cl_2O_2$; then the halogen acts as an oxidiser, and removes two atoms of hydrogen from this dichloro-compound, yielding dichlorodithymoquinone, $C_{20}H_{22}Cl_2O_2$. Finally, if the action of the chlorine is continued this derivative fixes two atoms of chlorine, and forms a compound, $C_{20}H_{22}Cl_4O_2$. From its reactions it does not appear to be a tetrachloride of dithymol, for it is insoluble in soda, and can be reduced by SO_2 in alcoholic solution, and by powdered zinc to dichlorodithymol. Hence it must be looked upon as the derivative obtained by fixing two atoms of chlorine to the quinone; *i.e.*, as the dichloride of dichlorodithymoquinone.

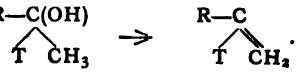
Products of the Action of Aluminium Chloride and Hydrochloric Acid on Benzene.—G. Gustavson.—When benzene containing finely-powdered aluminium chloride is saturated with gaseous hydrochloric acid, a dark brown layer of liquid is formed, which does not mix with the benzene floating on it. The action is very slow, and lasts some weeks, but it can be accelerated by heating. When this dark brown liquid is decomposed by water the products are benzene, a resinous residue, and hydrocarbons, from which, by the action of fuming sulphuric acid and barium carbonate, the barium salt of methylphenylcyclopentane is obtained. The free hydrocarbon may be prepared by decomposing the barium salt with hydrochloric acid in sealed tubes at 180—200°.

Derivatives of Phenylisoxazolone.—A. Wahl and André Meyer.—Phenylisoxazolone readily condenses with aromatic aldehydes in an alcoholic medium with or without a condensation agent. The condensation takes place slowly in the cold, but becomes rapid at the ordinary temperature in presence of a small quantity of piperidine. This condensation seems to show that phenylisoxazolone possesses a methylene group, although Moureu and Lazennec have shown that its constitutional formula is probably—



It appears to be capable of reacting in the tautomeric methylenic form.

Derivatives of Thiophene.—V. Thomas.—Magnesium dissolves very easily in thiophene iodide, $C_4H_3SI(\alpha)$, in presence of anhydrous ether, and the magnesium derivative thus formed behaves like phenyl magnesium iodide. It reacts with fatty ketones, giving tertiary alcohols from which ethylene hydrocarbons can be separated. The reaction is apparently—



R = fatty or aromatic radical; T = thienyl radical. Acetophenone reacts in the same way with thienyl magnesium iodide. Michler's ketone yields a green colouring matter possessing all the properties of thiophene, $[C_6H_4—N(CH_3)_2]_2=C(OH).C_4H_3S$.

MEETINGS FOR THE WEEK.

Tuesday, 19th.—Royal Institution, 3. "Why Light is believed to be a Vibration (2) What is it which Vibrates?" by Prof. F. T. Trouton, F.R.S., &c.

Wednesday, 20th.—Microscopical, 8. Exhibition of Microscopical Aquatic Life.

—— Royal Society of Arts, 8. "Industrial Entomology, or the Economic Importance of a Study of Insect Life," by F. Martin Duncan.

Thursday, 21st.—Royal Institution, 3. "The Chemistry of Photography" by Alexander Scott, F.R.S., &c.

—— Royal Society of Arts, 4.30. "The United Provinces of Agra and Oudh," by Sir James Digges La Touche, K.C.S.I.

—— Chemical, 8.30. "Hydroaromatic Ketones," by A. W. Crossley and C. Gilling. "Titanidihydroxymaleic Acid and the Detection of Titanium," by H. J. H. Fenton. "Some Experiments on Carbon at High Temperatures and Pressures and Apparatus therefor," by R. Threlfall. "The Sulphides and Oxysulphides of Silicon," by I. G. Rankin and S. M. Revington.

Friday, 22nd.—Royal Institution, 9. "Recent Researches in the Structure of the Universe," by Prof. Dr. J. C. Kapteyn, of the University of Groningen.

—— Physical, 5. "The Spectrum Top," by G. P. Sexton. "The Coefficient of Diffusion," by B. W. Clack. "Production of Small Alternating Currents of Variable Frequency suitable for Telephonic and other Measurements," by B. S. Cohen,

Saturday, 23rd.—Royal Institution, 3. "Japanese Prints," by Laurence Binyon.

THE CHEMICAL NEWS.

Vol. XCVII., No. 2530.

THE FREEZING-POINT OF MILK.

A Method of Detecting Adulteration, with some Considerations of Osmotic Pressures.

By W. R. GELSTON ATKINS.

The maintenance of temperature equilibrium in the animal body has long been studied, and its wonderful constancy in health is well known, but it is only in more recent years that the pressure has been considered. The osmotic pressure of blood was shown by v. Koranyi to be constant in health, a rise in pressure being a sure indication of grave disease. He studied the relation between the blood and urine, using the freezing-point method with a Beckmann thermometer to determine the osmotic pressures. A healthy kidney produces urine the osmotic pressure of which is from two to four times that of the blood. It is a great economy in water for an animal to produce this concentrated solution, but for the sake of this saving the animal has to do work against osmotic forces by means of the specialised tissue in the kidneys.

Consider now the production of milk; here no advantage will occur either to parent or offspring by concentrating the product so as to have a greater osmotic pressure than the blood and body generally. Thus it seems extremely unlikely that any special cells will have arisen in the milk glands, during the course of evolution, for the purpose of effecting this useless concentration. Accordingly, it appears reasonable to expect an upper limit to the osmotic pressure of milk, as shown by a maximum depression of freezing-point, this being the osmotic pressure of the blood. In other words, the freezing-point of milk can never lie below that of the blood of the animal producing it. This anticipation has been borne out by the examination of a hundred samples of milk extending over a period of two months.

Inspection of these results shows that the freezing-point of milk is nearly constant, being usually slightly higher than that of blood. Were the osmotic pressure of the milk much less than that of the blood, salts from the body would be driven into it tending to restore equilibrium. The intake of large quantities of water by the animal does not affect the milk, for the blood is kept at a constant concentration by the action of the kidneys, as in such cases they excrete nearly pure water. As the blood is maintained constant, or almost so, there is no reason why drinking large quantities of liquid should affect the concentration of the milk to a greater extent than it affects the concentration of the blood.

Nevertheless, there are undoubtedly greater variations in the milk than in the blood. This is to be expected, for its absolute constancy is not so important to the life of the animal; it is, as it were, accidentally constant, as the cells secreting it are nourished by a liquid, the blood, the osmotic pressure of which is constant. Now even in milk which has not been tampered with in any way cream may be deficient up to a large percentage of the average quantity. These variations are quite beyond the range of any I have met with in freezing-point determinations, and, indeed, such large variations in the osmotic pressure would be hard to account for. Thus it appears that milk deficient in fat may be of quite normal osmotic pressure, as shown by a normal freezing-point. The fat, of course, has no effect at all on the freezing-point, as it is not in solution, but present merely in minute globules.

Specimens of milk were bought daily from various Dublin dairies, and examined. As these were fairly constant in freezing-point, arrangements were made for obtaining specimens of morning and evening milk daily from the same cows. Specimens were supplied by the Lucan Dairy Co., and the values varied very little. The results are tabulated below. The letters denote Dublin dairies.

Date.	N.	L.	A.	C.	K,
Jan. 25..	−0·550	−0·525	−0·520	—	—
Feb. 6..	0·540	0·510	0·520	—	—
7..	0·520	0·530	0·545	—	−0·530
8..	0·540	0·520	0·520	—	0·550
10..	0·550	0·490	0·490	−0·570	0·570
11..	0·530	0·560	0·570	0·595	0·580
12..	0·570	0·570	0·580	0·580	0·535
13..	0·550	0·545	0·560	—	0·555
14..	0·550	0·550	0·545	0·550	0·575
17..	0·58c	0·590	0·555	0·580	—
24..	0·540	0·535	0·545	0·610	—
28..	—	—	—	—	0·570
Mean..	0·55	0·54	0·54	0·56	0·55

Morning and Evening Milk from Four Cows.

	B.		D.	
	6 a.m.	2 p.m.	6 a.m.	2 p.m.
Feb. 24 ..	—	−0·555	—	−0·545
25 ..	−0·535	0·560	−0·570	0·535
26 ..	0·550	0·550	0·540	0·545
27 ..	0·550	0·560	0·550	0·550
28 ..	0·540	0·555	0·555	0·560
29 ..	0·555	—	0·575	—
Mean ..	0·55		0·55	

	J.		S.	
	6 a.m	2 p.m.	6 a.m.	2 p.m.
Mar. 5 ..	—	−0·545	—	−0·560
6 ..	−0·550	0·570	−0·550	0·545
7 ..	0·560	—	0·550	—
8 ..	—	0·545	—	0·530
9 ..	0·560	—	0·540	—
11 ..	0·560	0·540	0·560	0·550
12 ..	—	0·550	0·550	0·550
13 ..	0·560	0·550	0·560	0·550
14 ..	0·560	—	0·560	—
15 ..	—	0·560	—	0·560
16 ..	0·560	—	0·570	—
Mean ..	0·55		0·55	

Dairy Milk.		*Milk of Individual Cows.*	
Mean of N ..	−0·55	Mean of B ..	−0·55
„ L ..	0·54	„ D ..	0·55
„ A ..	0·54	„ J ..	0·55
„ C ..	0·56	„ S ..	0·55
„ K ..	0·56		

Mean of all the samples (96) .. .. −0·55° C.

Thus, the mean freezing-point of cow's milk is −0·55° C., and the value does not usually vary by more than −0·03° C. above or below. Occasionally it may fall to −0·61° C., but not below −0·62° C., the freezing-point of cow's blood; the extreme variation on the other side met with was −0·49° C., which is 0·06° C. above the mean, just as much as the lower limit observed differs from it.

Application of the Freezing-point Method to Detection of Added Water.

It is possible to be perfectly certain whether a sample of milk is genuine by determining its specific gravity and freezing-point, unless it has been scientifically faked so as to give a correct result for the total solids, other than fat or casein, as ordinarily determined. For if the milk is undiluted and unskimmed, both values will be correct; if it is skimmed, the specific gravity will be too high, but the freezing-point will be unaffected, as fats have no effect

upon this; if, however, water has been added to bring the specific gravity to the correct value, the freezing-point will be too high; *i.e.*, will be closer to 0·00° C., the freezing-point of pure water. Water added without skimming can be at once detected by the freezing-point determination, and the amount present quantitatively measured.

Thus, if −0·52° C. were to be taken as the lowest numerical value for pure milk, a sample freezing at −0·44° C. would clearly contain the same amount of solids as normal milk, but in a volume of water −0·52/0·44 of the normal amount, 8 of water to 44 of milk, an addition of 18·2 per cent of water.

With a little practice the freezing-point determination can be carried out very rapidly; four samples were examined in fifty minutes on one occasion, two of the determinations being repeated a second time. The apparatus used was the ordinary one, Raoult's, with a Beckmann thermometer. The small error in the zero, owing to the glass of the thermometer bulb not having contracted fully when determinations are made rapidly, may be avoided by determining the scale reading corresponding to the freezing-point of pure water under exactly similar conditions as to degree and time of cooling. All measurements should be made on a rising column of mercury, when the liquid freezes and rises to its true freezing-point after supercooling. The best temperature for the freezing mixture employed is −5° to −6° C., as supercooling will then occur in the milk, but not to too great an extent.

Summary.

The mean freezing-point of cow's milk is −0·55° C.; the variations from this only rarely exceed 0·03° C., above or below the mean. The freezing-point of cow's blood is −0·62° C.

The determinations of the freezing-point and specific gravity of a sample of milk are sufficient to show, on the one hand, whether it has been diluted with water, and, on the other, whether fat has been removed. The freezing-point of milk is not affected by the presence or absence of fats.

University Chemical Laboratory,
Trinity College, Dublin.

THE

PREPARATION AND BEHAVIOUR OF POLONIUM.

By F. GIESEL.

I. *Preparation of Polonium.*

As polonium is known to be a derivative of radium, radium salts, if they are old enough, must be the best and purest material for its preparation. As a matter of fact, even before I knew of this relation, I had succeeded in precipitating polonium from pure radium solutions on metallic bismuth or platinum (*Ber.*, 1903, xxxvi., 2369). Later, I obtained polonium by precipitation with sulphuretted hydrogen. The invisible precipitate is retained by filter-paper, which then shows the effects of the best polonium.

Radium mother-liquors (resulting from the crystallisation of barium radium bromide) contain other active impurities besides the decay products of radium (*Ber.*, 1902, xxxv., 3611). With sulphuretted hydrogen a distinct precipitate is obtained, consisting chiefly of lead sulphide. When this is treated with hot concentrated hydrochloric acid the polonium goes into solution. In the residual lead chloride (mixed with undecomposed sulphide) there is another active substance; it is not polonium, and possesses a constant β-radiation. Evidently the lead chloride, which was previously obtained from radium mother-liquor, and which I sent to Demarçay in 1901 for spectroscopic examination, contained the same substance (*Ber.*, 1902, xxxv., 102). Recently, I proved the absence of radium in a similar preparation much more clearly than Demarçay could with the spark spectrum, by showing that its emanation is not present. It might be supposed that Radium D was in equilibrium with Radium E and Radium F, but a piece of copper immersed in the hydrochloric acid solution showed so little α-radiation—which bore no relation to the strong β-radiation of the preparation and the Radium D it was supposed to contain—that an unknown substance with a long duration of life seems to be present. This can be proved only by a further investigation.

To prepare larger quantities of polonium, we have, as before, to fall back upon the lead from pitchblende. In the middle of 1900 I first showed (*Ber.*, 1900, xxxiii., 1667; see also the subsequent articles on Polonium) that both α- and β-radiating polonium (thus, Radium E and Radium F) can be obtained from this lead, either by dissolving the lead chloride in water and using the insoluble residue, or by extracting the lead chloride with hydrochloric acid. These two methods always seemed to me the best, especially when it is remembered that most of the polonium is carried down with the barium-radium-lead sulphate.

At the beginning of 1907 I had about 40 kilogrms. of this lead chloride at my disposal. There was, undoubtedly, a considerable amount of polonium in it because a specimen reduced to metallic lead by means of carbon made a zinc sulphide screen scintillate. Radium, which was still present in traces in the lead chloride did not go over into the regulus, as Elster and Geitel showed (*Zeit. Phys. Chem.*, 1906, vii., 841).

The working up of the product was completed in about two months. The lead chloride was first dissolved in water, freed from the small quantities of insoluble substances, and a little dilute sulphuric acid was added to remove the radium as far as possible. (The polonium was obtained from this precipitate separately). The lead solution was then precipitated with ammonia, the precipitate digested with a large excess of pure concentrated hydrochloric acid, and the acid liquid was separated from lead chloride. The lead chloride, which separated in a fine state of division, was again subjected four or five times to the same extraction with pure hydrochloric acid. All the hydrochloric acid liquors were concentrated separately, and again concentrated after the removal of the lead chloride which crystallised out.

Sulphuretted hydrogen precipitated from the first extracts some grms. of a mixture of arsenic, lead, bismuth, copper, and traces of mercury. The subsequent extracts gave smaller precipitates consisting almost entirely of copper. (Only traces of radium were present in the last two extracts). After extraction of the sulphides with ammonium sulphide the lead-bismuth-sulphide was split up by boiling with concentrated hydrochloric acid, and the bismuth was precipitated as oxychloride, while the copper was obtained almost pure as undecomposed sulphide.

It was found that in these circumstances very little polonium (but much Radium E) goes over into the bismuth, and much more very pure polonium remains behind with the copper sulphide. If the copper sulphide is decomposed by nitric acid, and the solution is saturated with ammonia, the polonium is precipitated in the form of a few hardly visible white flakes, which, when collected on a filter and dried, leave behind a thin yellowish grey deposit.

II. *Behaviour of Polonium.*

The new precipitate is more active than deposits of polonium on metals. It is specially noteworthy that it causes strong ozonisation of the air with luminescence, besides bright phosphorescence of the zinc sulphide screen. This shows clearly the great purity of the preparation, as otherwise the α-particles could not appear in quantity. The paper near the precipitate is decomposed in a few days in such a way that the deposit can easily be removed with a knife. With two or three drops of hydrochloric acid a yellow-brown solution is obtained, like platinum chloride, which becomes colourless when an oxidising agent, *e.g.*, nitric acid or hydrogen peroxide, is added. I have already noticed this colouration of solutions containing much polonium in hydrochloric acid, and regard it as an indica-

tion of the presence of a good preparation. I have not made a statement on the subject before, because the polonium itself could not cause the colouration, for then it must disappear on immersing metallic bismuth in the solution, with the removal of the polonium. My suggestion that traces of vanadium and iron were carried down could not be absolutely disproved, owing to the difficulty of analysing such small amounts of costly substances, but from the method of preparation such large quantities of impurities, especially in new preparations, are not likely to be present. I am rather of the opinion that the colouration is connected with Radium D which in all probability is contained in the polonium preparation. This is shown by the fact that after a piece of bismuth has been made active, four pieces of copper one after the other, at intervals of about one month, can be made strongly active in the same solution. The intermediate product, Radium E, must undoubtedly have caused a considerable amount of β-radiation in the solution, but no sign of it was to be detected with the Röntgen screen.

The strip of bismuth turned brown or blue in the solution, like steel when tempered; it was used by Stark and Giesel for physical investigations (*Zeit. Phys. Chem.*, 1907, viii., 580). The deposit was on both sides, 2 cm. long and 4 mm. broad, and produced between two connected metallic plates, 3·5 cm. long and 2 cm. broad, facing one another at a distance of 2·2 cm., a current of $1{\cdot}3 \times 10^{-6}$ ampères with a difference of potential of 440 volts.

On the (polished) copper foil, besides corrosion, there appeared only a light greyish white film, so slight that the colour of the copper was hardly affected by it. Platinum was absolutely unaltered, although it also showed intense activity.

No relationship to tellurium could be discovered.

No helium could be detected in two-year-old vacuum tubes containing polonium.—*Berichte*, 1908, xli., 1059).

THE FERTILISING VALUE OF SNOW.

By FRANK T. SHUTT, M.A., F.I.C.,
Chemist, Dominion Experimental Farms.

In the month of February last analyses were made of certain river ices for the purpose of determining their relative purity. The blocks of ice examined were from 18 to 22 inches in thickness, the upper or first 6 to 7 inches forming a well-marked layer characterised by a somewhat porous structure and a certain opacity. Beneath this layer the ice was perfectly hyaline. The analysis of this surface layer revealed the fact that its free ammonia was considerably higher than that of the rest of the ice, and this fact, though explained in some degree by the well-known observation that purification during freezing results, in the case of thick ice, in the lower layers being purer than those nearer the surface, suggested the presence of snow in the ice, and that this snow possessed a high ammonia content. That the snow, if present, must be *in* and not *on* the ice was assured by removing from the surface all loosely attached snow before cutting the blocks from the river.

Our search for analyses of snow in Canada was not successful; apparently no such data are on record. The writer thought therefore that a chemical examination of the snow might furnish results that would prove interesting, especially from the agricultural standpoint, since the greater part of such nitrogen compounds as the snow contains must eventually serve to fertilise the soil.

The collection of the snow samples examined was made in the Arboretum of the Central Experimental Farm, an area of 65 acres devoted to the growth of trees and shrubs. The farm, comprising about 465 acres, is situated on the confines of the city of Ottawa, between the Ottawa and Rideau Rivers, and about 3 miles south-west from the General Post Office. The atmosphere of this locality, while naturally not free from smoke, may be considered as fairly pure—for Ottawa is not a city characterised by "tall chimneys," and besides the few residences on the farm there is only a single line of a little used railroad in the immediate vicinity.

Snow had lain since November, and this examination did not commence till nearly the end of February, consequently data cannot be presented in this paper for the snow-fall of the whole season of 1906-07. With the exception of the first collection, which represents the surface 1½ inches of the accumulated snow, the samples submitted to analysis were all freshly fallen snow, care being exercised to collect either during the snow-fall or within a few hours of its cessation. The snow was allowed to melt at room temperature (about 70° F.), in a clean covered glass vessel. Not one of the samples, as taken, appeared in the slightest degree dirty or soiled, all to the eye at the time of the collection were of the purest whiteness; nevertheless, on melting there was on the surface of the resulting water or clinging to the sides of the vessel a certain amount of sooty material, and frequently also there was a slight deposit.

The determinations made comprised nitrogen present as free ammonia, albumenoid ammonia, and nitrates and nitrites.

The tabulated data are as follows:—

Nitrogen (Parts per Million).

Date of collection. 1907.	As free ammonia.	As albumenoid ammonia.	As nitrates and nitrites.
February 21	0·243	0·045	0·136
February 25	0·276	0·078	0·300
March 4	0·161	0·044	0·170
March 4 (twelve hours after preceding) ..	0·171	0·047	0·170
March 15	0·412	0·045	0·390
March 20	0·284	0·058	0·128
March 25	0·095	0·049	0·111
April 8..	0·140	0·058	0·024
April 10	0·255	0·058	0·107
April 17	0·589	0·066	0·317
April 25	0·360	0·041	0·033
May 4	0·082	0·033	0·065
Average	0·256	0·052	0·163

Total nitrogen (average) = 0·471 part per million.

From the wide fluctuations noticeable in the nitrogen content of these samples it is evident that the condition of the atmosphere of a locality may change both frequently and considerably, though it may also be supposed that the size of the flakes and the temperature of the atmosphere during the fall exert an influence on the filtering and solvent powers of the snow. The writer thought it quite probable that when the period since the preceding snow-fall had been a brief one, say, a day, there would be a smaller nitrogen content than when a longer period, several days or a week, ensued, but the data do not show that this was always the case. Nor did we find any marked differences in purity between samples collected at the beginning and towards the close of the same snow storm, though in this matter we can only present data from one fall, that on March 4. Next winter we hope to obtain further results on this and one or two related points.

Of the total nitrogen, that of the free ammonia constituted the greatest part, that of the albumenoid ammonia the least; the nitrogen in the form of nitrates and nitrites occupies an intermediate position. This order is not invariably maintained, and in a few instances we further notice that the nitrates and nitrites are exceptionally high.

The total snow-fall at Ottawa for the winter 1906-07 was 85·5 inches, the amount per month being as follows:—

November, 1906	.. ..	7·75 inches
December „	.. ..	21·75 „
January, 1907	.. ..	12·50 „
February, „	.. ..	17·25 „
March, „	.. ..	11·50 „
April, „	.. ..	7·25 „
May, „	.. ..	7·50 „

The average snow-fall at Ottawa from data for the past sixteen years is 90·06 inches.

To estimate the amount of nitrogen in the snow-fall per acre, it will be necessary in the first place to accept the assumption that 10 inches of snow are the equivalent of 1 inch of rain, and secondly that the present averages are representative of the whole winter's fall. Since 1 inch of rain over one acre weighs, approximately, 113 tons 600 lbs., we have had, per acre, during the winter, 968 tons 1430 lbs. of snow-water. This contained 0·471 part per million of combined nitrogen, which, by calculation, gives 0·912 lb. of nitrogen in the snow over this area. With an average fall of 90 inches and with our present averages, we could state that the winter's snow furnished, approximately, per acre, 1 lb. of nitrogen valuable as a fertiliser.

We must not suppose that the whole of the fertilising, or to speak more correctly, the agricultural value of snow lies in the nitrogen it possesses; nevertheless, we have in these data some support for the widely accepted belief that snow is a direct fertiliser. It is very evident, however, that the value of snow in this respect has been greatly over-estimated by our farmers.

The annual rainfall at Ottawa has averaged for the past sixteen years 26·56 inches, practically three-fourths of the whole precipitation. If we assume that its nitrogen content is approximately that of the snow, we have a total of about 4 lbs. of combined nitrogen furnished per acre annually from the atmosphere, an amount very similar to that found in other countries.

In concluding this preliminary note on the snow as it falls at Ottawa, it may be stated that this work, it is hoped, will be continued next winter, and that during the next summer the nitrogen content of the rain will be ascertained. The present data are interesting, but their value will be much enhanced by further results of a confirmatory character.—*Transactions of the Royal Society of Canada*, [3], i., p. 35.

SOME NEW COMPOUNDS OF INDIUM.

By F. C. MATHERS and C. G. SCHLUEDERBERG.

THIS paper describes the preparation and properties of four new compounds of indium: the perchlorate, the iodate, the selenate, and the cæsium-selenium alum.

Indium Perchlorate, $In(ClO_4)_3.8H_2O$.—Metallic indium was dissolved in dilute perchloric acid. This solution was evaporated upon a hot plate to a concentration such that when cooled in a mixture of ice and salt, small crystals were formed. The beaker was then placed in a vacuum desiccator containing concentrated sulphuric acid, where the crystallisation continued in a satisfactory manner. The crystals were rapidly rinsed with a small amount of water, dried on filter-paper, and then placed in the vacuum desiccator for a short time.

The metallic indium that was used had been deposited electrolytically, and then fused in a charcoal crucible in a current of hydrogen. This fusion was necessary to remove salts that were occluded from the electrolyte. The perchloric acid that was used was purchased from Schuckhardt. It contained a small quantity of sulphuric acid, which was removed by the addition of the proper amount of barium hydroxide.

Two different methods were used to determine the indium in the indium perchlorate. The shorter procedure consists in heating the sample to a temperature of about 200°, at which decomposition of the perchlorate takes place, then evaporating with nitric acid, and finally igniting the nitrate to the oxide. In the other method the indium is precipitated as the hydroxide with ammonium hydroxide, and is weighed as the oxide. The second method is preferable, since it permits determinations of both the indium and the chlorine (ClO_4) in the same sample. To determine the chlorine, the filtrate from the indium hydroxide was treated with an excess of sodium carbonate and a few drops of potassium permanganate. It was then evaporated to dryness on a water-bath, and heated to near fusion, this treatment decomposing the perchlorate and yielding a chloride. The mass was dissolved in dilute nitric acid, and the solution was freed from the insoluble manganese dioxide by filtration. The chlorine in the filtrate was precipitated and weighed as silver chloride.

	Theory for $In(ClO_4)_3.8H_2O$ (per cent).	Found (per cent).		
Indium oxide .	24·92	24·82	24·73	24·83 (*a*)
Chlorine.. ..	19·08	19·05	18·67	—

(*a*) Determined by Method 1.

Attempts to make direct determinations of the water were unsuccessful on account of decomposition and the formation of a basic salt with a loss of chlorine. Samples of the crystals that had been dried for several hours in the vacuum desiccator gave higher values for the indium oxide, 25·4 and 25·7. These values agree with the theory for $In(ClO_4)_3.7H_2O$. This is evidently due to the loss of water of crystallisation, since several different samples that were dried for only a few minutes gave results that showed eight molecules of water.

Indium perchlorate is a colourless crystalline deliquescent compound that is soluble in water and in absolute alcohol, but much less soluble in ether. It easily forms saturated solutions in water. Basic salts are precipitated from a neutral water solution when the temperature is raised to 40°. When heated in the open air, the crystals fuse at about 80°, but do not form a clear liquid. When the heating is carried to a higher temperature, but not to a red heat, the substance decomposes with a liberation of chlorine. The residue is insoluble in water, but is easily soluble in dilute nitric acid, and this solution gives a strong test for chlorine.

Indium Iodate, $In(IO_3)_3$.—Anhydrous indium trichloride was prepared and sealed off in a glass tube by a method previously described (Mathers, *Journ. Am. Chem. Soc.*, 1907, xxix., 485). Potassium iodate was re-crystallised twice from water. This sample was analysed by treating it with dilute sulphuric acid and potassium iodide, and titrating the iodine that was liberated. Taken, 0·0750 grm. KIO_3; found, 0·0749 grm.

Equivalent quantities of the indium trichloride and of potassium iodate were dissolved separately, and then mixed. A precipitate formed immediately, but it showed no crystalline structure when examined with a microscope. The entire solution was evaporated to dryness upon a water-bath, and the residue was collected upon a Gooch crucible, and was thoroughly washed with cold water. (This is the method employed in his research upon iodates by A. Ditte, *Ann. Chim. Phys.*, 1890, [6], xxi., 145). The crucible and contents were dried over sulphuric acid in a vacuum desiccator. Analyses of several samples prepared in this way did not give constant results. The substance was then dissolved in boiling nitric acid (1 : 10 by volume). On evaporation of this solution, the indium iodate separated in imperfect broken crystals whose crystal system could not be determined. These crystals were washed with water, and dried in a vacuum desiccator. The results of the analyses were as follows:—

	Theory for $In(IO_3)_3$ (per cent).	Found (per cent).	
Indium oxide..	21·71	21·76	21·93
Iodine	59·53	59·19	59·30
Water at 125° .	0·08		
Loss at 160° ..	(Decomposition, brown colour)		0·40

The indium was precipitated as the hydroxide with ammonium hydroxide, and was weighed as the oxide. The iodine was calculated from the titration with sodium thiosulphate of the iodine that was liberated when a sample was treated with potassium iodide and dilute sulphuric acid.

Indium iodate is a white crystalline anhydrous compound. It is soluble in 1500 parts of water at 20°, and in 150 parts of 1 : 5 nitric acid at 80°. All attempts to grow large crystals from these solutions were unsuccessful. It is soluble in dilute sulphuric acid and in hydrochloric acid, but the latter causes a decomposition with the liberation of chlorine. The crystals decrepitate when heated with a free flame, become brown in colour, and give off iodine vapour. If touched with a red-hot wire they explode, and form a cloud of iodine vapour.

Indium Selenate, $In_2(SeO_4)_3.10H_2O$.—Indium selenate was prepared by dissolving indium hydroxide in selenic acid, which had been made according to the following method :—

Flue dust known to be rich in selenium was heated in a porcelain dish with a strong solution of potassium cyanide for several hours. On filtering, a clear amber-coloured solution of potassium selenocyanate, KCNSe, was obtained. A current of filtered air was passed through this solution for several hours in order to separate any tellurium that might have been dissolved with the selenium. A small quantity of a dark coloured precipitate that separated was filtered off. The filtrate was cooled to about zero degrees, and cold 50 per cent hydrochloric acid, sufficient to entirely precipitate the selenium, was added, care being taken to add the hydrochloric acid slowly to avoid an appreciable rise of temperature. The selenium is thrown down as a bright red amorphous precipitate, which was filtered off, and thoroughly washed. This was re-dissolved in a 10 per cent solution of potassium cyanide, treated with air, precipitated in the cold as before, filtered off, washed very thoroughly, and dried.

The selenium was then dissolved in concentrated nitric acid, and the solution evaporated to dryness on the water-bath, re-dissolved in very dilute hydrochloric acid, and again evaporated to dryness. The selenium dioxide thus obtained was dissolved in a little water, and added to chlorine water, through which a stream of chlorine was allowed to bubble, thus oxidising the selenium dioxide to selenic acid. After being thus treated for several hours with chlorine the liquid was freed as far as possible from excess of that gas by passing through it a current of air.

The solution of selenic acid was neutralised with copper carbonate and freshly precipitated copper hydroxide. The blue solution of copper selenate thus obtained was filtered, concentrated on the water-bath, and set aside to crystallise. Blue triclinic crystals of copper selenate separated. These were re-crystallised from water solution, and again dissolved in water, and the solution freed from copper by electrolysing in a platinum dish at low current density (R. Metzner, *Comptes Rendus*, 1898, cxxvii., 54). Electrolysis was continued until no test for copper could be obtained with either ammonium hydroxide, potassium sulphocyanate, or potassium ferrocyanide in small portions of the solution. The solution of pure selenic acid thus obtained was treated with indium hydroxide. Indium selenate crystallised out in white, easily soluble, hygroscopic crystals. Analysis gave the following results :—

	Theory for $In_2(SeO_4)_3.10H_2O$ (per cent).	Found (per cent).
Indium oxide ..	33·08	32·9—33·0
Selenium	28·30	28·3—28·2

Indium Cæsium Selenate, $CsIn(SeO_4)_2.12H_2O$.—Cæsium-indium-selenate, the alum, was made by crystallising a solution of cæsium selenate (prepared from cæsium hydroxide and selenic acid) and indium selenate.

The alum crystallises in beautiful colourless octahedra, belonging to the tetragonal system, which are soluble in water, efflorescent in the air, and are of the following composition :—

	Theory for $CsIn(SeO_4)_2.12H_2O$ (per cent).	Found (per cent).
Selenium	21·18	21·04
Indium	15·3	15·5
Cæsium	17·7	17·8

In the above analyses the selenium was determined by repeated precipitation with sulphur dioxide gas from a hot dilute solution of the salt. The precipitate was collected on a Gooch filter, and the filtrate was boiled down, and again treated with sulphur dioxide. It was found necessary to repeat this operation several times in order to remove all of the selenium from the solution. The Gooch filter was dried at 102—105°, and the selenium was weighed.

The indium was precipitated by ammonium hydroxide as the hydroxide from the hydrochloric acid solution of the salt, collected on an ashless filter, heated in a porcelain crucible, and weighed as In_2O_3.

For the determination of the cæsium, the selenium was first removed, and the cæsium was then precipitated from the chloride solution by chlorplatinic acid, and weighed as cæsium chlorplatinate.—*Journal of the American Chemical Society*, xxx., No. 2.

THE DETERMINATION OF VANADIC AND MOLYBDIC ACIDS IN THE PRESENCE OF ONE ANOTHER.

By GRAHAM EDGAR.

A METHOD has been recently proposed by Glasmann (*Ber.*, xxxviii., 600) for the estimation of vanadic and molybdic acids in the presence of one another, based on the different reducing action of zinc and magnesium upon the hydrochloric acid solution of these acids. In a previous paper from the Kent Chemical Laboratory of Yale University (Gooch and Edgar, *Am. Journ. Sci.*, xxv., 233) it has been shown that the action of magnesium is irregular, and not adapted to an accurate quantitative method. Vanadic acid, however, is reduced to the state of dioxide by a column of amalgamated zinc, and may be estimated by titration with potassium permanganate, if the receiver be charged with a solution of ferric alum to anticipate the oxidising action of the air (Gooch and Edgar, *loc. cit.*). That molybdic acid is under the same conditions reduced to the state of Mo_2O_3 has been shown by Dudley (unpublished, but privately communicated by Prof. Henry Fay), and, independently, by Randall (*Am. Journ. Sci.*, xxiv., Oct., 1907). The ease with which vanadic acid is reduced to the state of tetroxide by sulphur dioxide, and the difficulty, as has been found, with which this reagent attacks molybdic acid under proper conditions of acidity and concentration, suggest its use in one of two processes of differential action for the determination of these acids. To determine the conditions under which molybdic acid is unaffected by sulphur dioxide, a series of experiments was made in which solutions of molybdic acid of varying concentrations, acidified with varying amounts of sulphuric acid, were heated to boiling, and treated with a current of sulphur dioxide for varying lengths of time. The excess of sulphur dioxide was then removed by boiling the solution, a current of carbon dioxide being meanwhile passed into it, and the degree of reduction was determined by titration with nearly N/10 potassium permanganate. The solution of molybdic acid was standardised by the method of Randall (*loc. cit.*), and by evaporating a portion to dryness, and igniting at low red heat. The results of the experiments are given in Table I.

The results show that if the concentration be not greater than 0·2 grm. of MoO_3 in 50 cc. of solution, and the acidity not less than 1 cc. of sulphuric acid (sp. gr. 1·84) in the same volume, the molybdic acid is not reduced, and that if the acidity be increased to 5 cc. of sulphuric acid, reduction does not occur at even a concentration of 0·4 grm. in 25 cc.

Table I.

Volume of solution.	MoO_3.	H_2SO_4 (sp. gr. 1·84).	Time of treatment with SO_2.	$KMnO_4$ N/10 × 1·004.	Colour of solution.
Cc.	Grm.	Cc.	Mins.	Cc.	
25·0	0·200	Faintly acid	10	0·15	Light blue.
35·0	0·200	0·5	10	0·5	Faint blue.
50·0	0·200	1·0	10	—	Colourless.
75·0	0·200	2·0	10	—	,,
50·0	0·200	2·0	30	—	,,
25·0	0·200	5·0	10	—	,,
25·0	0·400	5·0	10	—	,,
50·0	0·400	5·0	10	—	,,
50·0	0·400	10·0	10	—	,,
50·0	0·400	15·0	10	—	,,

Table II.

Ferric alum (10 per cent).	Phosphoric acid syrup.	$KMnO_4$ N/10 × 1·052.	$KMnO_4$ N/10 × 1·052.	V_2O_5 taken as $NaVO_3$.	MoO_3 taken as $(NH_4)_2MoO_4$	V_2O_5 found.	MoO_3 found.	Error on V_2O_5.	Error on MoO_3.
Cc.	Cc.	Cc.	Cc.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
50	8	11·95	74·15	0·1144	0·1930	0·1146	0·1934	+0·0002	+0·0004
50	8	11·95	74·00	0·1144	0·1930	0·1146	0·1926	+0·0002	−0·0004
50	8	11·94	74·20	0·1144	0·1930	0·1145	0·1936	+0·0001	+0·0006
25	4	5·97	37·10	0·0572	0·0965	0·0572	0·0965	—	—
25	4	5·97	37·05	0·0572	0·0965	0·0572	0·0962	—	−0·0003
25	4	5·98	37·12	0·0572	0·0965	0·0573	0·0963	+0·0001	−0·0002
35	6	11·95	55·0	0·1144	0·0965	0·1146	0·0967	+0·0002	+0·0002
35	6	11·95	55·0	0·1144	0·0965	0·1146	0·0967	+0·0002	+0·0002
35	6	11·96	54·86	0·1144	0·0965	0·1147	0·0958	+0·0003	−0·0007
65	10	17·92	92·0	0·1716	0·1930	0·1719	0·1931	+0·0003	+0·0001
65	10	17·94	92·05	0·1716	0·1930	0·1720	0·1931	+0·0004	+0·0001
65	10	17·92	92·02	0·1716	0·1930	0·1719	0·1932	+0·0003	+0·0002

A series of experiments was then made in which solutions containing vanadic and molybdic acids were diluted to 75 cc., acidified with 2 to 3 cc. of strong sulphuric acid, heated to boiling, and subjected to a current of sulphur dioxide for a few minutes until the clear blue colour indicated the complete reduction of the vanadic acid to the state of tetroxide. The boiling was continued for some time, a current of carbon dioxide being passed into the liquid until the last traces of sulphur dioxide had been removed. Titration was then effected by nearly N/10 potassium permanganate, and the vanadic acid was calculated from the equation,—

$$5V_2O_4+2KMnO_4+3H_2SO_4 = 5V_2O_5+K_2SO_4+MnSO_4+3H_2O.$$

The solution, preceded by 100 cc. hot water and 125 cc. of dilute (2½ per cent) sulphuric acid, and followed by 100 cc. dilute sulphuric acid, and 200 cc. of hot water, was passed slowly through a column of amalgamated zinc in a Jones reductor ("The Chemical Analysis of Iron," Blair, p. 225), the receiver containing a solution of ferric alum. The hot solution was then titrated with nearly N/10 potassium permanganate, a little phosphoric acid being added to decolorise the ferric salt.

Since the reduction of vanadic acid is in this case to the condition of dioxide, V_2O_2, if the number of centimetres of permanganate used in the titration of the tetroxide be multiplied by three and the product subtracted from the total number of centimetres of permanganate used in the final titration, the result is the number of centimetres used in oxidising Mo_2O_3 to MoO_3, from which the amount of molybdic acid present may be easily calculated. The results, given in Table II., show that molybdic acid and vanadic acid may be accurately estimated in the presence of one another by two processes of reduction and oxidation, the reduction being made first by sulphur dioxide and last by amalgamated zinc.

In conclusion, the author desires to thank Prof. F. A. Gooch for many kind and helpful suggestions and criticisms during the progress of the work.—*American Journal of Science*, xxv., p. 332.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 2nd, 1908.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

(Concluded from p. 237).

81. "*The Hydrolysis of Amygdalin by Emulsin.*" Part I. By Samuel James Manson Auld.

By means of specially devised apparatus, the hydrolysis of amygdalin by emulsion has been studied in detail by estimating the hydrocyanic acid produced during the reaction. It has been shown that Jorissen and Hairs' "emulsin" is really a mixture of two enzymes, namely, true emulsin and a maltase-like ferment. The effect of varying the concentration of amygdalin and emulsin has been investigated, as also the action of many inhibitants. Of particular importance is the fact elucidated that the activity of emulsin is intimately bound up with basic and acidic groups, as both acids and alkalis only render the ferment inactive and do not destroy it except in high concentrations. Contrary to the statements of Tammann, the decomposition of amygdalin by emulsin nearly approaches completion, as much as 97 per cent of the available glucoside being decomposed as measured by the hydrocyanic acid formed. The end-point of the reaction has been found to be independent of the temperature, and the temperature-coefficients of the action have been measured over a range of 45°.

82. "*Complex Nitrites containing Potassium and Lead.*" (Preliminary Note). By Andrew Norman Meldrum.

The reaction between potassium nitrite and a lead salt (which may be the acetate, nitrate, chloride, bromide, or iodide) results in the production of complex-compounds, which, in addition to potassium, lead, nitrosyl, and water, may contain one or more equivalents of the negative ion with which the lead was originally associated. The

products vary in colour from bright yellow to orange, and they contain potassium and lead, as a rule, in the atomic ratio of 3 : 2.

In attempting to prepare the compound $K_2Pb(NO_3)_2,(NO_3)_4,H_2O,(KO.NO_3.PbO.NO_5 + HO$ (Hayes; *Quart. Journ. Chem. Soc.*, 1860, xiii., 335), the author finds that the product has always the composition, approximately, if not exactly, $K_2Pb(NO_2)_3NO_3,H_2O$.

Metallic lead is more easily attacked by solution of lead nitrate to which potassium nitrate has been added than by lead nitrate solution alone.

83. "*The Composition and Formula of Wells' Potassium Lead Periodide.*" By ANDREW NORMAN MELDRUM.

A potassium lead periodide has been described by Wells (*Am. Journ. Sci.*, 1893, xlvi., 190), who assigned to it the formula $K_3Pb_2I_{8,4}H_2O$, analogous to that of the perbromide, $K_3Pb_2Br_{8,4}H_2O$, described in the same paper. Actually, the analyses of six different preparations of the substance were in good agreement with one another, and with the formula $K_9Pb_4I_{19,10}H_2O$. In arriving at the formula $K_3Pb_2I_{8,4}H_2O$, Wells made the assumption that the material analysed was "contaminated with about 16·5 per cent of potassium iodide, and that an excess of water was present, possibly on account of the hygroscopic properties of that salt."

Potassium iodide (150 grms.), lead iodide (4 grms.), iodine (70 grms.), and water (90 cc.) were mixed, and the mixture was slowly heated to the boiling-point and filtered to remove any undissolved lead iodide. After some time, crystals separated, which were collected, drained on a porous tile, and exposed to the air until the odour of iodine was very faint. The product consisted of shining *violet* prisms, not unlike potassium permanganate, and hardly corresponded with Wells' "brilliant *black*, prismatic crystals."

The substance was analysed by methods different from those used by Wells. The lead and potassium were determined together as the sulphates, and the lead separately as chromate. Thiosulphate solution was used to determine (1) the total iodine (after addition of sulphuric acid and ferric alum, with subsequent distillation), and (2) the "extra" iodine. Water and "extra" iodine were determined together as loss on heating at 100°.

Found: mixed sulphates = 53·14, 52·97; Pb = 21·71, 21·67; total iodine = 64·19; "extra" iodine = 6·76, 6·81; loss at 100° = 11·33, 11·04.

$K_9Pb_4I_{19,10}H_2O$ requires mixed sulphates = 52·97; Pb = 21·95; total iodine = 63·96; "extra" iodine = 6·74; loss at 100° = 11·52 per cent.

Potassium iodide, if present in a mixture to the extent of 16·5 per cent, the assumption which Wells makes, would surely be visible to the naked eye, but the material which the author analysed, when examined under the microscope, had all the appearance of a single substance, and it was not hygroscopic. The formula of the periodide is therefore $K_9Pb_4I_{19,10}H_2O$, and it is probable that Wells, in assigning similar formulæ to the perbromide and the periodide, was led astray by the desire for uniformity.

84. "*The Molecular Complexity of Amides in various Solvents.*" By ANDREW NORMAN MELDRUM and WILLIAM ERNEST STEPHEN TURNER.

The authors have determined the molecular complexity by the boiling-point method of eleven amides, namely, benzamide, salicylamide, acetanilide, benzanilide, acetamide, monochloroacetamide, dichloroacetamide, trichloroacetamide, trichlorolactamide, carbamide, and malonamide in six solvents, so far as the solubility of the amides would allow (compare *Proc.*, 1907, xxiii., 165). The Lumsden-Walker apparatus was employed, and the boiling-points were specially corrected for the mere pressure effect of the accumulation of liquid in the boiling tube. The following table summarises the results, and includes also the dielectric constants of the solvents :—

A. Number of amides investigated.
B. Number of amides which form simple molecules.
C. Number of amides which form associated molecules.
D. Dielectric constant of solvent.

Solvent.	A.	B.	C.	D.
Benzene . .	8	1 doubtful	7	2·3 at 18°
Ether	5	1	4	4·4 at 18°
Chloroform . .	9	2	7	5 at 22°
Acetone . .	10	9	1	25 at 20°
Alcohol . .	11	9	2 doubtful	26 at 20°
Water	9	4 and 1 doubtful	4	80 at 17°

Except in the case of water, these results are in good accordance with the Nernst-Thomson theory that the smaller the dielectric constant of the solvent the greater is the association of the solute. Association in ether tends to be less than in benzene and much the same as in chloroform, just as would be inferred from the dielectric constant. Ether has hitherto been regarded as a non-associating solvent. In investigations into the physical properties of the amides and allied compounds, the most suitable solvent is alcohol, in which association is at a minimum.

Benzamide, salicylamide, acetanilide, and dichloroacetamide, the only instances of the kind known to the authors, have a greater molecular complexity in water than in alcohol. This is quite contrary to what would be expected from the Nernst-Thomson theory.

85. "*The Optical Activity of Compounds having Simple Molecular Structure.*" By WILLIAM JACKSON POPE and JOHN READ.

The authors described crystalline salts formed by chlorosulphoacetic acid and chlorobromomethanesulphonic acid with the optically active alkaloids, strychnine and quinidine. The two acids each contain an asymmetric carbon atom in the molecule, but, although their strychnine and quinidine salts crystallise well, no evidence was obtained that the acids are resolvable into enantiomorphously related components.

86. "*Acetylketen : a Polymeride of Keten.*" By FRANCES CHICK and NORMAN THOMAS MORTIMER WILSMORE.

It has been shown (*Nature*, 1907, lxxv., 510; *Trans.*, 1907, xci., 1938) that keten, both in the liquid and the gaseous states, condenses at the ordinary temperature to form a pungent-smelling, brown liquid. The latter has now been further studied. On distillation, a colourless liquid passes over, leaving a brown, non-volatile residue. This liquid boils at 126—127°, and solidifies in a freezing mixture to a white solid, which melts at −7° to −6°. It has an extremely pungent smell, suggestive both of acetic anhydride and of acrolein. On standing, even in absence of air, it slowly turns brown. Analysis gave C = 56·9, H = 5·0, whilst the depression of the freezing-point of benzene and the vapour density, determined by Gay Lussac's method, agreed in giving a molecular weight of nearly 85, showing that the substance has the composition $C_4H_4O_2$, which requires C = 57·1; H = 4·8 per cent M.W. = 84.

The liquid dissolves slowly in water, forming a strongly acid solution, which gives a violet colour with ferric chloride; on boiling the aqueous solution, carbon dioxide and acetone (recognised by the iodoform, benzaldehyde, and alkaline mercuric chloride reactions) are formed, and the solution becomes neutral. Hydrogen chloride facilitates the dissolution and decomposition. On boiling the substance with aqueous alkalis, acetates are formed, hence the substance combines with water to form acetoacetic acid. It reacts vigorously with aniline, forming acetoacetanilide melting at 84°.

The new substance is therefore *acetylketen*, having the formula $CH_3{\cdot}CO{\cdot}CH : CO$ or $CH_2 : C(OH){\cdot}CH : CO$.

It reacts with two molecular proportions of phenylhydrazine, forming the colourless *phenylhydrazone-phenylhydrazide*, which melts at 152—153°.

87. "*Saponification of Ethyl Formate by Water in presence of Acids as Catalytic Agents.*" By Arthur Lapworth.

Some statements in a recent paper by Stieglitz (*Am. Chem. Journ.*, 1908, xxxix., 402) have led the author to re-examine a suspicion, which he had some reason to entertain some six years ago, but which he did not then succeed in fully confirming. In recent experiments the velocity of saponification of ethyl formate in acetone solution has been measured, hydrogen chloride being used as catalyst, and the water being present in quantity small enough to be comparable with that of the ester.

Set I.—A = 10 cc. ethyl formate, 2 cc. water, made up with acetone to 50 cc. B = 10 cc. ethyl formate, 5 cc. water, made up with acetone to 50 cc.

Titre of 5 *cc.*

t = Hrs.	Mins.	A = Cc.	B = Cc.
0	0	(4·8)	(4·8)
0	4	6·1	6·55
0	10	7·5	7·4
0	27	10·45	9·75
0	59	16·35	15·2
2	58	36·3 ?	28·50 ?
6	28	41·40	42·4
22	30	43·2	57·0

Set II.—C = 10 cc. ethyl formate, 5 cc. water, made up with acetone to 50 cc. D = 10 cc. ethyl formate, 10 cc. water, made up with acetone to 50 cc.

Titre of 5 *cc.*

t = Hrs.	Mins.	C = Cc.	D = Cc.
0	0	(2·5)	(2·5)
0	1	2·7	2·5
0	6	3·3	3·0
0	29	5·85	5·75
2	0	16·05	15·8
9	18	51·0	48·9
21	9	62·6	72·5

Set III.—E = 5 cc. ethyl formate, 5 cc. water, made up with acetone to 50 cc. F = 10 cc. ethyl formate, 5 cc. water, made up with acetone to 50 cc.

Titre of 5 *cc.*

t = Hrs.	Mins.	E = Cc.	F = Cc.
0	0	(4·0)	(4·0)
0	2	4·15	4·4
0	25	6·7	8·45
0	54	9·65	15·10
1	5	11·1	17·95
1	31	14·4	25·45
6	20	32·8	58·7
18	50	42·8	65·1

The alkali used was about N/10, but was somewhat stronger in the case of Set I. The numbers in parentheses indicate about the amount of each titre due to hydrochloric acid used as catalyst in each set.

The results show clearly enough that, in the circumstances specified, the velocity of saponification is nearly independent of the concentration of the water present during a considerable part of the change, but that, when the mixture approaches equilibrium conditions, divergence is noticed for the first time.

Stieglitz has shown (*loc. cit.*, p. 417) that his own theory leads to the expression—

$$\frac{dx}{dt} = K \times k \times C_{ester} \times C_H \times [C_H \times C_{OH}]$$

or—

$$= \text{proportional to } C_{ester} \times C_H^{\cdots} \times C_{water},$$

and is therefore incorrect.

This chemist is also incorrect in asserting that the author's own theory (Mellor, "Chemical Studies and Dynamics," p. 289) fails to account for the catalysis of esters by hydrogen ions; it remains the only theory in accordance with the facts, in spite of Stieglitz's remarks on the velocity of "salt formation" (*loc. cit.*, p. 425). It accounts for the dependence of the equilibrium condition on the concentration of the water, and the independence of the initial velocity of hydrolysis on that factor.

The author intends to continue with his colleague the above work, and to study the influence of the concentration of alcohol and carboxylic acid on the velocity of esterification, as well as a number of analogous cases in which the influence of the substance generally used as solvent is not fully understood.

88. "*The Triazo-group.* Part III. *Bistriazo-Derivatives of Ethane and of Acetic Ester.*" By Martin Onslow Forster, Hans Eduard Fierz, and Walter Philip Joshua.

1 : 2-*Bistriazoethane*, $N_3 \cdot CH_2 \cdot CH_2 \cdot N_3$, prepared from ethylene dichloride and sodium azide, is a colourless, refractive liquid which boils at 53° under 9 mm. pressure, and has sp. gr. 1·178 compared with water at 19°; the odour resembles that of chloroform, and the vapour is explosive. Stannous chloride liberates two-thirds of the nitrogen, giving ethylenediamine; alcoholic alkali does not set free nitrogen, but slowly eliminates hydrazoic acid.

The *compound*, $C_{14}H_{16}N_6$, which probably has the constitution $C_6H_5 \cdot NH \cdot N : N \cdot CH_2 \cdot CH_2 \cdot N : N \cdot NH \cdot C_6H_5$, arises by the action of magnesium phenyl bromide on 1 : 2-bistriazoethane, and crystallises from petroleum in lustrous, square plates with brown tinge; it melts at 128°, evolving gas with vigour. Dilute mineral acids liberate two-thirds of the nitrogen, producing aniline.

Bistriazoacetic ester, $CH(N_3)_2 \cdot CO_2 \cdot C_2H_5$, produced from dichloroacetic ester and sodium azide, is a colourless liquid which boils at 70—72° under 2 mm. pressure, and has sp. gr. 1·222 compared with water at 18°; the odour is scarcely perceptible. The ester is highly explosive, and liberates nitrogen explosively when treated with sulphuric acid. Hydrazoic acid is eliminated by alcoholic ammonia, consequently bistriazoacetamide could not be obtained.

PHYSICAL SOCIETY.

Ordinary Meeting, May 8th, 1908.

Dr. Charles Chree, F.R.S., President, in the Chair.

A paper on "*A Modified Theory of Gravitation*" was read by Dr. C. V. Burton.

If we are to regard gravitational attraction as exerted through the medium of the ether, it appears to the author difficult to avoid the conclusion that the very great (or possibly infinite) velocity with which such attractions are propagated is due to the very great (or complete) incompressibility of the ether. This conception is embodied in the pulsatory theories of Hicks, and of subsequent writers; the chief outstanding difficulty has lain in providing for that agreement of phase which must be assumed to subsist amongst the centres of pulsatory disturbance associated with the mutually attracting masses. This difficulty is avoided if we suppose that primary waves of compressional-rarefactional type are being propagated through the ether with a velocity enormously transcending that of light. These primary waves may be travelling in directions indifferently distributed, or predominantly or exclusively in one direction; but an essential point is that all effective wave-lengths should be very great, measured even by astronomical standards. Thus the pressure-changes will be sensibly in the same phase over considerable regions, and if the etherial compressibility is locally increased (or diminished) by the presence of electrically neutral matter, every particle of such matter will act as a centre of pulsatory motion.

For the electron, so far as concerns this modification of etherial compressibility, a specification is assumed which involves no restraint on the free mobility of the electron through the ether. Incidentally the dynamics of the problem assumes a relatively simple form, and a value which could be quite insignificant attaches to a "gravitational (or non-electromagnetic) term" appearing in the expression for the total inertia of an electron.

It has to be shown that, in its primary aspect, the assumed wave-motion would give rise to no observable effects. This, in fact, follows from the assumptions made, and it is only through the feeble secondary effect of gravitation that any evidence of the wave-motion could be obtained.

In attempting to work out the theory on a numerical basis, values have to be found for a considerable number of physical quantities, several of these requiring to be independently conjectured, before the remaining quantities can be determined. But the range of the values which could be reasonably assumed is a good deal more restricted than might be supposed. The author gives a plausible set of values for these physical constants.

Mr. C. S. WHITEHEAD asked if the amount of energy stored in the ether was greater or less than it was in the past.

Prof. C. H. LEES asked if the ether considered was the old one or a new one. He referred to an interesting point in the author's representation of gravitation, namely, that matter was produced by the absence of something from the ether. In the theory advocated by Osborne Reynolds matter was produced by a deficiency in the normal piling, and recent theories seek to explain matter and gravitation by the absence of something which is present in free ether.

Dr. C. V. BURTON, in reply to Mr. Whitehead, said he was not aware whether the amount of energy in the ether varied with time or not.

A paper on "*An Examination of the Formulæ for the Grading of Cables*" was read by Mr. C. S. WHITEHEAD.

In the *Journal of the Institution of Electrical Engineers* both Mr. O'Gorman and Dr. Russell have shown that it would be advantageous if cables for electric lighting were constructed so that the component of the electric intensity along a radius (in cylindrical co-ordinates) was kept constant for all points in the dielectric in the same plane perpendicular to the axis. They both find that to attain this object λr ought to be kept constant if the current is alternating, and σ/r constant if the current is steady, where λ is the specific inductive capacity, σ the specific resistance, and r the distance from the axis. In this paper the question is regarded from a much more general point of view.

Maxwell's two curl relations are taken in cylindrical co-ordinates, and it is supposed, as is quite legitimate, that the electrical and magnetic quantities are symmetrical round the axis, and that they vary as $e^{i(mz+pt)}$. We can then solve the equation, and from the continuity of the tangential components of the electric and magnetic forces obtain an equation to find m.

If P is the component of the electric intensity along a radius, β the component of the magnetic force perpendicular to a radius in a plane perpendicular to the axis, we find—

$$P = -\frac{im}{\frac{4\pi}{\sigma} + \frac{\lambda i p}{c^2}}$$

where c is the ratio of the electrostatic to the electromagnetic unit of electrical quantity. Also if I be the total current in the wire parallel to the axis, and we neglect the displacement-current in the wire in comparison with I, we have—

$$\beta = \frac{2I}{r}.$$

Putting $m = -a+ib$, it is found that $\sqrt{a^2+b^2} = \sqrt{\lambda}.h$, where h involves no quantities which have reference to the dielectric. Taking the real parts and putting P_0 and I_0 for the factors of P and I which are independent of the trigonometrical factor, we obtain—

$$P_0 = 2I_0 e^{-bz} \frac{c^2}{\lambda r} \sqrt{\frac{a^2+b^2}{p^2 + \left(\frac{4\pi c^2}{\lambda\sigma}\right)^2}}.$$

If we suppose I_0, a, b to be constants of the cable which do not vary as we vary λ or σ, we get the rules given by Mr. O'Gorman and Dr. Russell. Thus, let σ be very great, then to keep P_0 constant we must make λr constant, but if $p = 0$, that is for steady currents, we must make σ/r constant. We have seen, however, that $\sqrt{a^2+b^2}$ varies as $\sqrt{\lambda}$, so that in the case of σ very great this process suggests the rule make $r\sqrt{\lambda}$ constant. When $p = 0$ it is shown that $a = 0$ and that b varies inversely as $\sqrt{\sigma}$, so that this case suggests the rule make $\sqrt{\sigma}/r$ constant. The equation for P_0 is, however, strictly true.

Dr. A. RUSSELL complimented the author on his interesting paper and on the skill with which he had handled the mathematical equations. The question of the grading of cables was one of great importance to the electrical engineer, and it was necessary to attack it both from the mathematical and the experimental side. The author took the case of an infinitely long concentric main, and assumed that the amplitude of the current remained constant. In the practical problem the main is of finite length and the amplitude of the applied voltage is constant. The mathematical difficulties in the way of getting a complete solution were great, and so he hoped the author would continue his investigations further. Dr. Russell exhibited a portion of a Jona graded cable which had successfully withstood a testing-pressure of 150 kilovolts applied between the core and the lead sheath. If the dielectric had been air a disruptive discharge would have ensued at 23 kilovolts.

A paper entitled "*Illustrations of Geometrical Optics*" was read by Mr. R. M. ARCHER.

The principles of geometrical optics are frequently illustrated by experiments in which the images of narrow obstacles are obscured by similar obstacles arranged in the line of vision. This method is tedious, and is open to the objection that the path of a shadow is traced rather than that of a beam. The author's method is free from these objections. Light from a narrow rectilinear source is allowed to pass through a slit and fall upon a flat white surface at almost grazing incidence. It is easy to obtain upon the surface a long narrow streak of light with sharp edges; and if a mirror be placed with its plane approximately normal to the surface, another streak corresponding to the reflected ray can be seen. Similarly, the path of the beam after its emergence from a glass block or prism may be traced. Interesting effects can be obtained by using many slits and casting the beam from a distant optical lantern upon them. This mode of illumination is useful in demonstrating the formation of caustics. Quantitative results can be obtained comparable in accuracy with those given by an ordinary optical bench.

The author exhibited a series of slides illustrating various cases of reflection and refraction, and showed also several experiments with the apparatus described in the paper.

Prof. C. H. LEES expressed his interest in the neatness of the experiments, and said the author's method of dividing up a beam was a very useful one.

Mr. A. CAMPBELL congratulated the author, and remarked that the methods described could be applied to other optical experiments. In using a vibration galvanometer or an oscillograph, an easy way to obtain a curve of the wave-form was to put obliquely in the path of the beam a sheet of white paper and vibrate it.

Dr. W. H. ECCLES also congratulated the author upon his paper.

NOTICES OF BOOKS.

The Spectroscope. By T. Thorne Baker, F.C.S., F.R.P.S. London: Baillière, Tindall, and Cox. 1907.

Students of advanced chemistry have undoubtedly felt the want of a text-book on spectrum analysis which explains the use of the spectroscope in analytical work sufficiently fully for all practical purposes, and serves as an introduction to the use of the larger treatises. This want is supplied by this book, which is admirably suited for chemical students with the usual elementary knowledge of physics. The general descriptions of different types of instrument explain their construction and give indications as to the reliability and cost of some of them, and notes on methods of carrying out determinations are also added. These might with advantage be somewhat fuller, though it must be remembered that the use of the spectroscope can only be explained really satisfactorily by a competent teacher to students who have every opportunity of handling and adjusting the instrument themselves. Spectrography is fully treated, and the formulæ for the development of different plates, which in the author's own experiments have been found to be trustworthy, are of special value.

Iron and Steel. By J. H. Stansbie, B.Sc. (Lond.), F.I.C. London: Archibald Constable and Co., Ltd. 1907.

In this book is given a short general review of methods of extracting iron from its ores and of the manufacture of steel, and the reader will be able to learn from it the outlines of every step in the processes, from the preparation of the ore to the treatment of masses of iron and steel necessary to enable the engineer to make use of the metal. A short introduction deals with the elements of chemical theory, but this is so sketchy that, except to the reader who has had some opportunity of previously studying the subject, it is more likely to be confusing than helpful. In the course of the text there is a short explanation of the application of the phase rule to problems in iron and steel chemistry, and this difficult subject is made very clear. The chapter on electric smelting gives an outline of the method of employing the energy of an electric current in these industries. The book is based upon notes used by the author for courses of lectures, and should be specially valuable for technical students to amplify and possibly add interest to their lecture work.

Kurzes Lehrbuch der Organischen Chemie. ("Short Text Book of Organic Chemistry"). By William A. Noyes. Translated into German by Walter Ostwald. Leipzig: Akademische Verlagsgesellschaft. 1907.

The American edition of this book showed great originality in many respects, and beginners have found that it has done much to smooth the path of their early studies in organic chemistry. Unless the student has much more time than is usually possible to spend on his elementary course, he is apt to be somewhat appalled by the mass of material which is put before him, and which appears to make such great demands upon his memory. Later in his work he finds that what appeared isolated facts and phenomena are really only illustrations of general reactions, and order is soon evolved from chaotic disorder in his mind. The author of the text-book, of which this is an excellent translation into German, conceived the plan of reversing the usual arrangement, and of putting before the beginner general reactions first, the individual substances being studied as illustrations of the previously learnt general methods of preparation and transformation. At the end of each chapter suggestions are given for suitable laboratory work in connection with the subject of the chapter. The book is prefaced by an appreciative introduction by Prof. Wilhelm Ostwald, in which he points out its special features, and recommends it as giving a thoroughly logical presentation of elementary organic chemistry.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 13, March 30, 1908.

Phenomena in the Spark Spectrum of Yttrium attributable to Positive Electrons.—Jean Becquerel.—The author has investigated whether the rare earths which, at a low temperature, exhibit phenomena attributable to positive electrons show the same effects at high temperatures. He has detected these phenomena in the spark spectrum of yttrium. In a magnetic field the light emitted parallel to the lines of force traverses a quarter wave plate, followed by a rhombohedron placed in front of the slit of a spectroscope, so that the spectra of two inverse circular vibrations can be observed simultaneously. In these conditions the isolated rays of the rare earths give the Zeeman effect in the usual direction with more or less intensity, but with yttrium two groups of rays do not resemble the isolated rays. These rays, which are situated in the orange, have been observed by Thalén, who regards them as characteristic of yttrium. They have also been studied by Urbain. In a spectroscope of feeble dispersion they appear as flutings, but with a grating a series of asymmetric rays appears, each possessing a sharp edge towards the violet, and a more indistinct edge, followed by a diminishing light towards the other side. They follow one another regularly at intervals of 1·6 to 1·8 $\mu\mu$, increasing slightly with the wave-length, and their intensity decreases as the wave-length increases. The most marked rays have wave-length 597·05 $\mu\mu$ and 613·10 $\mu\mu$, and they form two groups. Those of the second group give the Zeeman effect in the usual direction, while those of the first exhibit the phenomenon in the opposite direction. In each group the difference of the number of vibrations between two consecutive rays is constant. It seems possible that the positive electrons which cannot be separated from the atoms, either in electric discharges nor in radio-active phenomena, and which appear strongly bound to the atoms, can, nevertheless, acquire a sufficient degree of liberty to manifest themselves in optical phenomena.

Trichlorophenol, OH(1)Cl(2.4.6) and its Transformation into Chlorinated Quinones.—E. Léger.—It is most convenient to prepare this compound by the action of a commercial solution of sodium hypochlorite (Eau de Javel) upon phenol. When fuming nitric acid acts upon it in the cold the 2.6 dichloroquinone is obtained. If a small quantity of hydrochloric acid is added to the nitric acid a mixture of trichloroquinone and tetrachloroquinone is formed. These can be separated by fractional crystallisation with alcohol.

Styrolene Oxide.—MM. Tiffeneau and Fourneau.—This oxide can be prepared by the action of powdered caustic potash on an ethereal solution of styrolene iodohydrine in the cold. In its reactions sometimes it behaves normally, binary compounds being added symmetrically, and the chain being opened as follows:—$C_6H_5—\underset{|}{CH}—CH_2—O—$, and sometimes it behaves like the isomeric phenyl acetic aldehyde, $C_6H_5—CH_2—CHO$. It is impossible to decide whether this aldehyde is formed as an intermediate product, or whether after the migration of the hydrogen the binary compound adds itself on before this aldehyde is formed, *i.e.*, to the residue, $C_6H_5—CH_2—CH<^{O—}$.

β-$\alpha\alpha$-Dialcoholated Ketone Alcohols.—E. E. Blaise and I. Herman.—The action of alkalis on oxypseudobutylethyl ketone gives a ketone containing C_7. This is identical with methovinylisopropylketone, $CH_3>C—CO—CH<^{CH_3}_{CH_3}$. The formation of this compound is apparently due to a molecular transformation, dehydration first occurring, and then migration of a methyl group.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xli., No. 6, 1908.

Osmium.—O. Makowka.—When a solution of acetylene saturated with acetone is added to an osmium solution colloid osmium is at once formed, and may be separated by heating the solution in a closed tube to 100—110°. The residue, which contains metallic osmium, may readily be filtered off, and the separation is quantitative.

Formation of Hydrogen Peroxide.—Franz Fischer and O. Ringe.—Hydrogen peroxide is formed under the same conditions as ozone, if care is taken not to keep the substance when once formed for any length of time at a temperature at which its velocity of decomposition is high. Thus it is formed when mixtures of water vapour and oxygen are led rapidly over glowing magnesia capillaries, and when a blast of water vapour is blown on to a hydrogen flame. When oxygen is blown on to spark gaps or high voltage arcs ozone is obtained, and when water vapour is substituted for oxygen the product is hydrogen peroxide. In stagnant air the spark gives chiefly nitric oxide. Finally the ozone tube yields hydrogen peroxide if mixtures of oxygen and water at a sufficiently high temperature are led through it. Traces of ozone are also formed.

New Borneol.—Ossian Aschan.—When the hydrochloride of terecamphene (melting-point 148—149°) is treated with bases in presence of water a good yield of a new alcohol $C_{10}H_{17}.OH$ is obtained. Its properties show that it is neither borneol nor isoborneol; for instance, it readily gives up water when it is shaken for a few minutes with dilute mineral acids or boiled for a short time with glacial acetic acid. When it is oxidised it gives only small quantities of camphor and possibly a secondary reaction occurs. The new substance is a tertiary alcohol.

Lecture Experiments to Prepare Iodide Chlorides, Iodo and Iodinium Compounds.—C. Willgerodt.—I. *Preparation of Phenyl Iodide Chloride.*—The inner surface of a cylinder filled with chlorine is wetted with a solution of benzene iodide in chloroform. The chlorine instantly adds itself on to the iodide and crystals of phenyl iodide chloride cover the interior of the cylinder. II. *Preparation of Iodobenzene from Phenyl Iodide Chloride.*—Phenyl iodide chloride is rubbed up with a freshly prepared filtered calcium chloride solution and then boiled. White iodobenzene soon appears, the chlorine escaping quantitatively. The crystals of iodobenzene may be separated by cooling with ice-water. III. *Preparation of Diphenyl Iodinium Chloride and Iodide from Phenyl Iodide Chloride.*—A mixture of phenyl iodide chloride and caustic soda solution is heated till all the solid has disappeared. It is then filtered to separate off drops of benzene iodide, and divided into two parts. To one part concentrated hydrochloric acid is added, and a precipitate of sodium chloride and diphenyl iodinium chloride is at once obtained; the former may be separated by the addition of water. Potassium iodide is added to the second part of the solution, and thus diphenyl iodinium iodide is precipitated in white crystalline masses.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th instant, Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Earl Fitzwilliam, Dr. J. O'Conor Donelan, Mr. H. E. Donnithorne, Miss Helen Douglas, Mr. W. L. Dunn, Miss Farrer, Mr. H. E. Harrison, Mr. R. C. B. Kerin, Mrs. Carl Meyer, Lady O'Hagan, and Mr. H. T. Perkins, were elected Members. The Special Thanks of the Members were returned to Mr. J. Y. Buchanan, F.R.S., for his donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures. A Resolution of Condolence with the Duchess of Devonshire on the decease of the Duke of Devonshire was passed.

Royal Institution.—On Tuesday next, May 26, at 3 o'clock, Professor W. Stirling begins a course of two lectures at the Royal Institution on "Animal Heat and Allied Phenomena"; and on Saturday, May 30, Dr. H. Walford Davies commences a course of two lectures on "The Art of Bach and Future Developments" (with Musical Illustrations). The Friday Evening Discourse on May 29 will be delivered by Sir Ralph Payne Gallwey, on "Ancient and Mediæval Projectile Weapons other than Firearms"; and on June 5, by Professor Sir James Dewar, on "The Nadir of Temperature and Allied Phenomena."

Chemical Society Research Fund.—A meeting of the Research Fund Committee will be held in June next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, June 8, 1908. All persons who received grants in June, 1907, or in June of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Monday, June 1. The Council wish to draw special attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

Institute of Metals.—The objects of the Institute are similar to those of the well-known Iron and Steel Institute:—(1) To advance our knowledge of the non-ferrous metals and their alloys, more especially copper, zinc, tin, aluminium, lead, nickel, gold, silver, and platinum. (2) The publication, twice a year, of a volume of abstracts of papers and books on metallurgical subjects, likely to interest members. The volume will be a comprehensive bibliography of the practical and scientific work on non-ferrous metals of each year, both at home and abroad, and will be of great value. (3) To afford a means of communication between members of the trades in question, bearing upon their respective manufactures, excluding all questions connected with wages and trade regulation. (4) To arrange periodical meetings for the purpose of discussing practical and scientific subjects relating to the manufacture, working-up, and use of the non-ferrous metals. It is the desire of the founders to include not merely the copper and brass trades, but the spelter, lead, nickel, aluminium, and silver trades, in fact, all those engaged, producing, or working-up, the non-ferrous metals and their alloys. A Special Meeting is to be held in London on June 10th, at 2.30 p.m., at which the Committee will report progress, and it is hoped formally constitute the proposed Institute. All smelters, manufacturers, merchants, metallurgists, engineers, and scientific men who take an interest in the formation of the Institute of Metals, are requested to send in their names at once to WILLIAM H. JOHNSON, care of Rd. Johnson, Clapham, and Morris, Ltd., Manchester, who, during Professor Carpenter's indisposition, has undertaken to act as Secretary.

MEETINGS FOR THE WEEK.

TUESDAY, 26th.—Royal Institution, 3. "Animal Heat and Allied Phenomena," by Prof. William Stirling, M.D.
—— Faraday Society, 8. Presidential Address, "Some Aspects of the Work of Lord Kelvin," by Sir Oliver Lodge.

THURSDAY, 28th.—Royal Institution, 3. "The Chemistry of Photography" by Alexander Scott, F.R.S., &c.

FRIDAY, 29th.—Royal Institution, 9. "Ancient and Mediæval Projectile Weapons other than Firearms," by Sir Ralph Payne-Gallwey, Bart.

SATURDAY, 30th.—Royal Institution, 3. "The Art of Bach and Future Developments," by H. Walford Davies, Mus. Doc

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THE CHEMICAL NEWS.

VOL. XCVII., No. 2531.

ON THE CALCULATION OF THERMO-CHEMICAL CONSTANTS.

III.—THERMAL CONSTANTS OF ORGANIC OXYGEN COMPOUNDS.

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

WE find, generally in compounds of carbon, hydrogen, and oxygen, that the oxygen is combined in three primary ways, namely, the etheric, in which the oxygen atom is singly linked to two different carbon atoms; the hydroxylic, in which the oxygen atom is singly linked to a carbon and to a hydrogen atom; the ketonic, in which the oxygen atom is "doubly" linked to one carbon atom; each of these three classes will require a different constant, as follows hereinafter.

The molecular heats of combustion and formation of aromatic compounds will be calculated by means of the constants ζ = molecular heat of combustion of benzene (at constant volume) = 797·9 cals. (Thomsen), ζ' = molecular heat of formation of benzene (at constant volume) = −13·7 cals. (Thomsen), so that no assumptions regarding the constitution of the benzene nucleus are introduced.

1. *Molecular Heats of Combustion of Ethers.**

All ethers can theoretically be obtained by replacing $2c$ hydrogen atoms in one or more hydrocarbons by c oxygen atoms, each linked to two different carbon atoms, where c is some integer. The following constant will therefore be required:—ω = the algebraic sum of the following heats—(i.) due to the severance of two C.H links; (ii.) due to the combustion of two hydrogen atoms (to liquid water) minus the algebraic sum of the following heats—(iii.) due to the severance of two C.O links; (iv.) one-half that due to the formation of an oxygen molecule; or as it can be more simply written:—

ω = the sum of the following heats—(ii.) due to the combustion of two hydrogen atoms (to liquid water); (iii.) due to the formation of two C.O links, minus the sum of the following heats—(i.) due to the formation of two C.H links; (iv.) one-half that due to the formation of an oxygen molecule.

So that the general ether,—

$$nC+2(n+1-a-2b-p-c)H+(n+p-a-b-1)L_1+aL_2+ +bL_3+cO+2c(C.O) \text{ links},\dagger$$

can be written—

$$nC+2(n+1-a-2b-p)H+ +(n+p\cdots a-b-1)L_1+aL_2+bL_3-c\omega =na-(n+p\cdots a-b-1)\beta-a\gamma-b\delta-c\omega.$$

In Table I. will be found the molecular heats of combustion (corrected for constant volume) of eight ethers, determined by Thomsen; from these the value of ω has been calculated thus:—

Methyl ethyl ether is $CH_3.O.C_2H_5$, *i.e.*, $3\alpha-\beta-\omega$. M.H.C. found = 504·4 cals.

Therefore $\omega = 3\alpha-\beta-504{\cdot}4$ cals. = (632·4 − 52·5 − 504·4) cals. = 75·5 cals., &c.; these values are given in the table; the mean value of the six more consistent values is ω = 75·4 cals.

Using this value the molecular heats of combustion of all the ethers given have been calculated and are exhibited, together with the differences between them and the experimental, and the percentage errors in Table I., the agreement is quite satisfactory, except, perhaps, in the case of methylal.

The agreement in the case of anisol shows that ω has the same value in aromatic as in aliphatic substances.

2. *Molecular Heats of Formation of Ethers.*

The molecular heat of formation constant corresponding to ω is:—

ω' = the algebraic sum of the following heats—(i.) due to the decomposition of a hydrogen molecule; (ii.) due to the formation of two C.H links, minus the algebraic sum of the following heats—(iii.) one-half that due to the decomposition of an oxygen molecule; (iv.) due to the formation of two C.O links, or as it can be more simply written:—

ω' = the sum of the following heats—(ii.) due to the formation of two C.H links; (iii.) one-half that due to the formation of an oxygen molecule, minus the sum of the following heats—(i.) due to the formation of a hydrogen molecule; (iv.) due to the formation of two C.O links.

Therefore $\omega+\omega'$ = the heat due to the combustion of two hydrogen atoms (to liquid water) less the heat due to the formation of a hydrogen molecule = the molecular heat of combustion of hydrogen gas to liquid water = 67·5 cals.; whence,—

$\omega' = 67{\cdot}5 \text{ cals.} - \omega = (67{\cdot}5 - 75{\cdot}4) \text{ cals.} = -7{\cdot}9$ cals.

In Table I. will be found the molecular heats of formation (at constant volume) of eight ethers given by Thomsen; from these the value of ω' has been calculated in a similar manner as was the value of ω. The mean value is $\omega' = -7{\cdot}8$ cals., agreeing with the above.

Using this value ($\omega' = -7{\cdot}8$ cals.) the molecular heats of formation of all the ethers given have been calculated, and are exhibited together with the differences between them and the experimental in Table I.

3. *Molecular Heats of Combustion of Alcohols.*

All alcohols can theoreiically be obtained by replacing d hydrogen atoms in the corresponding hydrocarbon by d hydroxyl groups each linked to carbon, where d is some integer; the following constant will therefore be required:—

ω_1 = the algebraic sum of the following heats—(i.) due to the severance of a C.H link; (ii.) due to the combustion of a hydrogen atom (to liquid water) minus the algebraic sum of the following heats—(iii.) due to the severance of a C.O link; (iv.) due to the severance of an O.H link; (v.) one-half that due to the formation of an oxygen atom; (vi.) due to the combustion of a hydrogen atom (to liquid water); or as it can be more simply written:—

ω_1 = the sum of the following heats—(iii.) due to the formation of a C.O link; (iv.) due to the formation of an O.H. link, minus the sum of the following heats; (i.) due to the formation of a C.H link; (v.) one-half that due to the formation of an oxygen molecule.

So that the general alcohol,—

$$nC+2\left(n+1-a-2b-p-\frac{d}{2}\right)H+(n+p-a-b-1)L_1+ +aL_2+bL_3+d(C.O) \text{ links}+dO+d(O.H) \text{ links}+ +dH \text{ (linked to O, } \textit{not} \text{ to C)},$$

can be written—

$$nC+2(n+1-a-2b-p)H+(n+p-a-b-1)L_1+aL_2+ +bL_3-d\omega_1=na-(n+p-a-b-1)\beta-a\gamma-b\delta-d\omega_1.$$

Now, the heat of combustion of two hydrogen atoms to water vapour = the heat due to the formation of two O.H links less one-half that due to the formation of an oxygen molecule.

Therefore the heat due to the formation of two O.H links = the heat of combustion of two hydrogen atoms to water vapour plus one-half the heat due to the formation of an oxygen molecule.

Now, $2\omega_1$ = the sum of the following heats—(iii.) due to the formation of two C.O links; (iv.) due to the formation of two O.H links, minus the sum of the following heats—

* The consideration of ethylene oxide is postponed.

† For common ethers put $p = -1$.

TABLE I.—Ethers.

1. Substance.	2. Formula.	Molecular Heats of Combustion. 3. Formula.	4. M.H.C. found (Thomsen) constant vol. Cals.	5. ω Calculated. Cals.	6. M.H.C. calculated. Cals.	7. Difference between cols. 4 and 6. Cals.	8. Error. Per cent.	Molecular Heats of Formation. 9. Formula.	10. M.H.F. (Thomsen) constant vol. Cals.	11. ω′ Calculated. Cals.	12. M.H.F. calculated. Cals.	13. Difference between cols. 10 and 12. Cals.
Dimethyl ether	$CH_3.O.CH_3$	$2\alpha-\omega$	348·2	73·4	346·2	−2·0	−0·57	$2\alpha'-\omega'$	48·2	−5·8	50·2	+2·0
Methylethyl ether	$CH_3.O.C_2H_5$	$3\alpha-\beta-\omega$	504·4	75·5	504·5	+0·1	+0·02	$3\alpha'-\beta'-\omega'$	56·4	−7·8	56·4	0·0
Diethyl ether	$C_2H_5.O.C_2H_5$	$4\alpha-2\beta-\omega$	657·9	(80·3)	662·8	+4·9	+0·74	$4\alpha'-2\beta'-\omega'$	67·4	(−12·6)	62·6	−4·8
Methylallyl ether	$CH_3.O.C_3H_5$	$4\alpha-\beta-\gamma-\omega$	625·7	76·0	626·3	+0·6	+0·10	$4\alpha'-\beta'-\gamma'-\omega'$	32·1	−8·3	31·6	−0·5
Diallyl ether	$C_3H_5.O.C_3H_5$	$6\alpha-2\beta-2\gamma-\omega$	909·4	(72·4)	906·4	−3·0	−0·33	$6\alpha'-2\beta'-2\gamma'-\omega'$	9·9	(−4·7)	13·0	+3·1
Methylpropargyl ether	$CH_3.O.C_3H_3$	$4\alpha-\beta-\delta-\omega$	602·7	75·0	602·3	−0·4	−0·07	$4\alpha'-\beta'-\delta'-\omega'$	−12·4	−7·3	−11·9	+0·5
Anisol	$C_6H_5.O.CH_3$	$\zeta+\alpha-\omega$	934·8	73·9	933·3	−1·5	−0·16	$\zeta'+\alpha'-\omega'$	+13·8	−6·3	+15·3	+1·5
Methylal	$CH_2(OCH_3)_2$	$3\alpha-2\omega$	474·9	78·75	481·6	+6·7	+1·41	$3\alpha'-2\omega'$	85·9	−11·15	79·2	−6·7
		Mean .. .. ω = 75·4						Mean .. .. ω' = −7·8				

TABLE II.—Alcohols.

			ω_1 Calculated.					ω_1' calculated.				
Group 1.												
Phenol	$C_6H_5.OH$	$\zeta-\omega_1$	767·6	30·3	768·2	+0·6	+0·08	$\zeta'-\omega_1'$	16·6	−30·3	16·0	−0·6
Primary Alcohols—												
Methyl alcohol	$CH_3.OH$	$\alpha-\omega_1$	181·4	29·4	181·1	−0·3	−0·17	$\alpha'-\omega_1'$	50·6	−29·4	50·9	+0·3
Ethyl ,,	$C_2H_5.OH$	$2\alpha-\beta-\omega_1$	339·4	29·7	339·4	0·0	0·00	$2\alpha'-\beta'-\omega_1'$	57·0	−29·6	57·1	+0·1
Propyl ,,	$C_3H_7.OH$	$3\alpha-2\beta-\omega_1$	497·2	30·2	497·7	+0·5	+0·10	$3\alpha'-2\beta'-\omega_1'$	63·7	−30·1	63·3	−0·4
Isobutyl ,,	$(CH_3)_2CH.CH_2.OH$	$4\alpha-3\beta-\omega_1$	656·7	29·0	656·0	−0·7	−0·11	$4\alpha'-3\beta'-\omega_1'$	68·5	−28·7	69·5	+1·0
Isoamyl ,,	$(CH_3)_2CH.CH_2.CH_2.OH$	$5\alpha-4\beta-\omega_1$	818·0	(26·0)	814·3	−3·7	−0·45	$5\alpha'-4\beta'-\omega_1'$	71·7	(−25·7)	75·7	+4·0
Allyl ,,	$C_3H_5.OH$	$3\alpha-\beta-\gamma-\omega_1$	463·6	(27·3)	461·2	−2·4	−0·52	$3\alpha'-\beta'-\gamma'-\omega_1'$	29·8	(−27·2)	32·3	+2·5
		Mean .. .. ω_1 = 29·7						Mean .. .. ω_1' = −29·6				
Group 2.												
Propargyl alcohol	$C_3H_3.OH$	$3\alpha-\beta-\delta-\omega_1$	430·2	36·7	430·5	+0·3	+0·07	$3\alpha'-\beta'-\delta'-\omega_1'$	−4·4	−36·5	−4·5	−0·1
Ethylene glycol	$C_2H_4(OH)_2$	$2\alpha-\beta-2\omega_1$	297·2	71·9 × ½	296·3	−0·9	−0·30	$2\alpha'-\beta'-2\omega_1'$	+99·2	−71·8 × ½	+100·2	+1·0
Secondary Alcohol—												
Isopropyl alcohol	$(CH_3)_2CH.OH$	$3\alpha-2\beta-\omega_1$	491·9	35·5	491·0	−0·9	−0·18	$3\alpha'-2\beta'-\omega_1'$	69·0	−35·4	70·0	+1·0
Tertiary Alcohols—												
Trimethylcarbinol	$(CH_3)_3C.OH$	$4\alpha-3\beta-\omega_1$	639·6	(46·1)	649·3	+9·7	+1·52	$4\alpha'-3\beta'-\omega_1'$	85·7	(−45·9)	76·2	−9·5
Dimethylethylcarbinol	$(CH_3)_2C(OH)C_2H_5$	$5\alpha-4\beta-\omega_1$	808·4	35·6	807·6	−0·8	−0·10	$5\alpha'-4\beta'-\omega_1'$	81·3	−35·3	82·4	+1·1
		Mean .. .. ω_1 = 35·9						Mean .. .. ω_1' = −35·8				
		Final mean (see text) .. .. ω_1 = 36·4										

(i.) due to the formation of two C.H links; (v.) due to the formation of an oxygen molecule.

Hence, substituting the above value for the heat of formation of two O.H links:—

$2\omega_I$ = the sum of the following heats—due to the combustion of two hydrogen atoms to water vapour; (iii.) due to the formation of two C.O links, minus the sum of the following heats—(i.) due to the formation of two C.H links; (v.) one-half that due to the formation of an oxygen molecule (see the definition of ω).

Therefore $2\omega_I$ + the molecular latent heat of steam (corrected for constant volume) = ω.

Therefore $2\omega_I$ + 9·8 cals. = 75·4 cals., whence ω_I = 32·8 cals.

In Table II. will be found the molecular heats of combustion (corrected for constant volume) of twelve alcohols, &c., determined by Thomsen; from these the values of ω_I have been calculated thus:—

Methyl alcohol is CH_3OH; *i.e.*, $a - \omega_I$. M.H.C. found = 181·4 cals.

Therefore $\omega_I = a - 181{\cdot}4$ cals. = (210·8 − 181·4) cals. = 29·4 cals., &c.

These values are given in the table. It is seen that the alcohols divide themselves into two groups, thus:—

The first group contains the primary alcohols and phenol, and gives a value for ω_I somewhat below the theoretical (32·8 cals.). The mean of the five more consistent values is ω_I = 29·7 cals. Using this value the molecular heats of combustion of the members of this group have been calculated, and are exhibited, together with the differences between them and the experimental and the percentage errors in Table II. The agreement is quite satisfactory.

The second group contains the secondary and tertiary alcohols, ethylene glycol, and a primary alcohol (propargyl alcohol), and gives a value for ω_I somewhat above the theoretical.

The mean value (neglecting trimethyl carbinol) for this group is 35·9 cals. It will be shown, however, in the next paper in this series that the mean value of ω_I in monocarboxy acids is 37·0 cals. agreeing with this value above; the final mean, namely, 36·4 cals., is used in the calculations, and the molecular heats of combustion of the alcohols in this group have been calculated thereby, and are exhibited, together with the differences between them and the experimental, and the percentage errors in Table II. The agreement is quite satisfactory, except in the case of trimethylcarbinol.

This behaviour of the alcohols in thus dividing themselves into two groups with respect to the value of ω_I is remarkable, inasmuch as it appears that the mere position of the hydroxyl group exercises an influence upon its thermal equivalent, and is in marked contrast to the behaviour of the chlorine substituted hydrocarbons (CHEM. NEWS, xcvii., 183).

It may be, however, that the two hydrogen atoms in water are not bound to the oxygen atom with equal affinity; in some alcohols one hydrogen atom is replaced, in others the other hydrogen atom is replaced, depending possibly upon the configuration of the rest of the molecule; whereas the thermal value of either oxygen link with carbon is constant. This would explain why the value of ω_I deduced from a consideration of the ether constant and water is the arithmetic mean between the two values of ω_I obtained from the two groups of alcohols above.

4. *Molecular Heats of Formation of Alcohols.*

The molecular heat of formation constant corresponding to ω_I is:—

ω_I' = the algebraic sum of the following heats—(i.) one-half that due to the decomposition of a hydrogen molecule; (ii.) due to the formation of a C.H link, minus the algebraic sum of the following heats—(iii.) one-half that due to the decomposition of an oxygen molecule; (iv.) one-half that due to the decomposition of a hydrogen molecule; (v.) due to the formation of a C.O link; (vi.) due to the formation of an O.H link, or as it can be more simply written:—

ω_I' = the sum of the following heats—(ii.) due to the formation of a C.H link; (iii.) one-half that due to the formation of an oxygen molecule, minus the sum of the following heats—(v.) due to the formation of a C.O link; (vi.) due to the formation of an O.H link.

Hence, $\omega_I' = -\omega_I$.

In Table II. will be found the molecular heats of formation (at constant volume) of twelve alcohols, &c., given by Thomsen; from these the values of ω_I' have been calculated, similarly as were the values of ω_I. The mean values obtained are:—For the first group, $\omega_I' = -29{\cdot}6$ cals.; for the second group, $\omega_I' = -35{\cdot}8$ cals., in agreement with the above relation.

Using the values obtained from this relation ($\omega_I' = -\omega_I$), namely, −29·7 cals. and −36·4 cals., for the first and second groups respectively, the molecular heats of formation of all the alcohols, &c., given have been calculated, and are exhibited together with the differences between them and the experimental in Table II.

The Polytechnic, Regent Street, W.

(To be continued).

THE ETHER OF SPACE.*

By Sir OLIVER LODGE, LL.D., D.Sc., F.R.S.

THIRTY years ago Clerk Maxwell gave in this place a remarkable address on "Action at a Distance." It is reported in the *Journal of the Royal Institution*, vol. vii., and to it I would direct attention. Most natural philosophers hold, and have held, that action at a distance across empty space is impossible; in other words, that matter cannot act where it is not, but only where it is. The question "Where is it?" is a further question that may demand attention and require more than a superficial answer. For it can be argued on the hydrodynamic or vortex theory of matter, as well as on the electrical theory, that every atom of matter has a universal though nearly infinitesimal prevalence, and extends everywhere; since there is no definite sharp boundary or limiting periphery to the region disturbed by its existence. The lines of force of an isolated electric charge extend throughout illimitable space. And though a charge of opposite sign will curve and concentrate them, yet it is possible to deal with both charges, by the method of superposition, as if they each existed separately without the other. In that case, therefore, however far they reach, such nuclei clearly exert no "action at a distance" in the technical sense.

Some philosophers have reason to suppose that mind can act directly on mind without intervening mechanism, and sometimes that has been spoken of as genuine action at a distance; but, in the first place, no proper conception or physical model can be made of such a process, nor is it clear that space and distance have any particular meaning in the region of psychology. The links between mind and mind may be something quite other than physical proximity, and in denying action at a distance across empty space I am not denying telepathy or other activities of a non-physical kind; for although brain disturbance is certainly physical and is an essential concomitant of mental action, whether of the sending or receiving variety, yet we know from the case of heat that a material movement can be excited in one place at the expense of corresponding movement in another, without any similar kind of transmission or material connection between the two places: the thing that travels across vacuum is not heat.

In all cases where physical motion is involved, however,

* Abstract of a Discourse delivered at the Royal Institution, February 21, 1908.

I would have a medium sought for; it may not be matter, but it must be something; there must be a connecting link of some kind, or the transference cannot occur. There can be no attraction across really empty space. And even when a material link exists, so that the connexion is obvious, the explanation is not complete; for when the mechanism of attraction is understood, it will be found that a body really only moves because it is pushed by something from behind. The essential force in nature is the *vis a tergo*. So when we have found the "traces," or discovered the connecting thread, we still run up against the word "cohesion," and ought to be exercised in our minds as to its ultimate meaning. Why the whole of a rod should follow, when one end is pulled, is a matter requiring explanation; and the only explanation that can be given involves, in some form or other, a continuous medium connecting the discrete and separated particles or atoms of matter.

When a steel spring is bent or distorted, what is it that is really strained? Not the atoms—the atoms are only displaced; it is the connecting links that are strained—the connecting medium—the ether. Distortion of a spring is really distortion of the ether. All stress exists in the ether. Matter can only be moved. Contact does not exist between the atoms of matter as we know them; it is doubtful if a piece of matter ever touches another piece any more than a comet touches the sun when it appears to rebound from it; but the atoms are connected, as the comet and the sun are connected, by a continuous *plenum* without break or discontinuity of any kind. Matter acts on matter only through the ether. But whether matter is a thing utterly distinct and separate from the ether, or whether it is a specifically modified portion of it—modified in such a way as to be susceptible of locomotion, and yet continuous with all the rest of the ether, which can be said to extend everywhere—far beyond the bounds of the modified and tangible portion—are questions demanding, and I may say in process of receiving, answers.

Every such answer involves some view of the universal and possibly infinite uniform omnipresent connecting medium, the Ether of space.

It has been said, somewhat sarcastically, that the ether was made in England. The statement is only an exaggeration of the truth. I might even urge that it has been largely constructed in the Royal Institution; for, I will remind you now of the chief lines of evidence on which its existence is believed in, and our knowledge of it is based. First of all, Newton recognised the need of a medium for explaining gravitation. In his "Optical Queries" he shows that if the pressure of this medium is less in the neighbourhood of dense bodies than at great distances from them, dense bodies will be driven towards each other; and that if the diminution of pressure is inversely as the distance from the dense body, the law will be that of gravitation.

All that is required, therefore, to explain gravity is a diminution of pressure, or increase of tension, caused by the formation of a matter unit—that is to say, of an electron or corpuscle; and although we do not yet know what an electron is—whether it be a strain centre, or what kind of singularity in the ether it may be—there is no difficulty in supposing that a slight, almost infinitesimal, strain or attempted rarefaction should be produced in the ether whenever an electron came into being—to be relaxed again only on its resolution and destruction. Strictly speaking it is not a real *strain*, but only a "stress"; since there can be no actual *yield*, but only a pull or tension, extending in all directions towards infinity.

The tension required per unit of matter is almost ludicrously small, and yet in the aggregate, near such a body as a planet, it becomes enormous.

The force with which the moon is held in its orbit would be great enough to tear asunder a steel rod four hundred miles thick, with a tenacity of thirty tons per square inch; so that if the moon and earth were connected by steel instead of by gravity, a forest of pillars would be necessary to whirl the system once a month round their common centre of gravity. Such a force necessarily implies enormous tension or pressure in the medium. Maxwell calculates that the gravitational stress near the earth, which we must suppose to exist in the invisible medium, is 3000 times greater than what the strongest steel could stand; and near the sun it should be 2500 times as great as that.

The question has arisen in my mind, whether, if the whole sensible universe—estimated by Lord Kelvin as equivalent to about a thousand million suns—were all concentrated in one body of specifiable density, the stress would not be so great as to produce a tendency towards etherial disruption; which would result in a disintegrating explosion, and a scattering of the particles once more as an enormous nebula and other fragments into the depths of space. On doing the arithmetic, however, I find the necessary concentration absurdly great, showing that such a mass is quite insufficient; see Appendix). For the tension would be a maximum in the interior of such a mass; and, if it rose to the value 10^{28} dynes per square centimetre, something would have to happen. I do not suppose that this can be the reason, but one would think there must be *some* reason, for the scattered condition of gravitative matter.

Too little is known, however, about the mechanism of gravitation to enable us to adduce it as the strongest argument in support of the existence of an ether. The oldest valid and conclusive requisition of an etherial medium depends on the wave theory of light, one of the founders of which was your Professor of Natural Philosophy at the beginning of last century, Dr. Thomas Young.

No ordinary matter is capable of transmitting the undulations or tremors that we call light. The speed at which they go, the kind of undulation, and the facility with which they go through vacuum, forbid this.

So clearly and universally has it been perceived that waves must be waves of something—something distinct from ordinary matter—that Lord Salisbury, in his presidential address to the British Association at Oxford, criticised the ether as little more than a nominative case to the verb to undulate. It is truly *that*, though it is also truly more than that; but to illustrate that luminiferous aspect of it, I will quote a paragraph from that lecture of Clerk Maxwell's to which I have already referred:—

"The vast interplanetary and interstellar regions will no longer be regarded as waste places in the universe, which the Creator has not seen fit to fill with the symbols of the manifold order of His kingdom. We shall find them to be already full of this wonderful medium; so full, that no human power can remove it from the smallest portion of space, or produce the slightest flaw in its infinite continuity. It extends unbroken from star to star; and when a molecule of hydrogen vibrates in the dog-star the medium receives the impulses of these vibrations, and after carrying them in its immense bosom for several years, delivers them, in due course, regular order, and full tale, into the spectroscope of Mr. Huggins, at Tulse Hill." (It is pleasant to remember that those veteran investigators, Sir William and Lady Huggins, are still at work).

This will suffice to emphasise the fact that the eye is truly an etherial sense-organ—the only one which we possess, the only mode by which the ether is enabled to appeal to us, and that the detection of tremors in this medium—the perception of the direction in which they go, and some inference as to the quality of the object which has emitted them—cover all that we mean by "sight" and "seeing."

I pass then to another function, the electric and magnetic phenomena displayed by the ether; and on this I will only permit myself a very short quotation from the writings of Faraday, whose whole life may be said to have been directed towards a better understanding of these ethereous phenomena. Indeed the statue in your entrance hall may be considered as the statue of the discoverer of the electric and magnetic properties of the Ether of space.

Faraday conjectured that the same medium which is concerned in the propagation of light might also be the agent in electromagnetic phenomena. "For my own part," he says, "considering the relation of a vacuum to the magnetic force, and the general character of magnetic phenomena external to the magnet, I am much more inclined to the notion that in the transmission of the force there is such an action, external to the magnet, than that the effects are merely attraction and repulsion at a distance. Such an action may be a function of the æther; for it is not unlikely that, if there be an æther, it should have other uses than simply the conveyance of radiation."

This conjecture has been amply strengthened by subsequent investigations.

One more function is now being discovered; the ether is being found to constitute matter—an immensely interesting topic, on which there are many active workers at the present time. I will make a brief quotation from your present Professor of Natural Philosophy (J. J. Thomson), where he summarises the conclusion which we all see looming before us, though it has not yet been completely attained, and would not by all be similarly expressed:—

"The *whole* mass of any body is just the mass of ether surrounding the body which is carried along by the Faraday tubes associated with the atoms of the body. In fact, all mass is mass of the ether; all momentum, momentum of the ether; and all kinetic energy, kinetic energy of the ether. This view, it should be said, requires the density of the ether to be immensely greater than that of any known substance."

Yes, far denser—so dense that matter by comparison is like gossamer, or a filmy imperceptible mist, or a milky way. Nor unreal or unimportant—a cobweb is not unreal, nor to certain creatures is it unimportant, but it cannot be said to be massive or dense; and matter, even platinum, is not dense when compared with the ether. Not till last year, however, did I realise what the density of the ether must really be (see Lodge, *Phil. Mag.*, April, 1907), compared with that modification of it which appeals to our senses as matter, and which for that reason engrosses our attention. If I have time I will return to that before I have finished.

Is there any other function possessed by the ether which, though not yet discovered, may lie within the bounds of possibility for future discovery? I believe there is, but it is too speculative to refer to, beyond saying that it has been urged as probable by the authors of "The Unseen Universe," and has been thus tentatively referred to by Clerk Maxwell:—

"Whether this vast homogeneous expanse of isotropic matter is fitted not only to be a medium of physical interaction between distant bodies, and to fulfil other physical functions of which, perhaps, we have as yet no conception, but also . . . to constitute the material organism of beings exercising functions of life and mind as high or higher than ours are at present—is a question far transcending the limits of physical speculation."

And there for the present I leave that aspect of the subject.

I shall now attempt to illustrate some relations between ether and matter.

The question is often asked, is ether material? This is largely a question of words and convenience. Undoubtedly, the ether belongs to the material or physical universe, but it is not ordinary matter. I should prefer to say it is not "matter" at all. It may be the substance or substratum or material of which matter is composed, but it would be confusing and inconvenient not to be able to discriminate between matter on the one hand and ether on the other. If you tie a knot on a bit of string, the knot is composed of string, but the string is not composed of knots. If you have a smoke or vortex-ring in the air, the vortex-ring is made of air, but the atmosphere is not a vortex-ring; and it would be only confusing to say that it was.

The essential distinction between matter and ether is that matter *moves*, in the sense that it has the property of locomotion and can effect impact and bombardment; while ether is *strained*, and has the property of exerting stress and recoil. All potential energy exists in the ether. It may vibrate, and it may rotate, but as regards locomotion it is stationary—the most stationary body we know—absolutely stationary, so to speak; our standard of rest.

All that we ourselves can effect, in the material universe, is to alter the motion and configuration of masses of matter; we can move matter, by our muscles, and that is all we can do directly: everything else is indirect.

But now comes the question, how is it possible for matter to be composed of ether? How is it possible for a solid to be made out of fluid? A solid possesses the properties of rigidity, impenetrability, elasticity, and such like; how can these be imitated by a perfect fluid such as the ether must be? The answer is, they can be imitated by a fluid in motion; a statement which we make with confidence as the result of a great part of Lord Kelvin's work.

It may be illustrated by a few experiments.

A wheel of spokes, transparent or permeable when stationary, becomes opaque when revolving, so that a ball thrown against it does not go through, but rebounds. The motion only affects permeability to matter; transparency to light is unaffected.

A silk cord hanging from a pully becomes rigid and viscous when put into rapid motion; and pulses or waves which may be generated on the cord travel along it with a speed equal to its own velocity, whatever that velocity may be, so that they appear to stand still. This is a case of kinetic rigidity; and the fact that the wave-transmission velocity is equal to the rotatory speed of the material is typical and important, for in all cases of kinetic elasticity these two velocities are of the same order of magnitude.

A flexible chain, set spinning, can stand up on end while the motion continues.

A jet of water at sufficient speed can be struck with a hammer, and resists being cut with a sword.

A spinning disk of paper becomes elastic like flexible metal, and can act like a circular saw. Sir William White tells me that in naval construction steel plates are cut by a rapidly revolving disk of soft iron.

A vortex-ring, ejected from an elliptical orifice, oscillates about the stable circular form, as an indiarubber ring would do; thus furnishing a beautiful example of kinetic elasticity, and showing us clearly a fluid displaying some of the properties of a solid.

A still further example is Lord Kelvin's model of a spring balance, made of nothing but rigid bodies in spinning motion. (Address to Section A of British Association at Montreal, 1884).

If the ether can be set spinning, therefore, we may have some hope of making it imitate the properties of matter, or even of constructing matter by its aid. But how are we to spin the ether? Matter alone seems to have no grip of it. I have spun steel disks, a yard in diameter, 4000 times a minute, have sent light round and round between them, and tested carefully for the slightest effect on the ether. Not the slightest effect was perceptible. We cannot spin ether mechanically.

But we can vibrate it electrically; and every source of radiation does that. An electrified body, in sufficiently rapid vibration, is the only source of ether-waves that we know; and if an electric charge is suddenly stopped, it generates the pulses known as X-rays, as the result of the collision. Not speed, but sudden change of speed, is the necessary condition for generating waves in the ether by electricity.

We can also infer some kind of rotary motion in the ether; though we have no such obvious means of detecting the spin as is furnished by vision for detecting some kinds of vibration. It is supposed to exist whenever we put a charge into the neighbourhood of a magnetic pole. Round the line joining the two the ether is spinning like a top. I

do not say it is spinning fast: that is a question of its density; it is in fact spinning with excessive slowness, but it is spinning with a definite moment of momentum. J. J. Thomson's theory makes its moment of momentum exactly equal to $e\,m$, the product of charge and pole; the charge being measured electrostatically and the pole magnetically.

How can this be shown experimentally? Suppose we had a spinning top enclosed in a case, so that the spin was unrecognisable by ordinary means—it could be detected by its gyrostatic behaviour to force. If allowed to "precess" it will respond by moving perpendicularly to a deflecting force. So it is with the charge and the magnetic pole. Try to move the charge suddenly, and it immediately sets off at right angles. A moving charge is a current, and the pole and the current try to revolve round one another—a true gyrostatic action due to the otherwise unrecognisable etherial spin. The fact of such magnetic rotation was discovered by Faraday.

I know that it is usually worked out in another way, in terms of lines of force and the rest of the circuit; but I am thinking of a current as a stream of projected charges; and no one way of regarding such a matter is likely to exhaust the truth, or to exclude other modes which are equally valid. Anyhow, in whatever way it is regarded, it is an example of the three rectangular vectors.

The three vectors at right angles to each other, which may be labelled Current, Magnetism, and Motion respectively, or more generally E, H, and V, represent the quite fundamental relation between ether and matter, and constitute the link between Electricity, Magnetism, and Mechanics. Where any two of these are present, the third is a necessary consequence. This principle is the basis of all dynamos, of electric motors, of light, of telegraphy, and of most other things. Indeed, it is a question whether it does not underlie everything that we know in the whole of the physical sciences; and whether it is not the basis of our conception of the three dimensions of space.

Lastly, we have the fundamental property of matter called *inertia*, which, if I had time, I would show could be explained electro-magnetically, provided the etherial density is granted as of the order 10^{18} grms. per cubic centimetre. The elasticity of the ether would then have to be of the order 10^{22} c.g.s.; and if this is due to intrinsic turbulence, the speed of the whirling or rotational elasticity must be of the same order as the velocity of light. This follows hydrodynamically; in the same sort of way as the speed at which a pulse travels on a flexible running endless cord, whose tension is entirely due to the centrifugal force of the motion, is precisely equal to the velocity of the cord itself. And so, on our present view, the intrinsic energy of constitution of the ether is incredibly and portentously great; every cubic millimetre of space possessing what, if it were matter, would be a mass of a thousand tons, and an energy equivalent to the out-put of a million-horse-power-station for forty million years.

The universe we are living in is an extraordinary one; and our investigation of it has only just begun. We know that matter has a psychical significance, since it can constitute *brain*, which links together the physical and the psychical worlds. If anyone thinks that the ether, with all its massiveness and energy, has probably no psychical significance, I find myself unable to agree with him.

(To be continued).

New Method of Determining Phosphorus in Organic Matter.—Isidor Bay.—The organic matter is ignited in a tube with sodium carbonate and magnesia. The contents of the tube are dissolved in dilute acetic acid, and the phosphorus is determined in the solution by means of a titrated uranium nitrate solution, using potassium ferrocyanide as an indicator.—*Comptes Rendus*, cxlvi., No. 15.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

CONVERSAZIONE, *May 13th*, 1908.

SIR WILLIAM CROOKES exhibited—

1. Scandium, its Salts, and its position in the Scheme of the Chemical Elements.

Scandium is an exceedingly rare terrestrial element, occurring in very few minerals and in very small amount—usually not more than 0·01 per cent. The one exception is the rare mineral wiikite which contains scandium in considerable quantity.

Astronomical research has demonstrated the presence of scandium in comparative abundance in the sun and some of the brighter stars. To enable its spectrum lines to be identified with certainty, especially in some of the fainter celestial bodies, a thorough examination of its spectrum has been undertaken.

2. Rare Minerals containing Scandium: Auerlite, keilhauite, orthite, urdite, wiikite.

3. Salts of Scandium.

Scandium oxide, Sc_2O_3.

Scandium hydroxide, $Sc_2O_3,3H_2O = Sc(OH)_3$.

Scandium carbonate, $Sc_2(CO_3)_3,12H_2O$.

Hydrated scandium chlorides,—

$$Sc_2Cl_6,12H_2O = Sc_2O_3,6HCl,9H_2O,$$
$$Sc_2Cl_6,3H_2O = Sc_2O_3 + 6HCl.$$

Hydrated scandium bromides, $Sc_2Br_6,12H_2O$,

$$Sc_2Br_6,3H_2O = Sc_2O_3,6HBr.$$

Scandium chlorate.

Scandium perchlorate.

Scandium bromate.

Scandium sulphates,—

$$Sc_2(SO_4)_3,6H_2O, \qquad Sc_2(SO_4)_3,5H_2O.$$

Anhydrous scandium sulphate, $Sc_2(SO_4)_3$.

Basic scandium sulphate, $Sc_2O(SO_4)_2$.

Scandium and potassium double sulphate,—

$$3K_2SO_4,Sc_2(SO_4)_3.$$

Scandium selenates,—

$$Sc_2(SeO_4)_3,8H_2O, \qquad Sc_2(SeO_4)_3,2H_2O.$$

Scandium nitrates, $Sc(NO_3)_3,4H_2O$, $Sc(NO_3)_3$, $ScOH(NO_3)_2H_2O$, $Sc_2O(NO_3)_4$.

Scandium formate, $(HCOO)_2ScOH,H_2O$.

Scandium acetate, $(CH_3COO)_2ScOH,2H_2O$.

Scandium propionate, $C_2H_5COO)_2ScOH$.

Scandium butyrate, $(CH_3.CH_2.CH_2.COO)_2ScHO$.

Scandium iso-butyrate,—

$$\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH.COO\right)_2ScOH,2H_2O,$$

Scandium iso-valerate, $(C_4H_9COO)_2ScOH,2H_2O$.

Scandium oxalates,—

$$Sc_2(C_2O_4)_3,5H_2O, \qquad Sc_2(C_2O_4)_3,3H_2O,$$
$$Sc_2(C_2O_4)_3,2H_2O_3, \qquad Sc_2(C_2O_4),H_2O.$$

Scandium picrates, $[C_6H_2(NO_2)_3O]_2ScOH),14H_2O$, $[C_6H_2(NO_2)_3O]_2,ScOH,5H_2O$.

Scandium pyromellitate.

Scandium camphorate, $C_8H_{14}<\begin{matrix}COO\\COO\end{matrix}>ScOH$.

4. Photographed Spectra of Scandium and associated elements, from λ6305 to λ2625.

5. Lemniscate Curve, showing the author's scheme of the arrangement of the chemical elements in space, and the position of scandium with reference to its associated elements.

Such a figure will result from three very simple simultaneous motions. First, an oscillation to and fro (suppose east and west); secondly, an oscillation at right

angles to the former (suppose north and south); and thirdly, a motion at right angles to these two (suppose downwards), which, in its simplest form, would be with unvarying velocity.

Take any arbitrary and convenient figure-of-eight, without reference to its exact nature, divide each of the loops into eight equal parts, and then drop from these points ordinates corresponding to the atomic weights of the first cycle of elements. The model represents this figure projected in space; in it the elements are supposed to follow one another at equal distances along the figure-of-eight spiral, a gap of one division being left at the point of crossing. The vertical height is divided into 240 equal parts on which the atomic weights are plotted, from H = 1 to Ur = 239·59. The elements falling one under the other along each of the vertical ordinates, are :—

H He Li Gl B C N O F Na Mg Al Si P S
Cl Ne K Ca Sc Ti V Cr (Mn.Fe.Ni.Co) Cu Zn Ga Ge As Se
Br Ar Rb Sr Y Zr Cb Mo (Rh.Ru.Pd) Ag Cd In Sn Sb Te
I Kr Cs Ba Yb Th Ta W (La.Ce.Pr.Nd) Au Hg Tl Pb Bi
Ra Ur (Ir.Pt.Os)

The four elements, boron, scandium (Mendeleeff's "*ekaboron*, next on order to boron"), yttrium and ytterbium, have a close relationship, thus :—

B	atomic weight	11·0	× 16	= 176·0
Sc	,,	44·1	× 4	= 176·4
Y	,,	89·0	× 2	= 178·0
Yb	,,	173·0	× 1	= 173·0

CHEMICAL SOCIETY.

Ordinary Meeting, May 7th, 1908.

Prof. E. DIVERS, F.R.S., in the Chair.

MR. K. S. CALDWELL was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Charles Duncan Cooper, 776, Oxford Road, Reading; John Robert Cowburn, Belmont Villa, Birkbeck Grove, Acton, W.; Kaufman George Falk, B.Sc., Ph.D., 1070, Madison Avenue, New York City; Norman Holland, 4907, Sherbrooke Street W., Montreal; James Kirkman King, B.A., 55, Brewery Road, Plumstead; Lionel Gordon Larmuth, Grove House, Cheadle Hulme, Manchester; Henry Robert Lyell, Redcott, Dacres Road, Sydenham, S.E.; Haradham Ray, M.A., 4, Jhamapooker Lane, Calcutta; William Readwin, 6, Kirkfield Terrace, Morley, near Leeds; Alexander Mackintosh Stewart, Penang, Straits Settlements; Herbert Horace Ward, University College of Wales, Aberystwyth; Charles Harold Wright, B.A., Government Laboratory, Port of Spain, Trinidad; Charles Robert Young, B.Sc., 11, Low Pavement, Nottingham.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected :— Arthur John Allmand, M.Sc.; William Henry Benson Baker, B.A.; Josiah Leonard Bowen; Arthur Edward Coverdale; Bidhu Bhushan Dutt, M.A.; Albert Edward Findley, B.Sc.; Atul Chandra Gañguli, B.A.; Charles Gilling; Leonard Clifford Green, B.E.; William Hall, B.Sc.; Cyril Arden Hinds; George Edward Holden; Percy Hulme Hornby; Arthur Horrobin; Hugo Stefan Kohn, Ph.D.; Gerald Roche Lynch; Herbert Mansfield, B.Sc.; Frederick J. Maywald; Alwyne Harcourt Meade; Samuel Ernest Melling; Herbert Richard Neech; Pañchanan Neogi, M.A.; Thomas Richards Phillips; Francis Edward Richards, B.Sc.; William Seelhorst; Edwin John Watkins; William Wheatley, B.A.

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

*89. "*The Refraction and Dispersion of Triazo-compounds.*" By JAMES CHARLES PHILIP.

The molecular refraction and dispersion of a number of compounds containing the triazo-group have been determined. A study of these constants shows that the contribution which the N_3-group normally makes to the molecular refraction is 8·91 units, almost the same value as the atomic refraction of bromine. The contribution which the N_3-group normally makes to the molecular dispersion is 0·36—0·37, whilst the atomic dispersion of bromine is 0·35. In certain compounds, namely, ethyl triazoformate, phenylazoimide, and α-naphthylazoimide, the refractive and dispersive powers of the N_3-group are considerably above the normal values. Such "optical exaltation" (Brühl, *Ber.*, 1907, xl., 878) is generally associated with the existence in the molecule of contiguous unsaturated groups, and it will be seen that in each of the three triazo-compounds mentioned the N_3-group is in conjugation with an unsaturated group. The bearing of these results on the formulation of the N_3-group was discussed.

*90. "*The Dissociation Constants of Triazoacetic and α-Triazopropionic Acids.*" By JAMES CHARLES PHILIP.

The conductivity of solutions of these acids has been determined in the usual way. The values obtained for the expression $k = a^2(1-a)v$ diminish to some extent as the dilution increases, but are sufficiently constant to indicate the strengths of the two acids. The value of k for triazoacetic acid is 0·00090—0·00100, whilst that for α-triazopropionic acid is slightly less, about 0·00086. These values show that the introduction of the N_3-group into the molecule of acetic or propionic acid increases the strength of the acid nearly as much as the introduction of a bromine atom. It is noteworthy, also, that the conductivity of the triazoacetate ion is the same as that of the monobromoacetate ion.

DISCUSSION.

MR. H. STANLEY REDGROVE called attention to a paper (CHEMICAL NEWS, 1907, xcv., 193) in which he proved that in general the alleged atomic constants employed in calculating additive physico-chemical constants (such as Brühl's mol.-refractivity constants) were incorrect, and, in the present state of our knowledge, unobtainable.

This was due to the fact that the specific influence due to certain linkings (for example, the "ethane" carbon linking) is neglected. In the paper quoted, he had outlined a general method of calculation by means of the so-called "fundamental constants," whereby the above assumption is avoided, and was applying it with success to the calculation of thermal constants.

Allowing for this, Brühl's hydrogen constant was really the value of the hydrogen atom plus the C.H link decreased by half the value of a C·C link, and his carbon constant the value of the carbon atom increased by twice the value of a C·C link, &c., so that the triazo-constant would be the value of the triazo-group plus the link joining it to carbon decreased by half the value of a C·C link.

*91. "*The Fermentation of Mannose and Lævulose by Yeast-juice.*" (Preliminary Note). By ARTHUR HARDEN and WILLIAM JOHN YOUNG.

1. Mannose is fermented by yeast-juice at almost the same rate as dextrose.

2. Lævulose is fermented somewhat more rapidly than dextrose, the rate varying with different samples of yeast-juice from 1·2 to 1·8, compared with that of dextrose = 1.

3. Mannose and lævulose behave qualitatively towards phosphates in the presence of yeast-juice in a similar manner to dextrose.

a. When a phosphate is added to a fermenting mixture containing either of these sugars, the phosphate is converted into a hexosephosphate not precipitable by magnesia mixture; the rate of fermentation is temporarily greatly accelerated, and during this period an extra amount of carbon dioxide is evolved, equivalent to the phosphate added; the rate then rapidly diminishes, and falls to a value equal to, or slightly greater than, that which it had before the addition of the phosphate.

The fermentation of mannose and lævulose by yeast-juice therefore probably proceeds according to the same

two equations as have been previously proposed by the authors for dextrose :—

1. $2C_6H_{12}O_6 + 2R_2'HPO_4 = 2CO_2 + 2C_2H_6O + C_6H_{10}O_4(PO_4R_2')_2 + 2H_2O.$
2. $C_6H_{10}O_4(PO_4R_2')_2 + 2H_2O = C_6H_{12}O_6 + 2R_2'HPO_4.$

b. As in the case of dextrose, an optimum concentration of phosphate exists, which produces a maximum rate of fermentation. Increase of concentration beyond this maximum diminishes the rate of fermentation produced, until, with a sufficiently great concentration of phosphate, the rate is less than that of the juice in the absence of added phosphate.

4. The quantitative relations of mannose to phosphates are practically the same as those of dextrose.

The maximum rate produced by lævulose, on the other hand, is much greater than (about double) that produced by dextrose or mannose. The accelerated fermentation of lævulose in presence of phosphate, moreover, is much less readily inhibited than that of dextrose or mannose by the further addition of phosphate, the difference in this respect being very marked.

5. Lævulose possesses the property of inducing rapid fermentation in a mixture of dextrose or mannose with yeast-juice, in which fermentation has been inhibited by a large excess of phosphate and in which the concentration of free phosphate is maintained constant throughout the experiment. Dextrose and mannose have not a similar power. The amount of lævulose required to produce this effect is comparatively small. Thus, for a mixture of 15 cc. of yeast-juice with 15 cc. of a 0·6 molar solution of potassium phosphate and 2 grms. of dextrose fermenting at the rate of 0·7 cc. per five minutes, the addition of 0·05 grm. of lævulose was found to be sufficient, the maximum rate produced being 17 cc. per five minutes. The effect is not due to the preferential fermentation of the lævulose, as the amount of gas evolved far exceeds that which could be derived from this source.

The nature of this reaction is still under investigation.

Discussion.

Mr. Grant Hooper asked if Dr. Harden had examined the effect of phosphates on yeast as distinct from yeast-juice. In view of the fact that phosphates had been often used in the so-called "yeast foods" offered to or employed by brewers, it would be interesting to know whether the authors had observed whether the addition of phosphate to normal fermentations with yeast had the same effect as when added to yeast-juice.

Dr. Harden, in his reply, said that Slator had recently observed that the fermentation caused by yeast was not accelerated by phosphate.

*92. "*The Constituents of Olive Leaves.*" By Frederick Belding Power and Frank Tutin.

Air-dried olive leaves were percolated with hot alcohol, when they gave about 30 per cent of their weight of extracted material. This alcoholic extract yielded, besides some amorphous matter, the following products :—

(1) A new *monocarboxylic acid*, $C_{22}H_{45}\cdot CO_2H$ (m. p. 68—69°) ; (2) a small amount of a mixture of fatty acids, containing oleic acid ; (3) hentriacontane, $C_{31}H_{64}$ (m. p. 68—69°) ; (4) pentatriacontane, $C_{35}H_{72}$ (m. p. 74·5°) ; (5) *oleasterol*, $C_{20}H_{34}O$ (m. p. 174°), a new, crystalline alcohol related to the phytosterols ; (6) a new, crystalline alcohol, *olestranol*, $C_{25}H_{42}O_2$ (m. p. 217—218°), which appears to be a hydroxyphytosterol ; (7) *homo-olestranol*, $C_{27}H_{46}O_2$ (m. p. 210°) ; $[\alpha]_D$ +71°), a compound similar to olestranol ; (8) an amount of *d*-mannitol equivalent to about 3·4 per cent of the weight of air-dried leaves ; (9) a considerable amount of a sugar which yields *d*-phenylglucosazone ; (10) a trace of an essential oil ; (11) *oleanol*, $C_{31}H_{48}O(OH)_2,H_2O$ (m. p. 303—304° ; $[\alpha]_D$ +78·3°), a new, crystalline substance in an amount equivalent to nearly 3·4 per cent of the weight of air-dried leaves. This compound contains one alcoholic and one phenolic hydroxyl group. *Monomethyloleanol*, $C_{31}H_{48}O(OH)\cdot O\cdot CH_3$, melts at 194—195°, and on acetylation yields *acetylmethyloleanol*, $C_{31}H_{48}O_2(O\cdot CH)_3\cdot CO\cdot CH_2$ (m.p. 215·5°). *Diacetyloleanol*, $C_{31}H_{48}O_3(CO\cdot CH_3)_2$, when heated to about 210°, gives a *substance*, $C_{31}H_{48}O_3$, which does not fuse at 310°. *Monoacetyloleanol*, $C_{31}H_{48}O_2(OH)\cdot CO\cdot CH_3$, melts at 258°.

*93. "*The Constituents of Olive Bark.*" By Frederick Belding Power and Frank Tutin.

Air-dried olive bark, on percolation with hot alcohol, yielded about 30 per cent of its weighed of extracted material. From this alcoholic extract the following crystalline compounds were obtained, together with some amorphous products.

(1) A new *monocarboxylic acid*, $C_{34}H_{67}\cdot CO_2H$ (m. p. 69—70°), which yields an *ethyl* ester melting at 63° ; (2) a new *monocarboxylic acid*, $C_{24}H_{45}\cdot CO_2H$ (m. p. 79°), the *ethyl* ester of which melts at 66·5° ; (3) a new *monocarboxylic acid*, $C_{34}H_{69}\cdot CO_2H$ (m. p. 92°), which yields an *ethyl* ester melting at 87° ; (4) a new *monocarboxylic acid*, $C_{29}H_{57}\cdot CO_2H$ (m. p. 84°), the *ethyl* ester of which melts at 75° ; (5) a *substance*, probably a *tertiary alcohol*, $C_{35}H_{68}O$ (m. p. 70°) ; (6) pentatriacontane, $C_{35}H_{72}$ (m. p. 74—75°) ; (7) a phytosterol, $C_{27}H_{46}O$ (m. p. 136° ; $[\alpha]_D$ −35·2°), which yields an acetyl derivative melting at 119·5° ; (8) a *substance*, $C_{23}H_{38}O_2(OH)_2$ (m. p. 285—290°), which yields an *acetyl* derivative melting at 160°, and is identical with *ipuranol*, a compound recently isolated by Power and Rogerson from *Ipomoea purpurea* ; (9) a new phenolic substance, *olenitol*, $C_{14}H_{10}O_6$ (m. p. 265°), dilute solutions of which show a blue fluorescence. *Acetylolenitol* melts at 130° ; (10) *d*-mannitol, in an amount equivalent to 1·9 per cent of the weight of air-dried bark ; (11) a sugar which yields *d*-phenylglucosazone.

94. "*The Reaction of Diazonium Salts with Mono- and Di-hydric Phenols and with Naphthols.*" By Kennedy Joseph Previté Orton and Reginald William Everatt.

The behaviour of a series of typical diazonium salts, mainly hydrogen sulphates, with phenols in alcohol, water, and other solvents has been examined. All diazonium salts couple quantitatively with α- and β-naphthols in alcoholic media, but under similar conditions these salts do not combine with monohydric phenols.

The dihydric phenols, resorcinol and orcinol, resemble the naphthols, reacting readily with all diazonium salts in alcoholic solution. In aqueous solution, on the other hand, only those diazonium salts with a preponderance of negative substituents (halogen atoms) in the benzene nucleus couple completely with the two dihydric phenols. In other cases, unless the acidity has been reduced by sodium acetate, the coupling is either partial or absent, according to the character of the substituents of the benzene nucleus.

It is a remarkable fact that those diazonium salts possessing halogen atoms in the positions 2, 4, and 6 with respect to the diazo-group (for example, *s*-tribromodiazobenzene) will react rapidly and quantitatively with resorcinol and orcinol in solution in 50 per cent sulphuric acid.

Diazonium salts are converted by quinol in aqueous or alcoholic solution into the correspondlng hydrocarbon, thus :—

$$Ar\cdot N_2HSO_4 + OH\cdot C_6H_4\cdot OH = ArH + N_2 + H_2SO_4 + O : C_6H_4 : O.$$

With catechol, either coupling or a similar reaction to that with quinol takes place, according to the nature of the substituents in the benzene nucleus of the diazonium salt.

A number of azoresorcinols and azo-orcinols were described.

95. "*The Condensation of Benzoin with Methyl Alcohol.*" By James Colquhoun Irvine and David McNicoll.

It has already been noticed (*Trans.*, 1907, xci., 1384) that during the methylation of benzoin by Fischer's method two by-products (m. p. 185° and 285°) are formed in varying quantity, according to the conditions of the reaction. As one of the compounds appeared to be produced by the

condensation of benzoin methyl ether, the constitution and mode of formation of both substances have been further examined. The results show that the compounds are tetraphenylfuran derivatives, and the formulæ previously suggested are therefore no longer tenable. Both substances give the same triacetyl derivative when treated with acetic anhydride and sulphuric acid in the cold, and this in turn, when warmed with the reagent, is converted into acicular dibenzoylstilbene. The compound of lower melting-point is converted into the other by the action of methyl alcohol and hydrogen chloride, and both substances are formed when dibenzoylstilbene is subjected to a similar reaction. The compound melting at 185° is thus regarded as *αβ-dibenzoyl-α-methoxydibenzyl*—

$$C_6H_5\cdot C\text{———}C(OMe)\cdot C_6H_5$$
$$C_6H_5\cdot C<\overset{O}{\underset{O}{}}>C\cdot C_6H_5 \quad ,$$

and the second compound (m. p. 285°) as *2-hydroxy 3 : 5-dimethoxytetraphenyltetrahydrofuran*, conclusions which are supported by the action of hydrogen iodide on each. Apparently the formation of the compounds takes place during the methylation prior to the formation of benzoin methyl ether, and is doubtless owing to the dehydration of the benzoin to form dibenzoylstilbene, which then unites with two molecules of methyl alcohol in two successive stages.

The occurrence of similar side reactions has also been noticed in the methylation of anisoin.

96. "*The Mutual Solubility of 2-Methylpiperidine and Water.*" By OTTO FLASCHNER and BASIL MACEWEN.

The influence of constitution on one of the two critical solution temperatures of mutually soluble liquids was discussed. Nitrogen and oxygen atoms increase the mutual solubility when one of the liquids is water, whilst carbon and hydrogen atoms decrease it. In order to ascertain the influence of the position of a substituted group in a cyclic compound, the mutual solubility of 2-methylpiperidine and water has been examined. This is represented by a closed curve. The lower critical solution temperature is 79°, and the higher one 227°.

97. "*The Melting-points of the Anilides, p-Toluidides, and α-Naphthalides of the Normal Fatty Acids.*" By PHILIP WILFRED ROBERTSON.

The melting-points of the fatty amides do not exhibit any regularity even if the odd or even members are considered separately. The anilides also show the same exceptional behaviour, and, in order to obtain a more definite insight into the relationship between melting-point and number of carbon atoms in a homologous series, the missing members have been prepared as well as a complete series of the *p*-toluidides. The irregularities in these two series seem to tend always in the reverse direction to those observed in the case of the amides. On taking the mean melting-points of the amides and anilides, and of the amides and *p*-toluidides, the disturbing factor, which is considered to be a function of the lack of symmetry of the molecule, is to a great extent eliminated, as regular series of numbers are obtained.

In the fatty α-naphthalides, where the substituent group is heavier, irregularities tend to disappear: the melting-points of the even members descend to a minimum at the eighth member and then rise gradually, whilst there is a corresponding minimum in the case of the odd series at the ninth member.

98. "*The Absorption Spectrum of Camphor.*" By WALTER NOEL HARTLEY.

The absorption spectrum of solutions of camphor was examined in 1881 (Hartley, *Trans.*, xxxix., 153) and compared with the spectra of benzene and its derivatives. There was a difficulty in obtaining it free from impurities showing absorption bands. Camphor sublimed in sunlight and condensed in large crystals, showed no band, and was remarkably diactinic. In view of more recent work, it was decided to re-examine the spectrum of camphor very carefully. The result has been to show that when solutions of ten times the concentration usually employed in such experiments are examined, a band occurs in the spectrum, due to the occurrence of the CO and CH_2 groups in the molecule. This is in general agreement with the work of Baly, Marsden, and Stewart (*Trans.*, 1906, lxxxix, 979), but otherwise the substance is remarkably diactinic.

99. "*The Viscosity of Solutions.*" By CHARLES EDWARD FAWSITT.

In continuation of previous work (*Zeit. Phys. Chem.*, 1904, xlviii., 585; *Electrochemist and Metallurgist*, 1904, iii., 664), a number of colloidal solutions and alcoholic solutions have been examined. In dilute solutions, the viscosity is, in general, a linear function of the concentration. If the viscosities of solutions of the substances in a homologous series are compared, the relation of viscosity to composition appears to be largely additive.

100. "*The Action of Fused Potassium Hydroxide and of Hydrogen Peroxide on Cholesterol.*" (Preliminary Note). By ROBERT HOWSON PICKARD and JOSEPH YATES.

Cholesterol is slowly decomposed by prolonged fusion with potassium hydroxide. From the products of the decomposition, small quantities of two crystalline acids have been isolated. The *acid*, $C_{26}H_{44}(OH)\cdot CO_2H$, melts at 241°, is optically active, and forms an *acetyl* derivative (m. p. 163°) and an *ethyl* ester (m. p. 62°). The *acid*, $C_{24}H_{42}(CO_2H)_2$, melts at 190°, and forms an amorphous *silver* salt.

Cholesterol or its acetate is also rapidly attacked by hydrogen peroxide, which is employed to the best advantage under the conditions described by W. H. Perkin, jun., (*Proc.*, 1907, xxiii., 166). The main product is a neutral *substance*, $C_{27}H_{46(or\ 48)}O_3$, m.p. 239°, which is probably isomeric with dehydrocholestantriol (Windaus, *Ber.*, 1907, xl., 257). The *monoacetate* melts at 212°, the *diacetate* at 165°, and the *dipropionate* at 172°. It may be oxidised to a *keto-alcohol*, $C_{27}H_{44}O_3$ (m. p. 232°), which forms a *monoacetate*, m. p. 233°, and a *phenylhydrazone*, m. p. 164°. The substances melting at 239° and 232° contain the hydroxyl group of cholesterol, and are readily oxidised to the diketo-alcohol ("oxycholestendiol") described by Mauthner and Suida (*Monatsh.*, 1896, xvii., 590). Dicholesteryl ether behaves in an analogous manner with hydrogen peroxide, forming a neutral *substance*, $(C_{27}H_{45}O_2)_2O(?)$, which melts at 192° and forms a *diacetate*, m. p. 143°. The formation of these substances appears to confirm the deductions of Windaus (see summary in *Arch. Pharm.*, 1908, ccxlvi., 117) as to the relation between the constitution of cholesterol and that of some of the products of its oxidation by permanganic and chromic acids.

101. "*The Volumetric Estimation of Silver.*" By WILLIAM ROBERT LANG and J. C. WOODHOUSE.

The apparatus employed for the estimation of sulphates and salts of barium (*Trans.*, 1907, xci., 1370) was found unsuitable for the determination of silver, owing to the slowness with which the milky solution in the thin tube cleared. Some filtering medium appeared necessary, so, after several unsuccessful attempts with glass-wool and with asbestos, clean sand was used, held in position by a glass-wool plug in a curved tube. The packed sand filter necessitated the use of a filter-pump for washing, and was found a great convenience. Experiments were made with solutions containing a known amount (0·5 grm.) of silver, to which an excess of N/10 sodium chloride was added and the excess titrated with N/10 silver nitrate. Each titration occupied about half-an-hour, and the mean error of six determinations was 0·286 per cent. On using 1 grm. of silver, 100 cc. of N/10 sodium chloride, and titrating back with N/100 silver nitrate, the error was reduced to 0·198 per cent. The effect of free nitric acid in varying amounts on the estimation was also tried and found to reduce the error still further, as low as 0·063 per cent. The method and apparatus were then employed to determine silver in

bullion under the same conditions as obtained in the Gay-Lussac method, namely, 1 grm. of silver in nitric acid, 100 cc. of N/10 sodium chloride, and finishing with N/100 silver nitrate. The result of seven estimations done in this way, each occupying about half-an-hour, gave a mean error of 0·067 per cent. It seems reasonable to hope that this apparatus may prove of use to those requiring a rapid and accurate method of estimating silver.

102. "*A Criticism of Werner's Theory, and the Constitution of Complex Salts.*" By John Albert Newton Friend.

The author pointed out the disadvantages of Werner's theory, as applied to simple and complex salts, and suggested new structural formulæ which are free from these objections.

103. "*The Action between Potassium Sulphite and Potassium Pentathionate.*" By Edward Divers.

Debus published, in 1888, a paper on the polythionic acids (*Trans.*, liii., 278), which is still a classic on the subject, but can remain so only so long as later researches leave its accuracy in all essentials untouched. It is therefore important to point out that the accuracy of Debus' investigation of the action between a sulphite and a pentathionate is not affected by Colefax's quite recent work (*Trans.*, 1908, xciii., 798), as it would appear to be from pp. 803—804 of that author's paper. Debus is in agreement with Colefax, but his work is more comprehensive than Colefax's and with a wider object in view.

Colefax has found that potassium sulphite in solution is, nearly all, rapidly converted by potassium pentathionate into the thiosulphate, whilst Debus has stated (*loc. cit.*, p. 344) that "potassic sulphite and potassic pentathionate form potassic thiosulphate and potassic trithionate." The latter author's experimental proof of this is given on p. 332, but in an irregular form, for, instead of using potassium sulphite, he dissolved the potassium pentathionate in a concentrated solution of sulphur dioxide and then added barium carbonate. He gives two chemical equations in explanation of this procedure, which are equivalent to $K_2S_5O_6 + 2K_2SO_3 = K_2S_3O_6 + 2K_2S_2O_3$, an equation indicating a 50 per cent fall in iodine titration-value, in accordance with Colefax's observations. By using barium carbonate, Debus accomplished an easy separation of the products, obtaining the thiosulphate as insoluble barium salt, and the trithionate as potassium salt, in crystals. Colefax worked throughout his investigations on molecular proportions of his salts, as was proper for the end he had in view, but the addition to the above equation of a second molecule of pentathionate is without effect on the action it expresses or on the iodine value. Working quantitatively, and with the actual salts, Colefax has made, it should be added, a real addition to our knowledge of the reaction.

Debus did experiment with potassium sulphite itself, converting it into thiosulphate by the pentathionate, but he employed solutions a hundred times stronger than those used by Colefax, with the result, not met with by the latter, that he also obtained much sulphur dioxide. His explanation of this evolution of sulphur dioxide is a suggestion of deep theoretical significance, if well founded, with apparently no other explanation possible in place of it. His experiment has no bearing on Colefax's investigation with highly dilute solutions, and Debus's explanation of it is certainly quite inapplicable to the results obtained in other ways, both by himself and by Colefax, as the latter has rightly pointed out in connection with his own work.

104. "*Note on Phenolic Thetines and their Action with Benzoyl Chloride.*" By Edward de Barry Barnett and Samuel Smiles.

When phenol and phenetole *p*-sulphoxide are dissolved in concentrated sulphuric acid, *phenoxydiphenetylsulphonium sulphate* is formed. The *platinichloride* of the base is an orange-brown powder melting at 123—125°. The condensation of diphenyl sulphoxide with phenol does not take place in cold sulphuric acid, but it may readily be effected by warming with phosphoric oxide. *Phenoxydiphenylsulphonium platinichloride* occurs in orange crystals, which rapidly decompose at about 210°. The salts of these bases are colourless, viscous oils. On treatment with aqueous alkali hydroxide, they yield the phenolic thetines. These are unstable, yellow oils, which are soluble in water or chloroform and insoluble in concentrated aqueous alkali hydroxide. They are formed (by elimination of alkali salt) from the sodium salt of the sulphonium base—

$$(C_6H_5)_2(C_6H_4\cdot ONa)SCl = NaCl + (C_6H_5)_2{:}S\cdot C_6H_4\cdot O.$$

With benzoyl chloride in aqueous alkaline solution, the phenolic thetines yield benzoic anhydride, and in this respect they resemble certain tertiary nitrogen bases, for example, pyridine (Minunni, *Gazzetta*, 1892, xxii., 215). With hydrochloric acid they furnish the chlorides of the corresponding sulphonium bases.

105. "*The Relation between Dielectric Constant and Chemical Constitution.* Part I. *Stereoisomeric Compounds.*" By Alfred Walter Stewart.

The author has examined active and racemic compounds and also geometrical isomerides, and finds that the influence of the spacial arrangement of atoms on the dielectric constants of isomeric substances is not clearly marked. A difference in electric absorption was noticed in one case, the active isomeride having a stronger absorptive power than the racemic form.

106. "*An Apparatus for Determining the Specific Inductive Capacity of Organic Liquids.*" By Alfred Walter Stewart.

In this apparatus, Hertzian waves are generated and conducted along a secondary circuit in the usual manner. The secondary circuit is led through a vertical graduated tube, and an adjustable bridge between the wires of the circuit is obtained by moving mercury up and down within the tube. The apparatus is calibrated in the usual way, by means of liquids of known specific inductive capacity. The chief advantages over the previous method (Drude, *Zeit. Phys. Chem.*, 1897, xxiii., 267) lie in the regulation of temperature by jacketing the tube (which could not be done easily in the Drude apparatus), in the sharpness of contact between the mercury and the wires of the secondary circuit, and in the comparatively small quantity of substance required for the new apparatus. Reduced pressures can also be used.

107. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* Part XII. *Ethyl Tartrate in Aromatic Halogen Derivatives.*" By Thomas Stewart Patterson and David Paterson McDonald.

The rotation of ethyl tartrate has been examined in chlorobenzene, bromobenzene, iodobenzene, *p*-dichlorobenzene, and α-bromonaphthalene. The data were compared with others formerly obtained for benzene and for various aliphatic halogen derivatives. The relationship between rotation and molecular solution-volume in these solvents was discussed, as was also the influence of temperature change on the rotation of dilute solutions of ethyl tartrate in α-bromonaphthalene.

108. "*A New Test for Silver.*" By Arnold William Gregory.

When a solution of a silver salt is added to a mixture of 20 cc. of aqueous ammonium salicylate (20 grms. of salicylic acid neutralised with ammonium hydroxide, a slight excess of the latter added, and the solution made up to 1 litre), and 20 cc. of ammonium persulphate solution (50 grms. in 1 litre), an intense brown colour is produced. By this reaction, 0·01 milligrm. of silver can be detected. As lead does not give this reaction, silver may be tested for in presence of this element; 1·1 milligrm. of silver may be detected in this manner in the presence of 0·2 grm. of lead.

It was found that the brown substance formed in this reaction does not contain silver, and it is probable that the silver salt acts as a catalyst, since on boiling a solution of ammonium salicylate with ammonium persulphate a similar brown colour is produced.

109. "*The Spontaneous Crystallisation of Substances which form a Continuous Series of Mixed Crystals: Mixtures of Naphthalene and β-Naphthol.*" By HENRY ALEXANDER MIERS and FLORENCE ISAAC.

The object of this research was to ascertain whether there are definite temperatures of spontaneous crystallisation in mixtures which yield a continuous series of mixed crystals.

By means of experiments on mixtures of naphthalene and β-naphthol of known composition contained in sealed tubes, the authors have determined the supersolubility curve, and also the freezing-point curve and the melting-point curve for the whole series of mixtures.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 14, April 6, 1908.

Isomer of Diphenylcamphomethane.—A. Haller and E. Bauer.—Diphenylcamphomethane, which fuses at 106°, can be transformed into an isomer fusing at 136° to 137°. When the product of the reaction between phenyl magnesium bromide and benzylidene camphor is treated with benzyl chloride, a benzoate of diphenylcamphomethane is formed. This benzoate on saponification yields benzoic acid, and the same diphenylcamphomethane, fusing at 136—137°, as that resulting from the transformation of the isomer fusing at 106°. The authors have not as yet succeeded in determining the relation of the two compounds to one another.

Presence of Spark Lines in the Arc Spectrum.—Ch. Fabry and H. Buisson.—When the spark and arc spectra of a metal are compared it is found that certain lines belonging to the second are absent from the first or appear only very faintly. These lines are called spark lines (Lockyer's enhanced lines). The authors have discovered that in the spectrum of iron all the spark lines are emitted by certain parts of the arc. The arc appears to the eye to be formed of two flames which originate from a point situated on the drop of molten iron at the end of each electrode. These points emit all the spark lines, while the arc flames do not show them. The nickel and cobalt arcs exhibit the same phenomenon.

New Method of Determining Mercury Vapour in Air.—P. Ménière.—The method depends upon the preparation of intimate mixtures of the air containing mercury with the vapours of boiling nitric acid. The whole of the metal is thus fixed as nitrate, and can be determined colorimetrically by means of diphenylcarbazide. The apparatus for preparing the mercury nitrate consists of a 1500 cc. bulb furnished with two openings. Through the first is passed a tube for introducing the gas, while the second is connected with a Lebel-Schlœsing spiral. This apparatus is connected with a second, exactly like it to avoid loss. Nitric acid is placed in each bulb, and is boiled, while the air containing mercury is passed in. The nitrate solution thus obtained is slowly evaporated, and the mercury determined by Cazeneuve's method with diphenylcarbazide.

Combustion of Gases by Incandescence in presence of Oxidisable and Incombustible Substances.—Jean Meunier.—Incandescent substances localise combustion at their surface, and the experimental results are different according as the incandescent substance is oxidisable or incombustible. At ordinary temperatures the chemical affinity of oxygen for hydrogen, carbon, and their compounds is not revealed in gaseous mixtures. At the temperature of ignition, however, an attraction is exercised suddenly and violently between the molecules of the combustible substance and those of the oxygen. The chemical attraction is generally accompanied by a physical attraction. This is clearly shown when a combustible solid having given up all its volatile matter continues to burn without a flame. The molecules of oxygen are evidently attracted by those of the burning solid, when the latter is at a sufficiently high temperature. The author has illustrated this phenomenon by igniting piano-wire in oxygen and finding the increase of weight, which shows that some oxygen was attracted from a distance to the burning wire. The intensity of incandescence does not depend only upon the nature of the substance, but also upon the composition of the combustible mixture which surrounds it.

Variations in the Composition of Ammonium Phosphomolybdate.—G. Chesneau.—The amount of phosphorus in precipitates of ammonium phosphomolybdate appears to vary with the concentration of the phosphoric and molybdic acids and of the ammoniacal salts. If, however, Carnot's method of double precipitation is adopted, precipitates of perfectly constant composition are obtained, provided that—(1) 50 cc. of freshly prepared molybdic reagent and 5 grms. of ammonium nitrate are employed per grm. of metal; (2) the first precipitation is performed between 65° and 70°, and thus no ammonium tetramolybdate is formed; (3) the precipitate is always dissolved in the same quantity of ammonia. After re-acidifying with concentrated nitric acid the precipitate must be allowed to settle, and 15 cc. of the molybdic reagent added. The whole must be kept for two hours at 40°, and the precipitate washed with pure water.

Ammoniacal Chlorides of Dimercurammonium.—H. Gaudechon.—The study of the reactions and the thermochemistry of the two compounds, $(NHg_2Cl)_2H_2O$ and $NHg_2Cl.H_2O$, shows that two derivatives, $(NHg_2Cl)_2.NH_3$ and $NHg_2Cl.NH_3$, correspond to these compounds, the water molecule being replaced by the ammonia molecule. Thus the group NHg_2Cl, which has not yet been isolated, behaves like a true metallic chloride. Rammelsberg's compound, $NHg_2Cl.NH_4Cl$, may be regarded as the chlorhydrate of the complex ammonium base.

Arbutine and some of its Derivatives.—Em. Bourquelot and H. Hérissey.—Arbutine, $C_6H_4{<}^{OC_6H_{15}O_5}_{OH}$, and its methyl, benzyl, and dinitro derivatives, can be hydrolysed by emulsine. They are all derived from *d*-glucose, and are lævorotatory, and thus follow the general rules enunciated by the authors.

Comparative Study of the Dehydration of Atrolactic and *p*-Methoxyatrolactic Acids.—J. Bougault.—Atrolactic acid, or rather its ethyl ether, is dehydrated by prolonged boiling with hydrochloric acid (3 parts acid to 1 part water). It gives atropic acid and some of Fittig's isatropic acid. In the cold it yields β-chlorhydratropic acid, $C_6H_5—CH(CH_2Cl)—CO_2H$, and a little isatropic acid. When atrolactic acid is boiled with acetic acid or dilute mineral acid (10 per cent), no appreciable quantities of atropic acid are formed. *p*-Methoxyatrolactic acid is dehydrated much more readily. When boiled with acetic acid or dilute mineral acids, it gives good yields of *p*-methoxyatropic acid. With concentrated hydrochloric acid a new acid is formed by the condensation of two molecules of *p*-methoxyatropic acid. The author calls it di-*p*-methoxyatropic acid, $(C_{10}H_{10}O_3)_2$.

Formation of Mixtures of Isomers of Constant Melting-point in Friedel and Craft's Reaction.—G. Perrier and H. Caille.—When phenylnaphthylketone is

prepared by Friedel and Craft's method after decomposing with water a product is obtained which melts sharply at 54°. This is neither the α-derivative (melting-point 75°) nor the β-derivative (melting-point 82°). It can be separated into these isomers by crystallisation in ligroin and mechanical separation of the crystals, or by Rousset's method (formation in benzene of the insoluble β-picric derivative to the exclusion of the α-derivative). It appears to be a simple mechanical mixture which, like mixtures of salts or alloys, melts at a lower temperature than its constituents.

No. 15, April 13, 1908.

Action of Heat on the Hydrates of Lithium Hydroxide.—M. de Forcrand.—The evaporation of a concentrated solution of the pure hydroxide in cold pure air gives the compound $LiOH.H_2O$, which yields LiOH in a vacuum at the ordinary temperature. By heating the commercial hydroxide in a current of dry hydrogen it fuses at 445°, losing water. Its weight becomes absolutely constant at that temperature, and its composition is $LiOH+.125H_2O$. This is undoubtedly a definite compound; it can be heated for hours in a current of hydrogen without losing weight. After heating for eight to ten hours to 660° and two hours to 780°, the anhydrous oxide, Li_2O, or rather nLi_2O, is obtained.

Sulphur Compounds of Thorium.—A. Duboin.—The author prepared thorium chloride by passing a current of chlorine containing carbon tetrachloride over thorium hydroxide heated in a glass tube. The chloride thus obtained always contains a little oxychloride. Sulphuretted hydrogen begins to react on it at a dull red heat, and gives a dark brown amorphous product. In a porcelain tube at a red heat a very few crystals are obtained with amorphous brown and yellow products. If the chloride of thorium, to which an excess of sodium chloride has been added, is placed in a porcelain boat in the middle of a porcelain tube and heated in a reverberatory furnace, and a current of dry sulphuretted hydrogen is passed in, on cooling and extracting with water it is seen that the greater part of the product consists of brown micaceous shining lamellæ. These can be separated by sifting from the amorphous product, and small quantities of yellow crystals also formed. The yellow crystals can also be isolated by treating the sifted part with nitric acid, when the brown substance is attacked rapidly, and the yellow crystals much more slowly. The brown substance is thorium sulphide, ThS_2, whilst the yellow crystals are an oxysulphide.

Semicatalysis. Oxidation of Hydrocarbons in presence of Phosphorus.—Albert Colson.—When phosphorus is dissolved in terebenthene in presence of air the liquid becomes turbid, and a white curdy or colloidal deposit is formed. It is odorous, is insoluble in water, but soluble in ether and acetic acid. It does not contain free phosphoric acid. When the ethereal solution is dried in air a resinous substance of composition $PO_4H_3(C_{10}H_{16}O_3)_2$ is obtained. It is evident that the terebenthene has been oxidised, and since it does not oxidise in absence of phosphorus the phenomenon may be regarded as a sort of catalysis. Since, on the other hand, the phosphorus itself undergoes an alteration it is not a true catalytic action, but one which the author designates semi-catalysis.

Alloys of Platinum and Thallium.—L. Hackspill.—Platinum sponge dissolves readily in fused thallium, giving an alloy the melting-point of which is lower than that of pure thallium when the amount of platinum does not exceed 10 per cent. When more platinum is added the melting-point is first lowered, and then rapidly raised, reaching 855°, when 65 per cent of platinum is present. All these alloys are very brittle. The alloys rich in thallium contain white shining crystals, the number and dimensions of the crystals being at a maximum in the alloy, PtTl. This compound closely resembles PtPb.

Austenite.—Ed. Maurer.—The author has investigated the preparation of austenite from steel containing a little nickel and manganese and comparatively large amounts of carbon. Taking three specimens of the following composition—

	I.	II.	III.
Nickel	3·73	—	—
Manganese ..	—	1·83	2·20
Carbon	1·21	1·18	1·94
Silicon	0·28	0·88	0·94

he heated them for fifteen minutes to 1050°, and then tempered them in ice water. The two first specimens gave martensite and the third pure austenite.

No. 16, April 21, 1908.

Reducing Power of Ferropyrophosphates.—P. Pascal.—Concentrated and dilute solutions of ferropyrophosphates instantly reduce salts of gold and silver in the cold, but have no effect upon platinum salts even at 100°. Alkaline ferropyrophosphates reduce a solution of mercuric chloride, giving, first, mercurous chloride and then mercury. They precipitate cuprous iodide or bromide from copper salts on addition of alkaline iodide or bromide.

MEETINGS FOR THE WEEK.

Monday, June 1st.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "The 'Autolysator,' an Apparatus for the Automatic Estimation of Carbon Dioxide," by C. A. Keane and H. Burrows. "Some Modern Chemical Plant" and "Explosions and the Building of Explosive Factories," by O. Guttmann. "Estimation of Orcinol in Orchella Weed," by H. E. Watt.

Tuesday, 2nd.—Royal Institution, 3. "Animal Heat and Allied Phenomena," by Prof. William Stirling, M.D.

Wednesday, 3rd.—Society of Public Analysts, 8. "Studies in Steam Distillation—Part III., The Fatty Acids," by H. D. Richmond. "Detection of Poisonous Metals," by G. D. Lander and H. W. Winter. "Estimation of Cocoanut Oil in Butter," by R. Ross. "Ochoco Fat," by J. Lewkowitsch. "Detection of Small Quantities of Methyl Alcohol in the presence of Ethyl Alcohol," by L. E. Hinkel. "Separation of certain Volatile Fatty Acids by Extraction with Benzene or Toluene," by T. R. Hodgson.

Thursday, 4th.—Royal Institution, 3. "The Chemistry of Photography" by Alexander Scott, F.R.S., &c.
—— Chemical, 8.30. "Condensation Products from Pinene Aminodicarboxylic Acid," by W. Godden. "A Delicate Test for Bromides alone or in Solution with Chlorides," by J. S. Jamieson. "Experiments on the Synthesis of 1-Methylcyclohexylidene-4-acetic Acid," by W. H. Perkin and W. J. Pope. "The Triazo-group—Part IV., Allyl Azoimide," by M. O. Forster and H. E. Fierz.

Friday, 5th.—Royal Institution, 9. "The Nadir of Temperature and Allied Problems," by Prof. Sir James Dewar, F.R.S.

Saturday, 6th.—Royal Institution, 3. "The Art of Bach and Future Developments," by H. Walford Davies, Mus.Doc.

THE CHEMICAL NEWS.

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SOME OF THE NON-METALLIC ELEMENTS IN CONNECTION WITH VALENCY AND SPECIFIC GRAVITY.

By GEO. WOODIWISS.

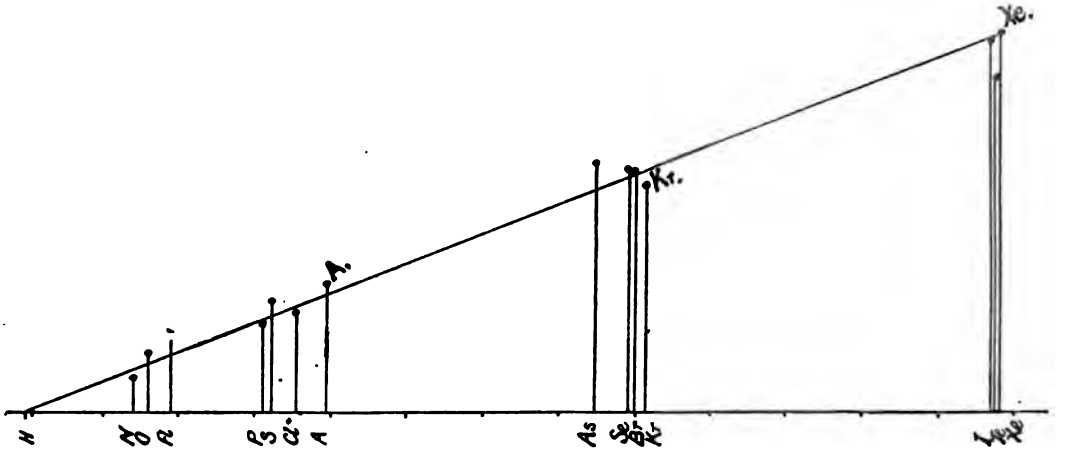
IT will probably readily be granted that one of the most interesting studies in chemistry is that of periodicity. What may possibly not be so evident is the order of the elements in the periods, different writers giving different versions of the matter. To the scientist with a full grasp of the whole subject this may be of little moment, but to the student with no desire for making this a speciality it is quite another thing. From one writer he may learn that lithium, sodium, copper, &c., follow each other in a natural grouping of the elements, casually from another he finds that lithium, potassium, &c., is considered to be more correct, and incidentally he may find that for their own purpose neither of the writers will adopt either of the orders given, but that each will place lithium, sodium, potassium, &c., in a group of alkali metals with copper altogether separate. The average student thus fails to appreciate the full importance of periodicity, and passes it by as a mere curiosity.

Again, he may be taught that there is a systematic change in valency progressing regularly from 1 to 8, after which there is a sudden drop to 0 for the argon group. The question will naturally arise, is the argon group by this method placed in a correct position? We find on taking a list of the elements in the order of atomic weight that this group as a rule falls between the alkali metals and the halogens, both of which are monovalent; and as valency has systematically decreased from either direction to this point, both with and against atomic weight, it is to be expected that it will further decrease and that for the argon group it will be of a value of less than 1. But are we justified in placing this amount definitely at 0? By so doing are we not giving a value to an unknown quantity, and precluding even the possibility of any element with a valency of a fraction of 1? Indirectly we may obtain evidence that it is not absolutely outside the bounds of possibility for such a valency to be, the indication pointing to this group possibly having a value of 0·5. No chemical action is known to take place with an exchange value of less than 1, consequently there would be no inconsistency if the above actually was the correct figure.

In support of this, if we take a list of the elements in the order of the atomic weight, we find that immediately preceding the argon group are the triads, diads, and monads of the non-metallic class, a characterising feature of which is the specific gravity being approximately directly proportionate to the atomic weight, as distinguished from the adjoining metals of similar valency (see CHEMICAL NEWS, xcvii., p. 122). A second feature is, the specific gravity of the groups vary, approximately, as the square root of the valency value. This singular connection between valency and specific gravity is only applicable to the argon group by adopting a value of 0·5.

In each case in the following lists the first set of figures is the specific gravity taken, and the last set is specific gravity divided by the square root of the valency value.

				Fl	1·1	÷ $\sqrt{1}$ =	1·1
A	1·21	÷ $\sqrt{0·5}$ =	1·7	Cl	1·33	,,	1·3
Kr	2·15	,,	3·0	Br	3·18	,,	3·2
Xe	3·52	,,	5·0	I	4·95	,,	4·9
O	1·13	÷ $\sqrt{2}$ =	0·8	N	0·88	÷ $\sqrt{3}$ =	0·5
S	2·07	,,	1·5	P	2·1	,,	1·2
Se	4·50	,,	3·2	As	5·7	,,	3·3
Te	6·23	,,	4·4	Sb = metallic.			



To show the connection more clearly the accompanying diagram is constructed, wherein the quotient of specific gravity, divided by square root of assumed valency value, is plotted against atomic weight. Here we see the inert elements argon, krypton, and xenon with an assumed valency of 0·5 behaving in accord with others of the non-metallic class.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st instant, the Duke of Northumberland, K.G., President, in the Chair. Mr. Franklin Adams, the Right Hon. the Duke of Devonshire, Dr. W. Heptinstall Millar, Lady Martin, Mr. P. Mavrogordato, and Mr. J. Ziffo were elected Members. The Chairman announced that he had nominated the following gentlemen as Vice-Presidents for the ensuing year;—The Right Hon. the Earl of Halsbury, Dr. Donald W. C. Hood, Dr. Ludwig Mond, the Right Hon. the Earl of Rosse, Mr. Alexander Siemens, The Right Hon. Sir James Stirling, Sir James Crichton-Browne (Treasurer), and Sir William Crookes (Honorary Secretary).

ON THE CALCULATION OF THERMO-CHEMICAL CONSTANTS.

IV.—THERMAL CONSTANTS OF ORGANIC OXYGEN COMPOUNDS (*continued*).

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

(Concluded from p. 255).

5. *Molecular Heats of Combustion of Ketones and Aldehydes.*

ALL ketones and aldehydes can theoretically be obtained by replacing 2ϵ hydrogen atoms in the corresponding hydrocarbon by ϵ oxygen atoms each "doubly linked" to carbon, where ϵ is some integer; the following constant will therefore be required:—

ω_2 = the algebraic sum of the following heats—(i.) due to the severance of two C.H links; (ii.) due to the combustion of two hydrogen atoms (to liquid water), minus the algebraic sum of the following heats—(iii.) due to the severance of a C:O link; (iv.) one-half that due to the formation of an oxygen molecule; or as it can be more simply written:—

ω_2 = the sum of the following heats—(ii.) due to the combustion of two hydrogen atoms (to liquid water); (iii.) due to the formation of a C:O link, minus the sum of the following heats—(i.) due to the formation of two C.H links; (iv.) one-half that due to the formation of an oxygen molecule.

So that the general ketone and aldehyde,—

$$n\mathrm{C}+2(n+1-a-2b-p-\epsilon)\mathrm{H}+ +(n+p-a-b-1)\mathrm{L}_1+a\mathrm{L}_2+b\mathrm{L}_3+\epsilon\mathrm{O}+\epsilon(\mathrm{C{:}O})\text{ links},$$

can be written—

$$n\mathrm{C}+2(n+1-a-2b-p)\mathrm{H}+ +(n+p-a-b-1)\mathrm{L}_1+a\mathrm{L}_2+b\mathrm{L}_3-\epsilon\omega_2 = na-(n+p-a-b-1)\beta-a\gamma-b\delta-\epsilon\omega_2.$$

The value of ω_2 can be shown from a consideration of carbon dioxide to be identical with that of $\frac{a}{2}$ in either of the following ways:—

1. a = molecular heat of combustion of methane (to gaseous carbon dioxide and liquid water) = the algebraic sum of the following heats—(i.) due to the combustion of one carbon atom; (ii.) due to the severance of four C.H links; (iii.) due to the combustion of four hydrogen atoms (to liquid water). But as carbon on combustion gives O:C:O, the heat of combustion of one carbon atom = the heat due to the formation of two C:O links, less the heat due to the formation of an oxygen molecule.

Therefore a = the sum of the following heats—(iii.) due to the combustion of four hydrogen atoms (to liquid water); (i.) due to the formation of two C:O links, minus the sum of the following heats—(ii.) due to the formation of four C.H links; (i.) due to the formation of an oxygen molecule.

Therefore $a = 2\omega_2$, whence $\omega_2 = \frac{a}{2} = 105{\cdot}4$ cals.

2. Otherwise, CO_2 can be written $a-2\omega_2$; its heat of combustion is zero, whence $a-2\omega_2=0$, so that $\omega_2 = \frac{a}{2} = 105{\cdot}4$ cals. as before.

This value of ω_2, as will be shown later, is in excellent agreement with the values obtained for the carbonyl oxygen in certain acids and esters.

In Table III. will be found the molecular heats of combustion, corrected for constant volume, of three aldehydes and two ketones given by Thomsen. These give lower values for ω_2, thus:—

Acetaldehyde is $CH_3.CHO$; *i.e.*, $2a-\beta-\omega_2$ M.H.C. found = 281·0 cals. Therefore $\omega_2 = 2a-\beta-281{\cdot}0$ cals. = (421·6 − 52·5 − 281·0 cals.) = 88·1 cals.

The values of ω_2 calculated thus from each aldehyde and ketone are given in the table. The mean value for the aldehydes is ω_2 = 87·7 cals., for the ketones ω_2 = 91·4 cals.; using these values the molecular heats of combustion of all the aldehydes and ketones given have been calculated, and are exhibited together with the differences between them and the experimental, and the percentage errors in Table III. The agreement is excellent.

It must, however, be noticed that probably the above two latter values are not the true values of ω_2, but are purely empirical, inasmuch that it seems very probable that all (or at least many) ketones and aldehydes are, under ordinary circumstances, mixtures of true carbonyl-oxygen compounds—the true ketones and aldehydes, and unsaturated secondary alcohols (*i.e.*, mixtures of the keto and enol forms); these latter it is worth while noticing have theoretically relatively high molecular heats of combustion.

6. *Molecular Heats of Formation of Aldehydes and Ketones.*

The molecular heat of formation constant corresponding to ω_2 is:—

ω_2' = the algebraic sum of the following heats—(i.) due to the decomposition of a hydrogen molecule; (ii.) due to the formation of two C.H links, minus the algebraic sum of the following heats—(iii.) one-half that due to the decomposition of an oxygen molecule; (iv.) due to the formation of a C:O link, or as it can be more simply written:—

ω_2' = the sum of the following heats—(ii.) due to the formation of two C.H links; (iii.) one-half that due to the formation of an oxygen molecule, minus the sum of the following heats—(i.) due to the formation of a hydrogen molecule; (iv.) due to the formation of a C:O link.

Therefore, $\omega_2+\omega_2'$ = the heat due to the combustion of two hydrogen atoms (to liquid water) less the heat due to the formation of a hydrogen molecule = the molecular heat of combustion of molecule hydrogen to liquid water = 67·5 cals.; whence ω_2' = 67·5 cals. $-\omega_2$.

Therefore ω_2' (CO_2, acids and esters; see hereinafter) = (67·5 - 105·4) cals. = −37·9 cals. ω_2' (aldehydes) = (67·5 − 87·7) cals. = −20·2 cals. ω_2' (ketones) = (67·5 - 91·4) cals. = −23·9 cals.

In Table III. will be found the molecular heats of formation (at constant volume) of the ketones and aldehydes given by Thomsen, from which the following values of ω_2' have been calculated in a similar manner as were those of ω_2:—

ω_2' (aldehydes) = −20·1 cals. ω_2' (ketones) = −23·55 cals.

Using the mean values ω_2' (aldehydes) = −20·2 cals., ω_2' (ketones) = −23·7 cals.; the molecular heats of formation of all the aldehydes and ketones given have been calculated, and are exhibited together with the differences between them and and the experimental in Table III.

7. *Molecular Heats of Combustion of Esters.*

The general formula for all esters derived from monobasic carboxy acids and mono-hydroxy alcohols is:—

$$n\mathrm{C}+2(n-a-2b-p-1)\mathrm{H}+(n+p-a-b-1) \mathrm{L}_1+a\mathrm{L}_2+b\mathrm{L}_3+2\mathrm{O}+1(\mathrm{C{:}O})\text{ link}+2(\mathrm{C.O})\text{ links}^* = n\mathrm{C}+2(n+1-a-2b-p)\mathrm{H}+ +(n+p\ \ a-b-1)\mathrm{L}_1+a\mathrm{L}_2+b\mathrm{L}_3-\omega-\omega_2, = na-(n+p-a-b-1)\beta-a\gamma-b\delta-\omega-\omega_2.$$

In Table IV. will be found the molecular heats of combustion (corrected for constant volume) of nine such esters given by Thomsen; from these the value of $\omega+\omega_2$ has been calculated, thus:—

Methyl formate is $H\cdot C\lessgtr^{O}_{OCH_3}$; *i.e.*, $2a-\omega-\omega_2$.

M.H.C. found = 240·6 cals.

Therefore $\omega+\omega_2 = 2a-240{\cdot}6$ cals. = (421·6 − 240·6) cals. = 181·0 cals.

* For common esters put $p=-1$.

TABLE III.—Aldehydes and Ketones.

1. Substance.	2. Formula.	Molecular Heat of Combustion. 3. Formula.	4. M.H.C. found (Thomsen) constant vol. Cals.	5. ω_2 Calculated. Cals.	6. M.H.C. calculated. Cals.	7. Difference between cols. 4 and 6. Cals.	8. Error. Per cent.	Molecular Heat of Formation. 9. Formula.	10. M.H.F. (Thomsen) constant vol. Cals.	11. ω_2' Calculated. Cals.	12. M.H.F. calculated. Cals.	13. Difference between cols. 10 and 12. Cals.
Aldehydes—												
Acetic aldehyde ..	$CH_3.CHO$	$2\alpha-\beta-\omega_2$	281·0	88·1	281·4	+0·4	+0·14	$2\alpha'-\beta'-\omega_2'$	47·9	−20·5	47·6	−0·3
Propionic aldehyde .	$C_2H_5.CHO$	$3\alpha-2\beta-\omega_2$	439·6	87·8	439·7	+0·1	+0·02	$3\alpha'-2\beta'-\omega_2'$	53·8	−20·2	53·8	0·0
Isobutyric aldehyde.	$C_3H_7.CHO$	$4\alpha-3\beta-\omega_2$	598·4	87·3	598·0	−0·4	−0·07	$4\alpha'-3\beta'-\omega_2'$	59·3	−19·5	60·0	+0·7
		Mean .. .. ω_2 =		87·7				Mean .. .. ω_2' =		−20·1		
Ketones—												
Dimethyl ketone ..	$(CH_3)_2CO$	$3\alpha-2\beta-\omega_2$	436·1	91·3	436·0	−0·1	−0·02	$3\alpha'-2\beta'-\omega_2'$	57·3	−23·7	57·3	0·0
Methylpropyl ketone	$CH_3.CO.C_3H_7$	$5\alpha-4\beta-\omega_2$	732·5	91·5	752·6	+0·1	+0·01	$5\alpha'-4\beta'-\omega_2'$	69·4	−23·4	69·7	+0·3
		Mean .. .. ω_2 =		91·4				Mean .. .. ω_2' =		−23·55		

TABLE IV.—Esters.

				$\omega+\omega_2$ calculated.						$\omega'+\omega_2'$ calculated.		
Esters—												
Methyl formate ..	$H.CO_2CH_3$	$2\alpha-\omega-\omega_2$; $1\frac{1}{2}\alpha-\omega$	240·6	181·0	240·8	+0·2	+0·08	$2\alpha'-\omega'-\omega_2'$	88·3	−45·9	88·1	−0·2
Methyl acetate ..	$CH_3.CO_2CH_3$	$3\alpha-\beta-\omega-\omega_2$; $2\frac{1}{2}\alpha-\beta-\omega$	398·4	181·5	399·1	+0·7	+0·18	$3\alpha'-\beta'-\omega'-\omega_2'$	95·0	−46·4	94·3	−0·7
Methyl propionate	$C_2H_5.CO_2CH_3$	$4\alpha-2\beta-\omega-\omega_2$; $3\frac{1}{2}\alpha-2\beta-\omega$	552·8	185·4	557·4	+4·6	+0·83	$4\alpha'-2\beta'-\omega'-\omega_2'$	105·0	−50·2	100·5	−4·5
Methylisobutyrate	$C_3H_7CO_2CH_3$	$5\alpha-3\beta-\omega-\omega_2$; $4\frac{1}{2}\alpha-3\beta-\omega$	715·5	181·0	715·7	+0·2	+0·03	$5\alpha'-3\beta'-\omega'-\omega_2'$	106·8	−45·8	106·7	−0·1
Ethyl formate ..	$H.CO_2C_2H_5$	$3\alpha-\beta-\omega-\omega_2$; $2\frac{1}{2}\alpha-\beta-\omega$	399·2	180·7	399·1	−0·1	−0·03	$3\alpha'-\beta'-\omega'-\omega_2'$	94·2	−45·6	94·3	+0·1
Ethyl acetate ..	$CH_3.CO_2C_2H_5$	$4\alpha-2\beta-\omega-\omega_2$; $3\frac{1}{2}\alpha-2\beta-\omega$	545·4	(192·8)	557·4	+12·0	+2·20	$4\alpha'-2\beta'-\omega'-\omega_2'$	112·4	(−57·6)	100·5	−11·9
Propyl formate ..	$H.CO_2C_3H_7$	$4\alpha-2\beta-\omega-\omega_2$; $3\frac{1}{2}\alpha-2\beta-\omega$	557·6	180·6	557·4	−0·2	−0·04	$4\alpha'-2\beta'-\omega'-\omega_2'$	100·2	−45·4	100·5	+0·3
Isobutyl formate .	$H.CO_2C_4H_9$	$5\alpha-3\beta-\omega-\omega_2$; $4\frac{1}{2}\alpha-3\beta-\omega$	718·4	178·1	715·7	−2·7	−0·35	$5\alpha'-3\beta'-\omega'-\omega_2'$	103·8	−42·8	106·7	+2·9
Allyl formate ..	$H.CO_2C_3H_5$	$4\alpha-\beta-\gamma-\omega-\omega_2$; $3\frac{1}{2}\alpha-\beta-\gamma-\omega$	527·0	(174·7)	520·9	−6·1	−1·16	$4\alpha'-\beta'-\gamma'-\omega'-\omega_2'$	63·3	(−39·5)	69·5	+6·2
		Mean .. .. $\omega+\omega_2$ =		181·2				Mean .. $\omega'+\omega_2'$ =		−46·0		

TABLE V.—Acids, &c.

				$\omega_1+\omega_2$ calculated.						$\omega_1'+\omega_2'$ calculated.		
Acids—												
Formic acid . ..	$H.CO_2H$	$\alpha-\omega_1-\omega_2$; $\frac{1}{2}\alpha-\omega_1$	69·1	141·7	69·0	−0·1	−0·14	$\alpha'-\omega_1'-\omega_2'$	95·4	−74·2	95·5	+0·1
Acetic acid . ..	$CH_3.CO_2H$	$2\alpha-\beta-\omega_1-\omega_2$; $1\frac{1}{2}\alpha-\beta-\omega_1$	224·8	144·3	227·3	+2·5	+1·11	$2\alpha'-\beta'-\omega_1'-\omega_2'$	104·1	−76·7	101·7	−2·4
Propionic acid ..	$C_2H_5.CO_2H$	$3\alpha-2\beta-\omega_1-\omega_2$; $2\frac{1}{2}\alpha-2\beta-\omega_1$	385·6	141·8	385·6	0·0	0·00	$3\alpha'-2\beta'-\omega_1'-\omega_2'$	107·7	−74·1	107·9	+0·2
		Mean.. .. $\omega_1+\omega_2$ =		142·4				Mean .. $\omega_1'+\omega_2'$ =		−75·0		
Acetic anhydride .	$(CH_3CO)_2O$	$4\alpha-2\beta-\omega-2\omega_2$; $3\alpha-2\beta-\omega$	459·5	—	452·0	−7·5	−1·63	$4\alpha'-2\beta'-\omega'-2\omega_2'$	130·8	—	138·4	+7·6

TABLE VI.—*The Fundamental Molecular Heat of Combustion and Formation, Oxygen Constants.*

Class of oxygen linkage.	Class of substance.	M.H.C. (cals.).	M.H.F. (cals.).
Etheric oxygen	Ethers, $R.O.R_1$	$\omega = 75{\cdot}4$	$\omega' = -7{\cdot}8$
	Esters, $R.C\overset{O}{<}_{OR_1}$		
Hydroxylic oxygen	Alcohols (Group 1, see text)	$\omega_1 = 29{\cdot}7$	$\omega_1' = -\omega_1 = -29{\cdot}7$
	Alcohols (Group 2, see text)	$\omega_1 = 36{\cdot}4$	$\omega_1' = -\omega_1 = -36{\cdot}4$
	Acids, $R.C\overset{O}{<}_{OH}$		
Ketonic oxygen	Aldehydes, $R.C\overset{O}{<}_{H}$ (?)	$\omega_2 = 87{\cdot}7$	$\omega_2 = -20{\cdot}2$
	Ketones, $R.C\overset{O}{<}_{R_1}$ (?)	$\omega_2 = 91{\cdot}4$	$\omega_2' = -23{\cdot}7$
	Carbon dioxide	$\omega_2 = \frac{a}{2} = 105{\cdot}4$	$\omega_2' = -37{\cdot}9$
	Esters, $R.C\overset{O}{<}_{OR_1}$		
	Acids, $R.C\overset{O}{<}_{OH}$		

The value of $\omega+\omega_2$ obtained from each acid is given in the table. The mean value (neglecting the values obtained from ethyl acetate and allyl formate, which diverge rather greatly from the mean) = 181·2 cals. It is at once evident that if we assign to ω_2 the values obtained from either aldehydes or ketones, values for ω will be obtained which are much higher than obtained before (CHEMICAL NEWS, xcvii., p. 253); but if, on the other hand, we assign to ω_2 the value 105·4 cals. obtained from a consideration of carbon dioxide, a value for ω, namely, 75·8 cals., is obtained in excellent agreement with that obtained from ethers, namely, 75·4 cals.

It is evident, therefore, that as the value of ω_2 in these esters is equivalent to $\frac{a}{2}$, their formulæ, in so far as molecular heats of *combustion* are concerned, can be simplified, the general formula becoming:—

$$(n-\tfrac{1}{2})a-(n+p-a-b-1)\beta-a\gamma-b\delta-\omega.$$

Both sets of formulæ are given in Table IV.; using the simplified one and the value $\omega = 75{\cdot}4$ cals., the molecular heats of combustion of all the esters given have been calculated, and are exhibited together with the differences between them and the experimental, and the percentage errors in Table IV. The agreement is quite satisfactory, except in the case of ethyl acetate, which gives an exceptional molecular heat of combustion, which has not yet been satisfactorily explained (see Thomsen, "Thermochemische Untersuchungen," iv., p. 310).

8. *Molecular Heats of Combustion of Acids.*

The general formula for all monobasic carboxy acids is—

$$\begin{aligned}&nC+2(n-a-2b-p-\tfrac{1}{2})H+(n+p-a-b-1)L_1+\\&\quad+aL_2+bL_3+2O+1(CtO)\text{ link}+\\&\quad+1(C.O)\text{ link}+1(O.H)\text{ link}+H\text{ (linked to O, not C).}\\&=nC2(n+1-a-2b-p)H+\\&\quad+(n+p-a-b-1)L_1+aL_2+bL_3-\omega_1-\omega_2.\\&=na-(n+p-a-b-1)\beta-a\gamma-b\delta-\omega_1-\omega_2.\end{aligned}$$

In Table V. will be found the molecular heats of combustion (corrected for constant volume) of three acids given by Thomsen; from these the value of $\omega_1+\omega_2$ has been calculated thus:—

Formic acid is $H.C\overset{O}{<}_{OH}$; *i.e.*, $a-\omega_1-\omega_2$. M.H.C. found = 69·1 cals. Therefore $\omega_1+\omega_2 = a-69{\cdot}1$ cals. = (210·8 − 69·1) cals. = 141·7 cals. The value of $\omega_1+\omega_2$ obtained from each acid is given in the table. Mean value $\omega_1+\omega_2 = 142{\cdot}4$ cals. It is at once evident that if we assign to ω_2 the values obtained from either aldehydes or ketones, values for ω_1 will be obtained which are much higher than obtained before (CHEMICAL NEWS, xcvii., p. 255); but if, on the other hand, we assign to ω_2 the value 105·4 cals. obtained from the consideration of carbon dioxide, we obtain for ω_1 a value 37·0 cals. in agreement with that found for the second group of alcohols, namely, 35·9 cals. The mean of these two values, namely, 36·4 cals., is therefore taken as the value of ω_1 for these classes of compounds.

It is evident therefore that as the value of ω_2 in these acids is equivalent to $\frac{a}{2}$ their formulæ, in so far as molecular heats of *combustion* are concerned, can be simplified as were the formulæ of their esters with monohydroxy alcohols, the general formula becoming:—

$$(n-\tfrac{1}{2})a-(n+p-a-b-1)\beta-a\gamma-b\delta-\omega_1.$$

Both sets of formulæ are given in Table V.; using the simplified fromulæ and the value $\omega_1 = 36{\cdot}4$ cals. the molecular heats of combustion of the acids (and also similarly that of acetic anhydride, using $\omega = 75{\cdot}4$ cals.) have been calculated, and are exhibited together with the differences between them and the experimental and the percentage errors in Table V. The agreement in the cases of the acids is quite satisfactory.

9. *Molecular Heats of Formation of Esters and Acids.*

The values of $\omega'+\omega_2'$ and $\omega_1'+\omega_2'$ have been similarly calculated from the molecular heats of formation of the esters and acids respectively, as were the corresponding molecular heat of combustion constants. The mean values are $\omega'+\omega_2' = -46{\cdot}0$ cals. and $\omega_1'+\omega_2' = -75{\cdot}0$ cals. in agreement with the values of ω', ω_1', and ω_2', as obtained respectively from ethers, alcohols (second group), and carbon dioxide. Using these values, namely, $\omega'+\omega_2' = -45{\cdot}7$ cals., $\omega_1'+\omega_2' = -74{\cdot}3$ cals., the molecular heats of formation of all these esters, acids, &c., given, have been calculated, and are exhibited together with the differences between them and the experimental in Tables IV. and V.

10. *Summary and Conclusion.*

In the two foregoing papers the molecular heats of combustion (and formation) of all the organic oxygen compounds given by Thomsen (excluding necessarily those containing elements whose thermal behaviours have not yet been considered; and also the following: carbon monoxide, whose formula is doubtful; carbonylchloride, trimethylorthoformate, and dimethyl and diethyl carbonates, which give anomalous results) have been considered, and by means of the author's system of "fundamental constants" (the values of which are exhibited in Table VI.) perfectly satisfactory results have been obtained for the molecular heats of combustion (and formation) of thirty-four substances out of the thirty-eight considered.

At a later date it is hoped that with the accumulation of data, explanations may be offered of the anomalous substances.

The Polytechnic, Regent Street, W.

THE ETHER OF SPACE.*

By Sir OLIVER LODGE, LL.D., D.Sc., F.R.S.

(Concluded from p. 258).

Appendix I.—On Gravity and Etherial Tension.

Stating the law of gravitation as $F = \gamma \frac{m\,m'}{r^2}$, the meaning here adopted for etherial tension at the surface of the earth is—

$$T = \int_R^\infty \frac{\gamma E}{r^2}\,dr = \frac{\gamma E}{R};$$

so that the ordinary intensity of gravity is—

$$g = -\frac{dT}{dR} = \frac{\gamma E}{R^2} = \frac{4}{3}\pi\rho\gamma R.$$

Accordingly, near the surface of a planet the tension is $T_0 = g R$, or for different planets in proportional to ρR_2.

The velocity of free fall from infinity to such a planet is $\sqrt{(2 T_0)}$; the velocity of free fall from circumference to centre, assuming uniform distribution of density, is $\sqrt{(T^0)}$; and from infinity to centre it is $\sqrt{(3 T_0)}$.

Expanding all this into words:—

The etherial tension near the earth's surface, required to explain gravity by its rate of variation, is of the order 6×10^{11} c.g.s. units. The tension near the sun is 2500 times as great. With different spheres in general, it is proportional to the density and to the superficial area. Hence, near a bullet one inch in diameter, it is of the order 10^{-6}; and near an atom or electron about 10^{-11}.

In order to set up a tension equal to the critical, or presumably disruptive, stress in the ether [10^{23} c.g.s.], a globe of the density of the earth would have to have a radius of eight light years. In order to generate a velocity of free fall under gravity equal to the velocity of light, a globe of the earth's density would have to be equal in radius to the distance of the earth from the sun, or say 26,000 times the earth's radius. If the density were less, the superficial area would have to be increased in proportion, so as to keep ρR^2 constant.

The whole visible universe within a parallax of 1/1000 second of arc, estimated by Lord Kelvin as the equivalent of 10^9 suns, would be quite incompetent to raise etherial tension to the critical point 10^{23} c.g.s., unless it were concentrated to an absurd degree; but it could generate the velocity of light with a density comparable to that of water.

If the average density of the above visible universe (which may be taken as $1{\cdot}6 \times 10^{-28}$ grms. per cc.) continued without limit, a disruptive tension of the ether would be reached when the radius was comparable to 10^{18} light years; and the velocity of light would be generated by it when the radius was 10^7 light years. But heterogeneity would enable these values to be reached *more* easily.

It is noteworthy how exceedingly small is the average or aggregate density of matter in the visible region of space; and Lord Kelvin has shown that throughout space in general it must be smaller still—in fact ultimately infinitesimal.

The estimated density of 10^{-28} c.g.s. means that the visible cosmos is as much rarer than a vacuum of a hundred millionths of an atmosphere, as that vacuum is itself rarer than lead.

It is, of course, because ordinary masses of matter likewise consist of separated particles, with great intervening distances in proportion to their size, that we are able to assert the minute aggregate density of ordinary stuff, such as water or lead, as compared with the continuous medium of which all particles are supposed to be really composed. The fundamental medium itself must be of uniform density everywhere, whether materialised or free.

* Abstract of a Discourse delivered at the Royal Institution, February 21, 1908.

Appendix II.—Explanatory Remarks concerning the Density of Ether.

I observe that it is surmised by at least one thoughtful and friendly critic—C. W. S. in the *Westminster Gazette*—that in speaking of the immense density or massiveness of ether, and the absurdly small density or specific gravity of gross matter by comparison, I intended to signify that matter is a *rarefaction* of the ether. That, however, was not my intention. The view I advocate is that the ether is a perfect *continuum*, an absolute *plenum*, and that therefore no rarefaction is possible. The ether inside matter is just as dense as the ether outside, and no denser. A material unit—say an electron—is only a peculiarity or singularity of some kind in the ether itself, which is of perfectly uniform density everywhere. What we sense as matter is an aggregate or grouping of an enormous number of such units.

How then can we say that matter is millions of times rarer or less substantial than the ether of which it is essentially composed? Those who feel any difficulty here should bethink themselves of what they mean by the average or aggregate density of any discontinuous system, such as a powder, or a gas, or a precipitate, or a snow-storm, or a cloud, or a milky way.

If it be urged that it is unfair to compare an obviously discrete assemblage like the stars, with an apparently continuous substance like air or lead, the answer is that it is entirely and accurately fair; since air, and every other known form of matter, is essentially an aggregate of particles, and since it is always their average density that we mean. We do not even know for certain their individual atomic density.

The phrase "specific gravity or density of a powder" is ambiguous. It may mean the specific gravity of the dry powder as it lies, like snow; or it may mean the specific gravity of the particles of which it is composed, like ice.

So also with regard to the density of matter, we might mean the density of the fundamental material of which its units are made—which would be ether; or we might, and in practice do, mean the density of the aggregate lump which we can see and handle; that is to say, of water or iron or lead, as the case may be.

In saying that the density of matter is small, I mean, of course, in the last, the usual, sense. In saying that the density of ether is great, I mean that the actual stuff of which these highly porous aggregates are composed is of immense, of well-nigh incredible, density. It is only another way of saying that the ultimate units of matter are few and far between—*i.e.*, that they are excessively small as compared with the distances between them; just as the planets of the solar system, or worlds in the sky, are few and far between—the intervening distances being enormous as compared with the portions of space actually occupied by lumps of matter.

Here it may be noted that it is possible to argue that the density of a *continuum* is necessarily greater than the density of any disconnected aggregate: certainly of any assemblage whose particles are actually composed of the material of the *continuum*. Because the former is "all there," everywhere, without break or intermittence of any kind; while the latter has gaps in it—it is here, and there, but not everywhere.

Indeed, this very argument was used long ago by that notable genius Robert Hooke, and I quote a passage which Professor Poynting has discovered in his collected posthumous works, and kindly copied out for me:—

"As for *matter*, that I conceive in its essence to be immutable, and its essence being expatiation determinate, it cannot be altered in its quantity, either by condensation or rarefaction; that is, there cannot be more or less of that power or reality, whatever it be, within the same expatiation or content; but every equal expatiation contains, is filled, or is an equal quantity of *materia*; and the densest or heaviest, or most powerful body in the world contains no more materia than that which we conceive to be the rarest, thinnest, lightest, or least powerful body of

all; as gold, for instance, and *æther*, or the substance that fills the cavity of an exhausted vessel, or cavity of the glass of a barometer above the quicksilver. Nay, as I shall afterwards prove, this cavity is more full, or a more dense body of æther, in the common sense or acceptation of the word, than gold is of gold, bulk for bulk; and that because the one, viz., the mass of æther, is all æther: but the mass of gold, which we conceive, is not all gold; but there is an intermixture, and that vastly more than is commonly supposed, of æther with it; so that vacuity, as it is commonly thought, or erroneously supposed, is a more dense body than the gold as gold. But if we consider the whole content of the one with that of the other, within the same or equal quantity of expatiation, then are they both equally containing the *materia* or body."—From the "Posthumous Works of Robert Hooke, M.D., F.R.S.," 1705, p. 171 (as copied in "Memoir of Dalton," by Angus Smith).

Newton's contemporaries did not excel in power of clear expression, as he himself did, but Professor Poynting interprets this singular attempt at utterance thus:—"All space is filled with equally dense *materia*. Gold fills only a small fraction of the space assigned to it, and yet has a big mass. How much greater must be the total mass filling that space."

The tacit assumption here made is that the particles of the aggregate are all composed of one and the same continuous substance, practically that matter is made of ether; and that assumption, in Hooke's day, must have been only a speculation. But it is the kind of speculation which time is justifying, it is the kind of truth which we all feel to be in process of establishment now.

We do not depend on that sort of argument, however; what we depend on is experimental measure of the mass, and mathematical estimate of the volume, of the electron. For calculation shows that however the mass be accounted for, whether electrostatically or magnetically, or hydrodynamically, the estimate of ratio of mass to effective volume can differ only in a numerical coefficient, and cannot differ as regards order of magnitude. The only way out of this conclusion would be the discovery that the negative electron is not the real or the main matter-unit, but is only a subsidiary ingredient, whereas the main mass is the more bulky positive charge. That last hypothesis, however, is at present too vague to be useful. Moreover, the mass of such a charge would in that case be unexplained, and would need a further step, which would probably land us in much the same sort of etherial density as is involved in the estimate which I have based on the more familiar and tractable negative electron.

It may be said why assume any finite density for the ether at all? Why not assume that, as it is infinitely continuous, so it is infinitely dense—whatever that may mean—and that all its properties are infinite? This might be possible were it not for the velocity of light. By transmitting waves at a finite and measurable speed, the ether has given itself away, and has let in all the possibilities of calculation and numerical statement. Its properties are thereby exhibited as essentially finite—however infinite the whole extent of it may turn out to be.

ON THE PURIFICATION OF PEATY WATERS BY FREEZING.

By FRANK T. SHUTT, M.A., F.I.C.,
Chemist, Dominion Experimental Farms.

In the course of an investigation to ascertain the relative purity of the ice from the Ottawa and Rideau Rivers, certain data were obtained of an interesting character, illustrative of the purification of "upland, surface" waters by freezing.

Both waters are "peaty" and highly coloured, and they are, further, characterised by a very small mineral content. The Ottawa river, by reason of its much larger body of water, its succession of rapids and water-falls, and its passage through a country less likely to contaminate it, naturally offers a more favourable source for supply than the Rideau river, which, in addition to its smaller volume and much shorter length, is at intervals through a considerable portion of its course rendered more or less stagnant by the locks which serve to convert the river into a canal system.

Analyses of these river waters made in the month of November are presented; they serve to show that the differences in the nature or quality of the waters is one of degree rather than of kind. Presumably, both rivers, at the point of collection, are unpolluted.

Analysis of Waters of Ottawa and Rideau Rivers (parts per million).

	Ottawa River (above Chaudiere Falls).	Rideau River (above Billings Bridge).
Free ammonia	0·012	0·024
Albumenoid ammonia	0·227	0·40
Nitrogen as nitrates and nitrites	0·113	0·034
Chlorine	0·6	2·5
Total solids at 212° F.	56·0	145·2
Solids after ignition .	24·8	82·8

That both waters contain large quantities of dissolved vegetable organic matter is evident from the high figures for the albumenoid ammonia; the Ottawa river water, however, it will be remarked, is in this respect much the purer. There would be no object for the purposes of this paper in critically considering and comparing these data, but it may be pointed out in passing, that they show the superior quality of the Ottawa river water in many respects—a conclusion that is in accord with our prediction from a knowledge of the rivers and the country through which they travel.

Ice from Ottawa and Rideau Rivers.

The ice blocks analysed were cut in February, when the thickness of the ice on the Ottawa river was about 22 inches; that on the Rideau river, about 18 inches. Both blocks showed from 4 to 6 inches on the surface of so-called "snow" or "slush" ice: *i.e.*, ice formed partly of snow. This layer of ice, which, though not so transparent as the rest of the block, was nevertheless fairly solid and clean. From inspection one would say that both ices were satisfactory, being clear, non-porous, and practically free from suspended matter.

Thoroughly representative samples were procured by sawing a section, about 5 inches wide, from the centre of each block and throughout its whole thickness. The ice thus obtained was broken up and allowed to melt in a clean covered vessel, the resulting waters constituting the first series as follows:—

Analysis of Ice (parts per million).

	From Ottawa River (above Chaudiere Falls).	From Rideau River (above Billings Bridge).
Free ammonia	0·04	0·06
Albumenoid ammonia	0·041	0·135
Nitrogen as nitrates and nitrites	0·049	0·049
Chlorine	0·05	0·15
Total solids at 212° F.	4·4	5·4
Solids after ignition .	Trace	Trace

Comparing these data with those of the waters previously given, it is at once apparent that, in freezing, a very large quantity of dissolved organic matter has been eliminated. Taking, first, the albumenoid ammonia as an index of this peaty matter, it will be noticed that the reduction by freezing in the case of the Ottawa river is from 0·227 p.p.m. to 0·041 p.p.m., and in that of the Rideau river from 0·400 p.p.m. to 0·135 p.p.m. Similarly with the "Total Solids," practically half of which is organic matter, the reduction from freezing has been from

56 p.p.m., and 145·2 p.p.m. to 4·4 p.p.m. and 5·4 p.p.m. respectively. The chlorine is also much reduced, and the mineral matter (solids after ignition) entirely disappears.

Purification by freezing has long been known, but the data on record in this regard refer more particularly to the exclusion of mineral matter. The extent to which dissolved vegetable matter may be thrown out by freezing, as made evident by these results, has seemed to the writer somewhat remarkable and worthy of note.

To obtain some further knowledge respecting this exclusion of peaty matter by freezing, 1000 cc. of the Ottawa river water were placed in a porcelain basin and submitted to the action of frost until the greater portion of the water was converted into ice. Upon removal of the ice it was found that 125 cc. of the original water still remained unfrozen, the ice representing 875 cc. Analyses of each were made, and the results show that under such conditions a very considerable elimination of the organic matter had taken place during the freezing process.

	Ice (p.p.m).	Water (p.p.m.).
Free ammonia	0·01	0·08
Albumenoid ammonia	0·175	0·40

A calculation from these results of the amounts of free and albumenoid ammonia in the original water furnishes data in close accord with those obtained by direct analysis.

The degree of purification is dependent on several factors. According to recognised authorities, ice forming on deep water is purer than that on shallow water—the quality of both waters being initially the same. The slower the ice formation, the purer the ice. The thicker the ice, within certain limits, the purer it is; and, lastly, it is held that the lower part of the ice block will be of better quality than that nearer the surface.

Purification by freezing is, after all, however, but partial. Undoubtedly under the most favourable conditions a very large proportion of the mineral and organic constituents may be thrown out, and the bacterial content considerably reduced; but it has been clearly shown that the elimination is never such that the ice cut from a polluted source is safe for domestic purposes.

The investigation has been continued to ascertain the purity of the ice in relation to its position in the block, but the data as yet are incomplete and are, therefore, reserved for presentation at some future time.—*Transactions of the Royal Society of Canada*, i., p. 31.

THE DETERMINATION OF ANTIMONY AND ARSENIC IN LEAD-ANTIMONY ALLOYS.

By GEORGE M. HOWARD.

THE separation and determination of antimony and arsenic in alloys with anything like commercial rapidity, and at the same time with a fair degree of accuracy, is by no means a simple matter. The apparent lack of satisfactory published methods led to the development several years ago of the method here described, which, while involving nothing radically new, has proved very serviceable in the author's laboratory.

One great advantage of this method is that tin does not interfere, and does not have to be removed, which makes it available for type metal, &c. Iron and copper in small amounts are also without effect, and in fact there seems to be nothing at all likely to be present which interferes. The method is applicable also to many other cases besides lead-antimony alloys—as, for instance, to the mixed sulphides of antimony and arsenic obtained in many analyses. Some operators object seriously to any method involving the use of hydrogen sulphide, but if the details of manipulation here given are followed there will be no inconvenience whatever from that source.

The procedure is as follows:—

The sample in fine filings, 0·5 to 2 grms. according to circumstances, is weighed into a 125 cc. Erlenmeyer flask, 60 to 70 cc. of strong hydrochloric acid added, and two or three drops (not more) of nitric acid (1·4). The flask is then placed on a hot plate where it will be just short of boiling until solution is complete. Frequent agitation considerably hastens the action. It is sometimes necessary to make further additions of nitric acid, but this should be done carefully, and an excess avoided. When the metal is all dissolved (ten to twenty minutes) the flask should be removed where it will boil vigorously for a few minutes until the colour changes from reddish yellow to colourless—or, if iron or copper is present, to straw-yellow. Now, while still hot, hydrogen sulphide is passed into the solution until it is completely saturated—fifteen minutes is usually sufficient. If insufficient hydrochloric acid has been used, or the solution has been boiled so long on the plate that much has been lost, antimony sulphide will be precipitated as the solution cools. The hydrogen sulphide treatment is most conveniently handled by fitting the flasks with two-hole stoppers and inlet and outlet tubes, and connecting several in series to the generator. If the outlet from the last flask is led into a bottle of caustic soda solution, no gas whatever comes off free. When saturated, the flasks are transferred to a current of air, still in series, and again absorbing the gas from the last flask in caustic soda, and the air passed until all the hydrogen sulphide is removed (half an-hour is sufficient for two flasks). The hydrogen sulphide precipitates nothing but arsenic as sulphide, but reduces all salts capable of reduction—antimony, tin, copper, iron, &c. The current of air then re-oxidises all of these except the antimony, which remains in the antimonious form.

To the now cold solution a little tartaric acid is added, and water until its bulk is about doubled, when it is filtered, best through a double filter, into a 16 oz. flask. Practically all of the lead chloride must be washed out of the precipitate with hot water, but it is not necessary to add all the washings to the filtrate, as the antimonious chloride is readily washed out by decantation with cold water.

Antimony.—The filtrate is nearly neutralised by adding powdered sodium carbonate in small portions, care being used not to reach the point of precipitation of the lead, or, if this is reached, making it slightly acid again with hydrochloric acid. The neutralisation is then completed with sodium bicarbonate, and a slight excess added (about one spoonful of powder). The antimony is then determined by titrating with standard iodine solution, using fresh starch solution as indicator. The precipitate of lead carbonate does not affect the titration, and with a little practice the end-point can be recognised just as easily as in a clear solution. Too much starch should be avoided, as it makes the end-point obscure. A convenient strength for the iodine solution is 1 cc. = 0·005 grm. antimony, then with 0·5 grm. samples 1 cc. = 1 per cent antimony.

If arsenic is negligibly low—which, with a little experience, can be pretty well gauged by the appearance of the precipitate—or for any reason is not to be determined, the filtering may be dispensed with. In this case the whole solution, with the arsenious sulphide, if any, and free sulphur in suspension, is merely transferred to a larger flask, neutralised and titrated. The suspended arsenious sulphide and free sulphur are without effect.

Arsenic.—The bulk of the arsenious sulphide and sulphur is washed off the filter back into the same flask in which the precipitation was made, using not over 20 cc. or so of water. A few drops of sodium hydroxide are added (five drops of 20 per cent solution is ample), the solution boiled for a few moments, and then decanted through the filter into an 8 oz. Erlenmeyer flask. This weak soda readily dissolves the arsenious sulphide, while taking up only a small part of the free sulphur. If the amount of precipitate is at all considerable, it is safer to give a second treatment with soda solution.

The filter is washed with hot water, and discarded. To the filtrate is added hydrogen peroxide solution, which

should be reasonably fresh, or else its strength known. Twenty cc. of 3 per cent solution is sufficient for arsenic up to several per cent. The hydrogen peroxide oxidises the arsenic, and also all sulphur compounds, giving a colourless solution. This is now boiled down to a small bulk, about 20 cc., the excess of peroxide being decomposed in the process. When cool, potassium iodide solution is added in amount equivalent to about 0·1 grm. KI, then 20 cc. of strong hydrochloric acid. After standing five minutes it is cooled and titrated with standard thiosulphate, adding three drops of starch solution only when the colour is almost gone. A convenient strength for the thiosulphate solution is 1 cc. = 0·001 grm. arsenic, and it should, of course, be frequently standardised. It is well, also, to run a blank titration, using the same amounts of reagents as in the analysis, to determine whether there is any constant to be deducted from the burette reading, due to impurities in the reagents.

The difficulty with the end-point experienced by many in this titration appears to be due to using too large an excess of potassium iodide and too much starch. With the proportions given above, the end-point is exceedingly sharp, and the reaction seems to be just as complete as when more potassium iodide is used. The heating due to adding the strong hydrochloric acid is sufficient without any digesting, as is sometimes recommended.

After oxidising and concentrating, the arsenic is in a form to be readily determined in several ways, although the above method is preferred on account of ease and rapidity. For instance, the arsenic may be precipitated with silver nitrate as silver arsenate, after neutralisation with acetic acid, and the combined silver titrated with thiocyanate, as in the well known modified Pearce method. In this case care must be used to wash the sulphide free from lead chloride, and also to have all reagents free from chlorine (most of the hydrogen peroxide solutions on the market contain hydrochloric acid). Or the arsenic may be determined gravimetrically by precipitation as ammonium magnesium arsenate. In this case it is better to use ammonia instead of sodium hydroxide to dissolve the arsenious sulphide.—*Journal of the American Chemical Society*, xxx., No. 3.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 21st, 1908.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

Messrs. G. Barr, C. Gilling, G. R. Lynch, W. E. Oakden, D. R. Pinnock, and W. H. Withey were formally admitted Fellows of the Society.

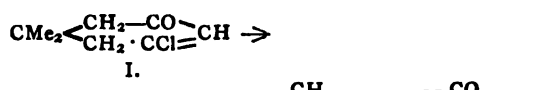
Certificates were read for the first time in favour of Messrs. William Henry Ballantyne, B.Sc., 99, Holmdene Avenue, Herne Hill, S.E.; Edward Morris Bevan, 10, Coronation Street, Aberkenfig, Glam.; James Brown, 20, Tower Road, Dartford, Kent; James Hill Fairweather, 62, Wythes Road, Silvertown, E.; Frank William Crossley-Holland, Connaught Club, Marble Arch, W.; Alfred Ash Meggitt, B.Sc., Dacca, Eastern Bengal, India; Clement Thomas Rutter, 4, Bath Terrace, Hanwell, W.; James Edward Southcombe, M.Sc., 138, Chester Street, Birkenhead, Cheshire; Edward Stokes, B.A., King William's College, Isle of Man; Harry James Yates, Redcroft, Four Oaks, Warwickshire.

A certificate has been authorised by the Council under By-law I. (Par. 3) in favour of Hari Prasad Vidyant, Etawah, U.P., India.

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

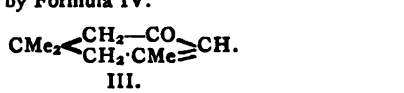
*110. "*Hydroaromatic Ketones.*" (Preliminary Note). By Arthur William Crossley and Charles Gilling.

5-Chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexenone-3 (I.) reacts readily with ethyl malonate in presence of sodium ethoxide to give *ethyl* 1 : 1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one*-5-*acetate* (II.). During the condensation, one of the carbethoxy-groups of the ethyl malonate is evidently hydrolysed by the sodium ethoxide, and the resulting carboxyl group loses the elements of carbon dioxide (compare Moore, *Trans.*, 1904, lxxxv., 165).

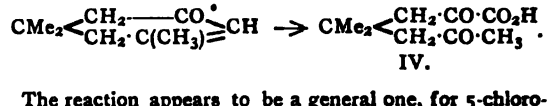


I. II.

The ester is a faintly yellow oil, boiling at 171°/22 mm., and possessing a slight ethereal odour. It gives a *semicarbazone* melting at 156—157° without decomposition. When hydrolysed with alcoholic potassium hydroxide, the corresponding acid cannot be isolated, as it at once loses carbon dioxide to give 1 : 1 : 5-*trimethyl*-Δ^4-cyclo*hexenone*-3 (III.) as a colourless, highly refractive liquid, boiling at 108°/35 mm., and possessing a slight camphoraceous odour. The *semicarbazone* crystallises from alcohol in clusters of flattened needles melting at 190—191°, and the *oxime* forms large transparent prisms melting at 78°. When oxidised with potassium permanganate, a variety of products are obtained, according to the conditions employed. One acid, melting at 98°, has been proved to have the composition $C_9H_{14}O_4$, and its constitution is most probably represented by Formula IV.



III.



IV.

The reaction appears to be a general one, for 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexenone-3 condenses with ethyl ethylmalonate in presence of sodium ethoxide, and the product on hydrolysis yields 1 : 1-*dimethyl*-5-*propyl*-Δ^4-cyclo*hexenone*-3, $CMe_2<^{CH_2\text{——}CO}_{CH_2\cdot C(C_3H_7)}>CH$, boiling at 125°/19 mm., and possessing an odour of celery and camphor. The *semicarbazone* crystallises from alcohol in rosettes of flattened needles melting at 156°. The work is being extended, and the products and by-products of the various reactions are under closer investigation.

*111. "*The Sulphides and Oxysulphides of Silicon.*" By Irvine Giles Rankin and Sidney Montagu Revington.

The white sulphide of silicon, first prepared by Berzelius, has been shown definitely to be the disulphide, SiS_2. The orange sulphide, SiS, prepared by Colson, has been investigated, and, in addition, the composition of two sulphoxides, SiSO and $SiSO_2$, has been determined; the former is mentioned by Colson, but was not analysed by him, whilst the latter has been hitherto unknown.

Discussion.

The President congratulated Mr. Revington and Mr. Rankin on the results they had obtained. He could testify to their perseverance, and, although the analyses which they had quoted were not so concordant as is usual, the difficulties of separating and obtaining in a pure state three such bodies as SiS_2, SiOS, and SiS were great, and at present, at all events, we had to be content with what were great improvements on former results.

*112. "*Apparatus for Experiments at High Temperatures and Pressures, and its Application to the Study of Carbon.*" By Richard Threlfall.

The author described a small and inexpensive laboratory apparatus for exposing carbon or other substances to very high temperatures and pressures. It was shown how small quantities of material may be heated up to the temperature of the melting-point of magnesia at pressures up to 100 tons per square inch. These results are rendered possible by taking advantage of the practically perfect fluidity of crystalline graphite under high pressures. Instead of using compressed gases, as has hitherto been done in order to obtain high pressures, it is only necessary to make use of crystalline graphite, which is, of course, very much more easily and safely handled. The graphite itself acts as a conductor whereby electric heating is rendered possible.

Some experiments on heating graphite or amorphous carbon up to the melting-point of magnesia at pressures up to 100 tons per square inch were described. In no case was anything produced but soft crystalline graphite, the results obtained agreeing precisely with those already published by Parsons (*Proc. Roy. Soc.*, 1907, lxxix., A, 532).

A summary was given of our present information in regard to the transformation of carbon, and the view is taken that the formation of diamond under certain conditions is not so much a direct transformation of carbon as the result of the liberation of carbon by decomposition of carbides in presence of certain substances which induce it to crystallise in any of the well known forms of diamond. These substances can be recognised by a study of the ash left when diamonds are burnt. The only condition as to temperature is that it must be low enough for the velocity of transformation into graphite to be small. The results obtained by Hasslinger and others were examined from this point of view.

*113. "*Acids as Accelerators in the Acetylation of Amino-groups.*" By Alice Emily Smith and Kennedy Joseph Previté Orton.

When the basic properties of amino-groups are in abeyance, acids act as powerful accelerators of acetylation by means of acetic anhydride. Such amino-groups are present in anilines with two negative groups in the ortho-positions with respect to the amino-group.

All strong acids, very small quantities of which are alone needed, act in this manner. Sulphuric, hydrochloric, perchloric, trichloroacetic, nitric, and chromic acids have been tested; the two latter behave exceptionally, yielding respectively nitroaminobenzene, $Ar{\cdot}NH{\cdot}NO_2$, and products of oxidation of the aniline.

The formation of diacetyl as well as of monoacetyl derivatives of the anilines is aided by the presence of acids.

In the case of basic amino-groups, the reaction of which with acetic anhydride, even when largely diluted by a neutral solvent, is extremely rapid, acids act as mild inhibitors of acetylation.

Details of the preparation of typical mono- and di-acetanilides with the aid of strong acids were described.

*114. "*The Chemical Action of Radium Emanation.* Part III. *On Water and certain Gases.*" By Alexander Thomas Cameron and Sir William Ramsay, K.C.B.

The decomposition of water and the re-combination of hydrogen and oxygen, when treated with radium emanation, have been confirmed by numerous experiments. Carbon dioxide is decomposed into carbon, oxygen, and the monoxide. The last named gives carbon, oxygen, and the dioxide. Ammonia breaks up into its components. These re-combine, but in smaller quantity, for the same amount of emanation. Hydrogen chloride is decomposed into hydrogen and chlorine. At 130°, hydrogen and oxygen re-combine during five hours at a steady rate; steam is apparently undecomposed. The time rates of the various reactions were measured; the volume was kept constant, and change of pressure indicated the rate of change. This was in all cases proportional to the rate of change of the emanation. In other words, it obeyed the same exponential law; the amount of change in any time was strictly proportional to the amount of emanation disintegrating in that time. Hence, other conditions being the same, each atom of emanation, as it disintegrates, produces a certain definite chemical effect.

*115. "*The Chemical Action of Radium Emanation.* Part IV. *On Water.*" By Alexander Thomas Cameron and Sir William Ramsay, K.C.B.

The results obtained in a previous experiment (*Trans.*, 1907, xci., 1593) have been confirmed; radium emanation in presence of water breaks up into neon. The neon was conclusively identified by its spectrum; the lines were almost as bright as those of the helium visible at the same time. The spectrum was photographed successfully, and a large number of the neon lines identified. It faded rapidly; the neon lines practically disappeared in ten minutes.

116. "*Titani-dihydroxymaleic Acid and the Detection of Titanium.*" By Henry John Horstman Fenton.

Dihydroxymaleic acid reacts in cold dilute aqueous solution with quadrivalent titanium compounds, giving an intensely reddish brown solution. The reaction is so sensitive that it serves for the detection of minute traces of titanium. It is very much more delicate than the hydrogen dioxide test, and has the additional advantage that it is not given by vanadium.

From more concentrated solutions, a voluminous chocolate-coloured precipitate separates which has the empirical composition $C_4H_4O_6{,}2TiO_2{,}2\frac{1}{2}H_2O$. This compound acts as an acid, giving, when treated with alkalis, bright orange-coloured salts.

Compounds having a similar composition have previously been obtained with many other aliphatic acids, but they are all colourless.

The coloured compound obtained with dihydroxymaleic acid is at once destroyed by hydrofluoric acid or soluble fluorides, and may, as in the case of the hydrogen dioxide reaction, be employed for the detection of fluorides. Owing to the marked difference in colour between the acid and its salts, the compound may also be used as an alkali-acid indicator.

117. "*The Preparation of Diselenides. Dibenzyl Diselenide.*" (Preliminary Note). By Thomas Slater Price and Lionel Manfred Jones.

The method employed by Price and Twiss (*Trans.*, 1907, xci., 2021) for the preparation of disulphides has been extended to the preparation of diselenides. A solution of sodium selenosulphate was obtained by digesting excess of selenium with a solution of sodium sulphite, and then filtering. On adding this solution to an alcoholic solution of benzyl chloride, a turbid liquid was obtained, which, however, soon cleared when heated on a water-bath under reflux. After a short time, sulphur dioxide was evolved, and a small quantity of a yellow oil separated, which, after removal from the remainder of the liquid, solidified on cooling; on re-crystallisation from alcohol, it was obtained in lustrous yellow crystals, melting at 90·5°, and had all the characteristic properties of dibenzyl diselenide, as described by Jackson (*Annalen*, 1875, clxxix., 1). It had probably been formed according to the following equations, the evidence for which the authors hope to publish later:—

$$C_6H_5{\cdot}CH_2Cl + Na_2SeSO_3 = C_6H_5{\cdot}CH_2{\cdot}Se{\cdot}SO_3Na + NaCl,$$

$$2C_6H_5{\cdot}CH_2{\cdot}Se{\cdot}SO_3Na + H_2O = (C_6H_5{\cdot}CH_2{\cdot}Se)_2 + Na_2SO_4 + H_2O + SO_2.$$

On allowing the mother-liquor to stand, a further quantity of diselenide slowly separated, sulphur dioxide being continuously evolved. The diselenide was also obtained from the mother-liquor, after the addition of potassium hydrogen carbonate, by electrolysis in a divided cell, the method being similar to that used in the preparation of disulphides (Price and Twiss, *loc. cit.*).

118. "*The Optical and Sensitising Properties of the* iso*Cyanine Dyes.*" By SAMUEL EDWARD SHEPPARD.

The absorption spectra and sensitising power for gelatino-bromide plates have been investigated for a series of dyes of the *iso*cyanine group. It was shown that solutions in alcohol and chloroform conform to Beer's law, and that the colour is probably independent of ionisation. Further, in different solvents, the absorption follows Kundt's rule, the bands being shifted to the red as the dispersive power of the solvent increases. The influence of different substituted groups on the absorption and sensitising power was measured. It is found that for a group of dyes of similar chemical constitution the photo-chemical activity is proportional to the rate of fading in light. Comparison of the sensitising and absorption spectra shows that the bands in the latter are regularly displaced to the red some 10 $\mu\mu$, as would be expected from their behaviour in different solvents. The investigation of the conditions of sensitising by bathing shows that the "taking-up" of the dye is an absorption process comparable with substantive dyeing.

119. "*The Polarimetric Study of Intramolecular Rearrangement in Inactive Substances.*" By THOMAS STEWART PATTERSON and ANDREW MCMILLAN.

Continuing previous work (*Trans.*, 1907, xci., 504; *Ber.*, 1907, xl., 2564), the authors have applied their new method for studying intramolecular re-arrangement in inactive compounds to measure the rate of inversion of piperonal-*syn*oxime at a number of temperatures. The increase of velocity with rise of temperature was found to obey van't Hoff's law. The method was also applied for the measurement of the inversion of *p*-iodobenz*syn*aldoxime in *n*-propyl tartrate, and to the transformation of *ω-iso*nitrotoluene into *ω*-nitrotoluene, satisfactory constants being obtained. It was shown that by the same method the dynamic isomerism of ammonium thiocyanate and thiocarbamide and of ammonium cyanate and carbamide could be followed.

120. "*Mercuric Zinc Cyanide.*" (A Correction). By WYNDHAM ROWLAND DUNSTAN.

In a paper communicated to the Society in 1892 (*Trans.*, 1892, lxi., 666), the author described the results of an investigation of the "antiseptic cyanide" which had been introduced into surgery by Lord Lister. The conclusion was arrived at that the substance was an unstable double mercuric zinc cyanide, for which the formula proposed was $Zn_4HG(CN)_{10}$, and this was stated to correspond with 40·65 per cent of mercuric cyanide. This is a miscalculation, as the formula actually requires 35 per cent of mercuric cyanide, and must therefore be rejected.

The formula which most nearly corresponds with the maximum percentage of mercuric cyanide found, namely, 38·5, and which is also in accordance with the curves plotted from numerous experimental data, is $Zn(CN)_2,\frac{1}{4}HgCN)_2$, which requires 41·6 per cent of mercuric cyanide.

The salt, prepared as described, may therefore be regarded as a trizincic monomercuric octacyanide of the formula $Zn_3Hg(CN)_8$, which, as shown, inevitably suffers some decomposition by the water present during its precipitation.

121. "*Ethyl 6-Methyl-2-pyrone-3 : 5-dicarboxylate and its Derivatives.*" By JOHN LIONEL SIMONSEN.

When ethyl ethoxymethylenemalonate reacts with ethyl sodioacetoacetate, *ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate* is obtained:—

$$(CO_2Et)_2{:}C{:}CH{\cdot}OEt + CHNaAc{\cdot}CO_2Et \rightarrow (CO_2Et)_2{\cdot}C{:}CH{\cdot}CHAc{\cdot}CO_2Et,$$

$$CH\!\leqq\!\begin{matrix}C(CO_2Et){\cdot}CO_2Et\\ C(CO_2Et){:}CMe{\cdot}OH\end{matrix} \rightarrow CH\!\leqq\!\begin{matrix}C(CO_2Et)\text{—}CO\\ C(CO_2Et){:}CMe\end{matrix}\!\geqq O.$$

The same product results from the interaction of (I.) ethyl ethoxymethyleneaceteoacetate and ethyl sodiomalonate; (II.) ethyl ethoxymethyleneacetoacetate and the ethyl sodiocyanoacetate; and (III.) ethyl ethoxymethylene-cyanoacetate and ethyl sodioacetoacetate.

Ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate readily reacts with ammonia, with formation of *ethyl ammonium 6-hydroxy-2-methylpyridine-3 : 5-dicarboxylate*,—

$$CH\!\leqq\!\begin{matrix}C(CO_2{\cdot}NH_4){\cdot}C(OH)\\ C(CO_2{\cdot}E\text{—}CMe\end{matrix}\!\geqq N,$$

which on hydrolysis with alcoholic potash yields 6-hydroxy-2-methylpyridine-3 : 5-dicarboxylic acid,—

$$CH\!\leqq\!\begin{matrix}C(CO_2H){\cdot}C(OH)\\ C(CO_2H)\text{—}CMe\end{matrix}\!\geqq N,$$

which has already been described by Errera (*Ber.*, 1900, xxxiii., 2969). The action of aniline on ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate has also been investigated.

122. "*Contributions to the Chemistry of the Amidines.* Part II. *2-Anilinobenzoxazole and the supposed Anilodihydrobenzoxazole.*" By GEORGE YOUNG and ALBERT EDWARD DUNSTAN.

The authors have re-investigated the two substances described in the literature as anilinobenzoxazole and anilodihydrobenzoxazole. They confirm the nature and constitution of the anilino-compound, but find that the supposed isomeride is in reality carbanilide.

The following substances were described:—

Acetylanilinobenzoxazole, $C_{13}H_9ON_2Ac$, m. p. 91°; *p-chlorophenylcarbamide*, $C_7H_7ON_2Cl$, m. p. 212°; di-*p*-chlorocarbanilide, m. p. 289°; *trichlorocarbanilide*, $C_{13}H_9ON_2Cl_3$, m. p. 262°; and di-*p*-tolylcarbamide, m. p. 265°.

123. "*The Slow Decomposition of Ammonium Chromate, Dichromate, and Trichromate by Heat.*" By WALTER CRAVEN BALL.

When ammonium dichromate is heated at temperatures between 185° and 205°, it gradually becomes dark brown, and finally black, and nitrogen, water, and ammonia are evolved. After heating for several days, the remaining black substance has the approximate percentage composition:—Cr_2O_3, 83·89; active oxygen, 9·00; and water, 6·93. This corresponds fairly well with the formula $3CrO_2,H_2O$, but the composition is not quite constant.

If the heating is interrupted at an intermediate stage, it is found that part of the dichromate has decomposed, with production of a black insoluble substance, nearly half the nitrogen of the decomposed dichromate being contained in it. This black substance also varies in composition, but approximates to the formula $2CrO_3,Cr_2O_3,2NH_3,H_2O$.

The slow decomposition of ammonium dichromate is therefore partly a dehydration to this insoluble compound containing ammonia, and partly a combustion of the hydrogen of the ammonium to form water, with production of nitrogen.

The author has studied quantitatively the decomposition of ammonium chromate and of ammonium trichromate under similar conditions; the substances decompose in a similar manner.

FARADAY SOCIETY.

Ordinary Meeting, May 12th, 1908.

MR. LEON GASTER in the Chair.

DR. F. MOLLWO PERKIN and Mr. L. O'DOWD read a paper on "*Determination of Boiling-points of very Small Quantities of Liquids.*"

The determination of boiling-points of small quantities of liquids by distillation is not satisfactory, owing to the considerable loss which may take place, and also because of the difficulty of accurately arriving at the boiling-point before the liquid has distilled away. In the method described a small test-tube, made of thin glass, is passed through a hole in the cork in such a way that the end of it comes against the bulb of the thermometer. Through another hole a stirrer is passed. The heating vessel contains about 100 cc. of sulphuric acid or glycerin. About a quarter of a cc. of the liquid, the boiling-point of which

is to be determined, is placed in the small test-tube; this amount will rise nearly a centimetre up the tube. A small capillary tube, about 1 cm. long and sealed at one end, is dropped into this in such a manner that the open end rests upon the bottom of the test-tube. The external liquid is then heated fairly rapidly until a constant stream of bubbles is seen to rise from the end of the capillary tube. The source of heat is then removed, when the speed at which the bubbles are given off slackens, and, finally, when the last bubble makes its appearance and shows a tendency to suck back, the thermometer is immediately read. This is the boiling-point of the liquid, because it is the point at which the vapour pressure of the liquid is equal to the pressure of the atmosphere.

This method is really a modification of an older method, which, however, gives results which cannot be depended upon. The authors have determined the boiling-points of a large number of liquids and found the results to be perfectly accurate, both with low boiling-point substances such as ether and with high boiling-point substances such as safrol.

Mr. F. MOLLWO PERKIN read a paper entitled "*The Industrial Uses of Ozone, particularly in connection with Water Purification.*"

A brief account was first given of the various methods for obtaining ozone, and of the different processes employed for water purification and sterilisation. The method used by Siemens and Halske was then described in detail. The apparatus consists of two concentric electrodes, the inside one being of aluminium and the outside one of glass. The aluminium one, in order to keep it cool, is hollow and has water circulating through it. The external one is also kept cool by water contact, and as the water is in an iron container which is earthed, this acts as a negative pole, and of course water is a conductor on the high tensions which are employed. Dried air is passed up the annular space between the two electrodes, and, by means of the silent electric discharge which is there taking place, is ozonised. From the ozoniser the air passes up towers which are filled with pebbles, and over which the water trickles; by this means the water is divided up into a number of small streams, and consequently a very large surface is exposed to the action of the ozone. After the water has been thus treated it is allowed to flow into the reservoir in a series of cascades. By this means it comes in contact with the air, and any excess of ozone which may be in it is removed.

It is found that the water purified in this way becomes almost absolutely sterile, and any bacteria which may happen to remain are not of a pathogenic nature, consequently the water is absolutely safe for potable purposes.

Messrs. Siemens and Halske have a large installation for dealing with water at Wiesbaden and another for purifying the water supply at Paderborn.

They have also erected experimental plant in several other places. The process can be very cheaply carried out, as it does not cost more than ¼d. for every cubic metre of water which is treated. A portable plant has also been devised and is of particular use in case of war; in fact, some of them were employed in the late Russo-Japanese war. They should also be of value for other purposes—if the water supply of any town were to become contaminated with typhoid, for example.

The paper finally discusses other uses for ozone, such as the oxidation of eugenol in the preparation of artificial vanilla and the bleaching and sterilising of flour, a process used in a very large number of mills in this country. Flour so sterilised is capable of export for long distances, and may be kept for a very long time without deteriorating.

Dr. T. M. LOWRY thought that a simpler method of sterilising on a large scale was to soften the water and bring down the bateria in the precipitated chalk.

Dr. H. BORNS pointed out that water from rapidly-flowing rivers needed little further purification.

Dr. G. SENTER referred to the difficulties of removing the last traces of ozone from the sterilised water.

Dr. V. H. VELEY remarked that germs that could not easily be destroyed were, as a rule, harmless.

The CHAIRMAN described an ozonising plant he had lately visited in Philadelphia, where the water purified was practically diluted sewage. This plant was capable of treating water for a population of 30,000, but occupied only thirty by fifty feet of ground, as against acres required for sand filters. He also gave some particulars of the Lahmeyer process.

Dr. V. H. VELEY, F.R.S., exhibited an Apparatus for the Determination of the Dielectric Constants of Non-conducting Liquids.

In the usual bridge method balance is obtained by varying a resistance. In the author's apparatus a capacity is varied in such a way that variations are proportioned to the distance traversed by the movable condenser plate. These are read off directly, and a simple calculation gives the specific inductive capacity under measurement.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 17, April 27, 1908.

Ionisation of the Air by Ultra-violet Light.—Eugène Bloch.—Lenard has studied the ionising action of ultra-violet light upon gases, especially air, and has shown that the negative ions are small ions of high mobility, and the positive ions are large ions of low mobility. The Lenard effect appears to be a particular case of the Hertzian photo-electric effect. The author has experimented with different sources of ultra-violet light and with gases at rest and in motion, and has found that the greater part of the Lenard effect is attributable to the presence of photo-electric particles in suspension in the gas. When no dust is present the Lenard effect is much less marked than when dust is present.

Detection of Helium in Minerals containing Uranium.—F. Bordas.—Helium is very abundant, and seems to be combined with the uranium in samarskite, noegeite, euxenite, yttrotantalite, and anneroedite; less helium is found in woehlerite, pyrochlore, polycrase, troegerite, xenotime, gummite, thorite-orangite, and niobite-columbite. The minerals in which the salts of uranium are sharply defined or crystallised do not yield helium, *e.g.*, torbernite, autunite, carnotite. Helium has been detected by its line $\lambda = 5878$ in a sample of native bismuth from Saxony, and of bismuth with smaltine from Cornwall.

No. 18, May 4, 1904.

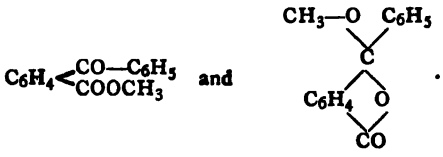
Carrying down of Soluble Substances by certain Precipitates.—Paul Frion.—In a basic medium more of a soluble substance is carried down by a precipitate than in a neutral medium, and more in a neutral than in an acid medium. The amount carried down increases as the concentration of the ion carried down increases, and also increases with the valency of the ion. The precipitate carries down most when it is in a dilute liquid. These different results can be interpreted by applying the laws of electrification by contact—thus the charge which each grain of the precipitate takes appears to be due to the ions H^{+ve} or OH^{-ve}, and is much diminished by the presence of polyvalent ions of opposite sign.

Determination of Halogens in Chloro-brominated Organic Compounds.—H. Baubigny.—The sulpho-chromic mixture can be used to determine chlorine and bromine in derivatives containing both halogens as follows;—The compound is treated with the mixture as

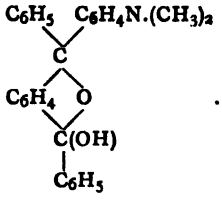
usual in presence of silver sulphate, and the volatile products are received in an alkaline solution of sulphite. The alkaline liquid must be divided into two equal parts. In one the chlorine and bromine are determined by precipitation, and in the other the alkali is neutralised, and after concentration the excess of sulphite is destroyed by potassium permanganate. The bromine is eliminated by drying *in vacuo* after the addition of copper sulphate and potassium permanganate. Thus the bromine is set at liberty, and the dry residue contains all the chlorine. The bromine can be calculated by difference.

New Method of Preparing the Homologues of Naphthalene.—G. Darzens and H. Rost.—When α-acetylnaphthalene is led over reduced nickel, water-vapour and α-ethylnaphthalene are produced, $C_{10}H_7—CO—CH_3+4H = C_{10}H_7—CH_2—CH_3 + H_2O$. Under the same conditions β-acetylnaphthalene yields β-ethylnaphthalene, α-isobutyrylnaphthalene yields α-isobutylnaphthalene, and the β-iso-compound gives β-isobutylnaphthalene. These two last homologues of naphthalene had not previously been prepared.

Action of Phenyl Magnesium Bromide upon the Second Methyl Ether of Para-dimethylamido-orthobenzoyl Benzoic Acid.—J. Pérard.—Meyer has recently prepared the methyl ethers corresponding to the two tautomeric forms of orthobenzoyl-benzoic acid :—



By an analogous method the authors have obtained the second methyl ether of para-dimethylamido-orthobenzoyl-benzoic acid, and have found that the product obtained when phenyl magnesium bromide acts upon it is the same as when the first ether is used, *i.e.* :—



Fixation of Hydrocyanic Acid by Benzoyl Acrylic Acid.—J. Bougault.—Benzoyl acrylic acid and analogous compounds readily fix one molecule of hydrocyanic acid. The addition is made at the ethylene bond, and the acid obtained is α-cyanbenzoylpropionic acid, $C_6H_5—CO—CH_2—CH(CN)—CO_2H$. It appears to be identical with Klobb's phenacylcyanacetic acid. On saponification it yields β-benzoylisosuccinic acid, $C_6H_5—CO—CH_2—CH(CO_2H)_2$.

MISCELLANEOUS.

Central Technical College.—The Third Year Students of the Central Technical College are holding their Annual Dinner at the Gaiety Restaurant on Thursday, June 18, at 7.30 punctually. All Old Centralians are cordially invited to attend. Professor Dalby has kindly consented to preside. Tickets may be obtained from the Hon. Sec., C. H. RUSSELL, Ingram House, Stockwell, S.W., at 7s. each.

Infants' Health Exhibition.—This special Exhibition, under the auspices of the Incorporated Institute of Hygiene will be opened from the 15th to the 27th of June, at the Institute buildings in Devonshire Street, Harley Street, W., and is intended to demonstrate the progress and recent advances in connection with the health, comfort, and training of children. A most attractive and instructive display is assured, and as space is limited only those exhibits can be shown that represent merit or improvement and are of public interest. A great influx of visitors, in connection with various events, is expected in London between the 15th and 22nd of June, and such an Exhibition as this, held in the heart of the Metropolis, will be a source of interest, attraction, and education to many. It will appeal especially to mothers and heads of families, to medical men, matrons, and nurses, as well as to school teachers. The exhibits will represent and be shown in the following sections, viz. : — Foods, Clothing, the Nursery, the Bedroom, Recreation, Physical Exercise, School Life, Education.

MEETINGS FOR THE WEEK.

TUESDAY, 9th.—Faraday Society, 8. "Utilisation of Atmospheric Nitrogen in the Production of Calcium Cyanamide, and its Use in Agriculture and Chemistry," by Dr. A. R. Frank.

FRIDAY, 12th.—Physical, 8. "Experiments on a Directive System of Wireless Telegraphy," by Messrs. Bellini and Tosi. "Lateral Vibration and Deflection of Clamped Directed Bars," by Dr. Morrow. "On the Resistance of a Conductor of Uniform Thickness whose Breadth suddenly changes, and on the Shapes of the Stream-lines," by Prof. Lees. "Self-inductance of two Parallel Wires," by Dr. Nicholson. "Homogeneous Secondary Radiation," by Dr. Barkla and Mr. Sadler. "Notes on the Motion of a Corpuscle and on Cloud Formation," by Prof. Morton.

THE CHEMICAL NEWS.

VOL. XCVII., No. 2533.

NOTES ON GIESEL'S ARTICLE ON POLONIUM.

By W. MARCKWALD.

A RECENT number of the *Berichte* (1908, vol. xli., p. 1059; CHEMICAL NEWS, 1908, xcvii., 242) contains an article by Giesel on the preparation of polonium and its behaviour. Some statements in this article call for notice from me.

The second section begins with the statement that "The new precipitate is more active than deposits of polonium on metals." The separation of polonium as oxide (hydroxide) is not new, but was described by me three years ago (*Berichte*, 1905, xxxviii., 591). The three milligrms. of polonium separated from fifteen tons of pitchblende were obtained by specific reactions, which enable polonium to be separated from any known element. For this reason this polonium cannot have been appreciably impure, and cannot therefore be considerably inferior in activity to any other specimen. The effects of his preparation which Giesel mentions have almost all been observed by me in a polonium preparation which I exhibited in 1903 (*cf.*, *Berichte*, 1903, xxxvi., 2662) at the International Congress for Applied Chemistry, and which was about one-tenth as pure as the polonium afterwards obtained. I have repeatedly mentioned the strong ozonising power and the rapid destruction of the filter-paper (*cf.*, *Sitzungsbericht des Vereins für Gewerbefleiss*, Jan. 2, 1905).

The last sentence but one in Giesel's article reads, "No relationship to tellurium could be discovered." It is not clear what Giesel means by this sentence. The only "relationship" to tellurium which I assumed for polonium and which—it may prove to be true or not—served me excellently as a working hypothesis for the systematic preparation of polonium, consists in the position of polonium in the periodic system of the elements. After this hypothesis has served its purpose there is, of course, no reason for retaining it; but, on the other hand, in the observations which Giesel communicates I see not the least reason for rejecting it.—*Berichte*, 1908, xli., 1378.

THE ULTRA-VIOLET SPARK SPECTRUM OF DYSPROSIUM AND THE REMARKABLE MAGNETIC PROPERTIES OF THIS ELEMENT.

By G. URBAIN.

I. *Spectrum.*

THE only known spark spectrum of dysprosium is the visible spectrum obtained by Lecoq de Boisbaudran (*Comptes Rendus*, 1886, cii., 155) and containing only five nebulous lines, 583·5, 575·0, 570, 526·9, 525·9. This spectrum has been attributed to the element $Z\gamma$. Demarçay, moreover (*Comptes Rendus*, 1900, cxxxi., 388), has given some ultra-violet lines of dysprosium as characteristic of the element Δ.

The dysprosium, which I have obtained in a state of purity and which shows no variation in properties after systematic multiple fractionation, shows these lines very clearly, to the exclusion of other earths, and in the fractionations these lines behave like the absorption spectrum, by means of which Lecoq de Boisbaudran discovered and defined dysprosium.

There can be no doubt that these lines are as characteristic of the element as its absorption bands. Nevertheless, the knowledge of these lines appearing insufficient, I have made many more measurements with different photographs of the spark spectrum of dysprosium in the ultra-violet. This spectrum is one of the richest in lines of the family of the rare earths. In the following table only the principal lines are given, or those which are undoubtedly correct, for my apparatus did not enable me to take measurements which were precise enough to leave no doubt about the very faint lines.

The numbers in the following list are correct to two-tenths of an Angström unit:—

2872·0	Strong.	3498·8	
2904·1	Fairly strong.	3501·5	
2948·5	Fairly strong.	3504·5	
2950·4	Strong.	3506·8	
2955·4	Fairly strong.	3512·8	
2969·2	Strong.	3517·3	
3029·7		3524·2	Strong.
3038·4	Strong.	3527·3	
3052·3	Fairly strong.	3529·3	
3060·6	Fairly strong.	3531·9	Very strong.
3062·7	Fairly strong.	3535·1	Strong.
3109·8		3536·2	Strong.
3128·6	Fairly strong.	3538·5	Strong.
3135·5	Very strong.	3542·5	Fairly strong.
3140·7	Fairly strong.	3544·5	
3146·1		3546·8	
3152·4		3550·4	Strong.
3163·0	Strong.	3551·7	Strong.
3170·4		3574·0	
3206·5	Fairly strong.	3576·3	
3215·3	Strong.	3591·3	Fairly strong.
3216·7	Very strong.	3594·8	Fairly strong.
3221·5	Fairly strong.	3606·3	Fairly strong.
3223·3	Fairly strong.	3613·1	
3235·8	Strong.	3620·3	
3236·7	Fairly strong.	3630·5	Strong.
3245·3	Fairly strong.	3645·4	Very strong.
3251·5	Very strong.	3648·9	
3266·4	Very strong.	3695·0	Strong.
3309·0	Very strong.	3724·6	
3320·2	Strong.	3747·7	
3341·1	Strong.	3753·8	Fairly strong.
3385·9	Very strong.	3757·3	Strong.
3393·9	Very strong.	3786·3	
3396·3	Strong.	3788·6	
3420·0		3816·8	
3423·0		3872·3	Strong.
3434·7		3944·8	Very strong.
3439·1		3978·7	Fairly strong.
3445·7	Strong.	3997·0	
3447·2		4000·7	Strong.
3456·7	Fairly strong.	4045·7	Strong.
3461·1	Very strong.	4078·0	Strong.
3471·3	Strong.	4104·0	
3477·0	Strong.	4187·0	Fairly strong.
3494·6	Very strong.	4195·0	Fairly strong.
3496·5		4212·5	Very strong.
3498·0		4221·3	

This spectrum was obtained with solutions of the chloride, the spark being condensed.

II. *Magnetism.*

Stéphan Meyer (*Sits. Ber. der R. Acad. zu Wien*, cx., 492) in 1901 published a certain number of magnetic measurements which he carried out with the rare earths fractionated by Cleve and by Nilson. Naturally no values are given for dysprosium in this note; dysprosium has only recently been isolated (G. Urbain, *Comptes Rendus* 1906, cxlii., 785), but under the heading "oxide of holmium" very high values of magnetic susceptibility are given.

From the publications of Cleve, his pupils, and the spectroscopists who examined their products I can easily

deduce what is the true nature of the substances called holmium. They are earths containing, besides yttrium and erbium and some other impurities, a notable proportion of true holmium, and possibly a still higher proportion of dysprosium; so much so that the values of $x \cdot 10^6$ obtained by Meyer for these substances have only a limited scientific value, in spite of the interest attached to them.

I have determined the coefficient of magnetisation of the oxides of dysprosium Dy_2O_3, obtained from consecutive members of one of my fractionations, by means of Curie and Chéveneau's magnetic balance. The following table gives the results of the experiments:—

No. of fraction.	Wt. of substance.	Deviation.	$x \cdot 10^6$.
31.	0·1974	26·27	289·5
32.	0·2031	26·77	286·9
33.	0·2256	29·98	289·3
34.	0·2796	37·48	291·7
35.	0·2476	33·03	290·4
36.	0·2491	33·23	290·4

Cobalt sulphate taken for comparison gave a deviation of 3·60 for 0·1974 grm. of sulphate. If the value $39·7 \times 10^{-6}$ recently given by Meslin (*Ann. de Phys. et de Chim.*, 8th Series, 1906, vii., 182) is taken for the coefficient of magnetisation of this salt, we get for the different terms of this fractionation values lying irregularly between $286·9 \cdot 10^{-6}$ and $291·7 \cdot 10^{-6}$, *i.e.*, values which may be regarded as constant and of which the mean value is roughly $290 \cdot 10^{-6}$.

This high value gives dysprosium the first place amongst the paramagnetic elements. Its oxide Dy_2O_3 is about 12·8 times as magnetic as iron oxide Fe_2O_3.—*Comptes Rendus*, 1908, cxlvi., 922).

YTTRIUM EARTHS.*

FIRST PAPER.

By VICTOR LENHER.

THE methods which we have at our disposal for the separation of the earths of the yttrium group may be classified under the following heads:—(1) Fractional precipitation; (2) Fractional crystallisation; (3) Fractional decomposition of such salts as the nitrates by heat.

Under fractional precipitation, we have methods which depend largely on the differences in basic properties, such as the fractional precipitation by ammonia, magnesia, &c. The speed by which separations are effected by use of this principle depends largely on how quickly the system can be brought into equilibrium.

In the methods of fractional crystallisation we must depend necessarily on the differences in solubility of various salts and as a rule with the mixtures which are found in the rare earth minerals; the solubilities of a given salt of the various metals are not widely different. On this account separation by the crystallisation of the nitrates or double nitrates is not rapid, while with the chromates accurate conditions must be observed, in which case this method gives splendid results.

The decomposition of the nitrates by heat is slow, but can, by patience, be carried out with success. The basic nitrate method of Welsbach (*Monatshefte*, v., 508) which can be applied to the yttrium group is a combination of this method and that of fractional precipitation. It is more rapid and successful than either method alone.

The successful use of any of the methods for separating the metals of the yttrium group depends largely on the ratios of the various constituents present in the mixtures, as well as on the character of the elements to be separated. We note, for example, that Dennis and Dales (*Journ. Am. Chem. Soc.*, xxiv., 428) in their study of the yttrium earths from sipylite find that magnesia, as a precipitating agent, causes little change in the atomic weights and absorption spectra, while James (*Ibid.*, xxix., 495) was more successful in using this method on gadolinite earths. James used the nitrate solution, while Dennis and Dales used a chloride solution. The author in working in a nitrate solution with yttrium earths from monazite has found that various fractions acted quite differently towards magnesia; some showed marked differences in atomic weight and absorption spectra after treatment with magnesia, while others showed little change. It has been observed, moreover, that in order to work this method with any appreciable degree of success the magnesia must be freshly ignited. The various degrees of success with different methods can also be illustrated by the Welsbach method (*Monatshefte*, xxvii., 935) of crystallising the oxalates from an ammoniacal solution or by the James method (*Journ. Am. Chem. Soc.*, xxix., 495) in which the "oxalate-carbonates" are crystallised from an ammonium carbonate solution of the oxalates. This method with gadolinite earths in the hands of James yielded first yttrium and successively fractions with higher atomic weight to ytterbium. In the author's hands, it has worked similarly with the yttrium earths from samarskite, but on applying the same method to certain oxalates from monazite, atomic weight determinations showed that the elements with heavier atomic weight appeared first, while the more soluble portion yielded fractions whose atomic weight was far below the more insoluble portions. In other words, we here have the same method producing opposite results with different mixtures of earths.

From time to time it has been proposed to use salts of organic acids. The oxalates can be crystallised from either ammoniacal or ammonium carbonate solution, yielding a fairly rapid method of fractionation, or the oxalates can be crystallised from nitric acid solution, yielding fractions of different atomic weights. The ethyl sulphates and the acetyl acetonates have been used by Urbain and others as means of separation in this group. The formates have been repeatedly used for fractionations. Salts of a number of organic acids have been prepared, but little has been done in the application of the derivatives as means of separation. Such salts as the tartrates, citrates, and succinates have been prepared, but little has been attempted in the way of separation.

The tartrates and citrates of the yttrium earths appear as white gelatinous precipitates when a neutral salt of potassium, sodium, or ammonium is added to a solution of the yttrium salt. In a similar manner insoluble derivatives are formed with neutral salts of fumaric, maleic, tartronic, malic, and malonic acids. The neutral succinates of the alkalis or ammonium deport themselves in a very interesting manner with the neutral nitrates of the yttrium earths.

When neutral ammonium or sodium succinate is added to a neutral nitrate solution of the yttrium earths and the solution allowed to stand, a finely divided crystalline precipitate forms slowly; in fact, in the cold a few hours are necessary to insure complete precipitation. On the other hand, when the solution is hot or boiling, complete precipitation is effected in much less time, from ten minutes to half-an-hour being sufficient time for complete formation of the insoluble succinates. The ready formation of this finely divided precipitate and the fact that the reaction is far from instantaneous appears to us as promising to be a satisfactory method for fractionation. The fact that it forms as slowly as it does would indicate that there should be plenty of time for equilibrium to be established, and the physical character of the salt and its insolubility enables it to be quickly filtered and readily washed.

That the yttrium earths form succinates was shown by Berlin in 1835 (*Pogg. Ann.*, xliii., 108). He showed that with sodium succinate the yttrium earths form a fine crystalline powder. Ekeberg in 1802 (*Gilb. Ann.*, xiv., 247; *Ann. Chim. Phys.*, xliii., 228) thought that the yttrium earths were not precipitated by the alkaline succinates, while beryllium was, which was contrary to the

results found by Berlin and to the work of Cleve and Höglund (*Ber.*, vi., 1468) who showed that ammonium succinate precipitates yttrium but not erbium from nitrate solution, but out of a mixture precipitates both.

In the thorium cerium group, Berzelius showed in 1829 (*Pogg. Ann.*, xvi., 385) the formation of an insoluble succinate of thorium. This reaction has been later studied by Kaufmann (Dissertation Rostock University, 1899) and Schilling (Dissertation Heidelberg University, 1902, p. 141). The use of an alkaline succinate has been recommended as a means of separation of iron from the gadolinite earths by Gadolin, Vauquelin, Berzelius, Berlin, and Hermann, after Klaproth had shown that iron would be first precipitated from such a solution.

The yttrium earths from samarskite have been studied with the view of testing the applicability of the succinates as a means of separation in this group.

Treatment of Samarskite.

Fifteen pounds of samarskite containing very little gangue minerals were treated with concentrated hydrofluoric acid according to the method of J. Lawrence Smith. The mineral dissolved with effervescence. The columbium and tantalum passed into solution, while the earths appeared as insoluble fluorides. These insoluble fluorides were thoroughly washed with water by decantation, after which they were dried and treated with concentrated sulphuric acid. After the first copious evolution of hydrofluoric acid, the mass was warmed and finally heated until the heavy fumes of the sulphuric acid came off. The pasty mass was allowed to cool; when it was extracted with water, and the insoluble residue, which consisted of more or less of the oxides of columbium and tantalum, insoluble sulphates, and a little undecomposed mineral, was thoroughly washed with water by decantation. This sulphate solution of the earths and uranium was nearly neutralised with sodium hydroxide. Oxalic acid was then added, and the oxalates precipitated. These crude oxalates were ignited to oxides, dissolved in nitric acid, and treated with a hot saturated solution of potassium sulphate, with the addition of the sold salt. The soluble yttrium double sulphate solution was precipitated with oxalic acid, the oxalates were roasted to oxides, from the nitric acid solution of which it was again treated with potassium sulphate. Three such treatments with potassium sulphate from the nitrate solution were found necessary to completely remove the more insoluble group of earths, and after three such treatments the didymiums could not be detected in a strong solution of the nitrates by means of their characteristic absorption spectra, nor could cerium be detected by means of hydrogen peroxide.

Fractionation of the Succinates.

(With R. C. Benner).

About one hundred grms. of the oxides were dissolved in nitric acid and the slight excess of free acid neutralised in ammonia. This neutral nitrate solution was diluted to a litre, brought to boiling, and a saturated solution of neutral sodium succinate added in portions of 100 cc. By this means twelve fractions were obtained. After the addition of each portion of the sodium succinate, the solution was boiled fifteen minutes, after which the succinates were filtered and washed with 400 cc. of hot water. The fractions thus obtained were dried and ignited to oxide, small portions being taken for the determination of the atomic weight and the study of the absorption spectra.

The fractions thus obtained were combined and refractionated, selection being made of the portions whose atomic weights were close to each other; thus, for the second series, 2, 3, and 4 were combined, and 5, 6, 7, and 8 were united, while the lightest material, 9, 10, and 11, was similarly combined.

These oxides were dissolved in nitric acid, the excess of nitric acid removed by evaporation and in a dilution similar to that in Series I. were fractionated by addition of sodium succinate in fractions as before. By again combining fractions of close atomic weight in three such series of fractionations the most soluble succinate fraction gave a nearly white oxide, whose nitrate solution showed only very weak absorption bands. The atomic weight of the element in the most soluble portion was 93, and the fraction corresponds to yttrium containing small amounts of samarium, europium, and holmium as shown by the absorption spectra.

Series I.

	Weight of fraction as oxide. Grms.	Atomic weight in R_2O_3.
1.	22·2	114·2
2.	15·8	111·83
3.	10·0	110·06
4.	8·8	111·30
5.	9·0	108·5
6.	7·1	107·2
7.	7·0	105·6
8.	6·1	104·4
9.	7·0	101·0
10.	6·4	97·0
11.	4·0	95·8
12.	3·0	—

On the other hand, the third fraction at the other end of the series or the most insoluble portion gave a yellow earth whose atomic weight corresponded to 139. This oxide dissolved in nitric acid to a pink solution and showed absorption bands, and was doubtless a mixture of yttrium with terbium, holmium, europium, samarium, and erbium. Further study of these earths is being continued.

It has been considered well worth the while in making these studies on the samarskite earths and on the work which is in progress on the yttrium earths from monazite to determine the atomic weight in each fraction and also to study the absorption spectra.

The determination of the atomic weight for control purposes can be carried out sufficiently accurately by the estimation of the oxalic acid and of the earth oxide in the oxalate. While it is true that this method has some serious defects, yet very good results can be obtained if it is properly handled.

Baxter (*Journ. Am. Chem. Soc.*, xxviii., 1684) has recently shown in splendid detail that when the oxalates of neodymium, praseodymium, yttrium, and certain other of the rare earths are precipitated in neutral or nearly neutral solution, they exhibit a strong tendency to carry down ammonium oxalate. This carrying down of ammonium oxalate by the insoluble oxalates of the yttrium earths is very pronounced and is difficult to prevent without going to the opposite extreme and making the solution too acid, in which case we have the factor of the solubility of the oxalate in acid appearing and the obviously incomplete precipitation of the oxalate. In the first case, the result due to the presence of additional oxalic acid in the precipitated oxalate would cause the atomic weight to be too low, while if considerable free nitric acid is present, the more soluble yttrium oxalate is incompletely precipitated, and the result is to obtain a high atomic weight, due to the greater solubility of yttrium oxalate in nitric acid than of those earths of higher atomic weight.

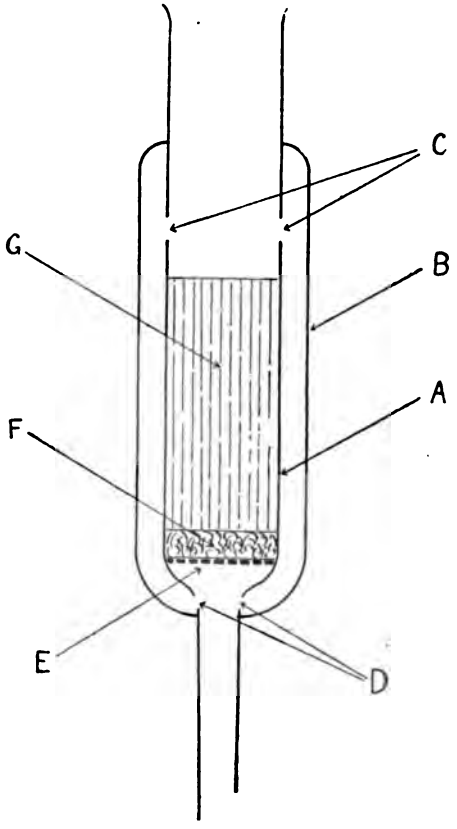
The most accurate method for the precipitation of the oxalate of the yttrium earths which has come to the attention of the author has been to use a grm. or less of the nitrate in very slightly acid solution and to use a dilution of about 500 cc. The oxalate is precipitated from the boiling solution by means of a dilute solution of pure oxalic acid.

In conclusion, the author wishes to acknowledge his appreciation of the courtesy of Mr. H. S. Miner, of the Welsbach Co., of Gloucester, N.J., who has placed at our disposal a large quantity of rare earth residues from Carolinian monazite, and who has been able to secure for us a quantity of rare minerals for the study of the chemistry of the metals of the yttrium group. — *Journal of the American Chemical Society*, xxx., No. 4.

AN APPARATUS FOR SIMULTANEOUSLY EXTRACTING A SOLID AND FILTERING THE SOLUTION SO OBTAINED.

By FREDERICK RECORD, B.Sc.

THE apparatus, shown in section in the accompanying figure, was designed to obviate the loss of substance which occurs in the course of filtration subsequent to the extraction of solids with such solvents as ether and alcohol. It consists or an inner tube, A, sealed to a shorter concentric jacket, B. In that portion of A which is within B there are two pairs of holes, C and D. The apparatus is prepared for use by inserting in A a filter disc, E, and covering this, first with one or two pieces of filter-paper, and then with a layer, F, of asbestos. Above the latter is



placed the substance, G, which is to be extracted. A reflux condenser is attached to the upper part of the apparatus, and a flask containing the solvent to the lower end. On boiling the solvent its vapour rises through the apertures at D into the annular space between A and B, from whence it passes through C into A again, and finally into the condenser. The liquid formed by condensation drops on to G and percolates through it, dissolving a little on the way. The solution thus obtained falls through F and E and is filtered by them. This process continues until the whole of the soluble material has passed into the flask.

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THE SEPARATION OF MAGNESIUM FROM THE ALKALIS BY ALCOHOLIC AMMONIUM CARBONATE.

By F. A. GOOCH and ERNEST A. EDDY.

NEARLY fifty years ago Schaffgotsch (*Ann. Phys.*, 1858, civ., 482) brought out the ammonium carbonate method for the separation of magnesium from the alkalis. According to this process, the very concentrated solution of the sulphates, nitrates, or chlorides of magnesium, sodium, and potassium is treated with a concentrated solution of ammonium carbonate. The voluminous precipitate which first falls is acted upon by an excess of the precipitant, sometimes dissolving completely, and crystalline ammonium magnesium carbonate, $MgCO_3.(NH_4)_2CO_3.4H_2O$, is soon formed. After standing twenty-four hours the precipitate is filtered off, washed with the concentrated ammoniacal solution of ammonium carbonate, dried, and strongly ignited. In the absence of salts of potassium, the residue is weighed at once as magnesium oxide, and from the filtrate sodium salts are recovered by evaporation. When a salt of potassium is originally present, with or without a salt of sodium, the ignited magnesium oxide is to be washed out, and again ignited before weighing, and the washings are to be added to the filtrate containing the greater part of the alkalis.

When Schaffgotsch published this method it was customary to deal in analysis with larger amounts of material than at present, and the requirements as to results were not so exacting. (A similar method was published by H. Weber, *Jahresb. Chem.*, 1858, p. 606). In eight complete determinations, upon which Schaffgotsch rested, weights of salts taken ranged between 1·75 grms. and 3·69 grms., and the magnesium oxide taken approximated 0·6 grm.; while the error in the weight of magnesium oxide found varied from 0·0007 grm. to 0·0082 grm., with an average error amounting to 0·6 per cent.

Though these results do not meet the modern requirements of a good analytical method, the process has been recently recommended and applied in rock analysis by Wuelfing (*Ber.*, 1899, xxxii., 2214), and mentioned by Hillebrand (*Bull.* 305, 149, U.S. Geol. Survey). It has seemed to us desirable therefore that the method should be again submitted to careful testing, and to that end the following work was undertaken.

Experimental.

Schaffgotsch's reagent was prepared by dissolving 230 grms. of ammonium carbonate in 180 cc. of ammonium hydroxide, diluting the solution to 1 litre, and filtering.

A solution of magnesium chloride was prepared by the following process:—Presumably pure magnesium oxide, 20 grms., was treated with nitric acid not quite sufficient in amount to act upon all the oxide. The solution thus obtained was diluted somewhat, and boiled and filtered to remove traces of the elements of the iron group. From this filtrate the greater part of the magnesium was precipitated by concentrated ammonium carbonate, thrown upon a filter, washed, and nearly dissolved in nitric acid. The solution, containing some undissolved magnesium carbonate, was first boiled and filtered to remove traces of the elements of the calcium group, and then treated again with ammonium carbonate to precipitate magnesium carbonate. The insoluble magnesium carbonate was washed and dissolved in the least possible amount of hydrochloric acid; and the solution was suitably diluted, and standardised by heating definite portions in a large platinum crucible with sulphuric acid, evaporating, removing the excess of sulphuric acid by careful heating over a radiator, and bringing to constant weight the residue of magnesium sulphate. With the Schaffgotsch reagent and the standard solution of pure magnesium chloride the following experiments were made:—

In Table I. are given results of experiments made to test the solubility of the ammonium magnesium carbonate in an

TABLE I.

MgO taken as $MgCl_2$. Grm	MgO weighed. Grm.	Error MgO. Grm.	MgO found as $Mg_2P_2O_7$ in filtrate. Grm	Volume of precipitant. Cc.	Volume of reagent used in washing. Cc.
		A.			
0·0029	—	−0·0029	0·0024	100	—
0·0289	0·0286	−0·0003	0·0007	10	—
0·1444	0·1430	−0·0014	0·0006	50	—
0·1444	0·1427	−0·0017	0·0009	50	50
		B			
0·0034	—	−0·0034	0·0033	100	—
0·0342	0·0342	—	0·0002	10	—
0·1708	0·1694	−0·0014	0·0012	50	—
0·1708	0·1696	−0·0012	0·0012	50	—
0·1708	0·1698	−0·0010	0·0020	50	25
0·1708	0·1683	−0·0025	0·0024	100	10
0·1708	0·1670	−0·0038	0·0043	200	10

TABLE II.

MgO taken as $MgCl_2$. Grm.	MgO weighed. Grm.	Error in MgO. Grm.	MgO found as $Mg_2P_2O_7$. Grm.	Original volume. Cc.	Volume of alcohol added. Cc.	Volume of precipitant. Cc.	Volume of solution used in washing. Cc.
			A.				
0·1444	0·1446	+0·0002	0·0001	—	—	50	—
0·1444	0·1449	+0·0005	—	—	—	100	—
0·1444	0·1445	+0·0001	—	—	—	100	50
0·1444	0·1445	+0·0001	—	—	—	100	50
			B.				
0·1444	0·1443	−0·0001	—	50	50	50	—
0·1444	0·1440	−0·0004	0·0002	50	50	50	—

TABLE III.

MgO taken. Grm.	NaCl taken. Grm.	KCl taken. Grm.	NH_4Cl taken. Grms.	MgO weighed. Grm.	Error MgO. Grm.	MgO found as $Mg_2P_2O_7$. Grm.	Volume of water solution. Cc.	Volume of alcoho added. Cc.	Volume of precipitant. Cc.	Volume of solution used in washing. Cc.	Time of standing.
					A.						
0·1444	—	0·1	—	0·1455	+0·0011	—	1—2	—	100	50	Over night
0·1444	0·1	—	—	0·1446	+0·0002	—	1—2	—	100	50	„
					B.						
0·1444	—	0·1	—	0·1445	+0·0001	0·0001	50	50	50	50	20 minutes
0·1444	—	0·1	—	0·1444	—	0·0001	50	50	50	50	20 „
0·1444	0·1	—	—	0·1445	+0·0001	0·0002	50	50	50	50	20 „
0·1444	0·1	—	—	0·1449	+0·0005	0·0001	50	50	50	50	20 „
0·1444	0·2	—	—	0·1449	+0·0005	0·0002	50	50	50	50	20 „
0·1444	—	0·2	—	0·1461	+0·0017	—	50	50	50	50	20 „
0·1444	—	—	3·0	0·1444	—	0·0001	50	50	50	50	20 „
0·1444	—	—	3·0	0·1447	+0·0003	0·0002	50	50	50	50	20 „
					C.						
0·1444	0·2	—	—	0·1446	+0·0002	0·0002	50	50	50	50	20 „
0·1444	—	0·2	—	0·1442	−0·0002	0·0002	50	50	50	50	20 „

excess of the precipitant of full strength or half strength. Definite portions of the standard solution of magnesium chloride were evaporated in a beaker of 250 cc. capacity nearly to dryness, and the precipitant was added in the amount indicated. The mixture, stirred vigorously until the flocky precipitate had disappeared, and the crystalline double carbonate had begun to form, was allowed to stand at least twenty-four hours. The precipitate, filtered off on asbestos in a perforated crucible, the filtrate being used to effect the transfer without addition of other liquid, was dried, ignited, and weighed as magnesium oxide. The filtrate was treated with microcosmic salt, and, after standing over-night, was again filtered on asbestos in a weighed perforated crucible, and the precipitate was washed with water faintly ammoniacal, dried, ignited, and weighed. The increase in weight of the crucible was taken as magnesium pyrophosphate from which the magnesium oxide was calculated. In the experiments of A, Schaffgotsch's reagent of full strength was used as the precipitant. In B the same reagent was used of half strength.

These experiments show plainly that ammonium magnesium carbonate is noticeably soluble in Schaffgotsch's solution of full strength, and rather more so in the same reagent of half strength. So, it is evident that an exact separation of magnesium from the alkalis, in solutions of reasonable volume, cannot be made without some modification of the method. The effect of adding to the mixture certain proportions of alcohol was therefore tried, and, after some preliminary attempts, a series of experiments was performed for which the precipitant used was made by saturating with ammonium carbonate a mixture of 180 cc. of ammonium hydroxide, 800 cc. of water, and 900 cc. of absolute alcohol, and filtering, after some hours, from the undissolved ammonium carbonate. In the experiments of Table II. (A), portions of the standard solution of mag-

nesium chloride were evaporated nearly to dryness, and to the residue was added a definite amount of the alcoholic solution of ammonium carbonate. The precipitates, after stirring and standing over-night, were filtered upon asbestos in the perforated platinum crucible, washed with the precipitant, dried, ignited strongly, and weighed. The filtrates were examined as before for dissolved magnesium by the phosphate method. In the experiments of Table II. (B) an equal volume of alcohol was added to the solution of magnesium chloride taken, and to this mixture was added, as a precipitant, a volume of the saturated alcoholic solution of ammonium carbonate equal to that of the magnesium chloride. The precipitate was filtered, washed, dried, ignited, and weighed as in the former experiments. The filtrate was examined as before for magnesium.

From the results of Section A of this table, it appears that the precipitation of the magnesium brought about in 100 cc. of a saturated ammoniacal ammonium carbonate solution containing 50 per cent of alcohol is complete. From the result of Section B it appears that the precipitation produced in 150 cc. of a one-third saturated solution of ammonium carbonate containing 50 per cent of alcohol is reasonably complete.

Table III. shows the details of certain experiments in which the separation of magnesium from the alkalis was attempted by the precipitation processes of Table II. In the experiments of A the precipitation was brought about by treating the solution of magnesium chloride and the alkali chlorides, concentrated in the highest degree, with the saturated ammoniacal ammonium carbonate solution containing 50 per cent of alcohol. In the experiments of B an equal volume of absolute alcohol was added to the water solution containing magnesium chloride and the alkali chlorides, and to this mixture was added the saturated ammoniacal ammonium carbonate solution containing 50 per cent of alcohol. In the experiments of C the precipitate was made as in the experiments of B, but, after pouring off the supernatant liquid through the asbestos felt of a weighed perforated platinum crucible, was dissolved in the beaker by warming with the least possible amount of hydrochloric acid. The solution was diluted with water to 50 cc., and treated as in the first precipitation. The second precipitate was collected upon the asbestos felt through which the supernatant liquid had been filtered after the first precipitation, ignited, and weighed. The filtrates were tested for dissolved magnesium as in former experiments. In experiments in which the filtration was made after twenty minutes it was found advisable to hurry the crystallisation by stirring the mixture for not less than five minutes after adding the precipitant.

The results of each method of treatment are plainly very good, but it is more convenient to add alcohol to a water solution than to evaporate a solution, and then treat the residue. Re-precipitation is shown to be advisable when large amounts of the alkalis are present. For amounts comparable to those which we have handled, the procedure is very rapid and simple. The solution containing the salts of magnesium and the alkalis is brought to a volume of about 50 cc., and an equal amount of absolute alcohol is added, precipitation is made by addition of 50 cc. of the saturated ammoniacal ammonium carbonate solution containing 50 per cent alcohol, and the mixture is allowed to stand twenty minutes with stirring for five minutes. If the amount of alkali salt originally present is small, the precipitate may be collected on asbestos in a perforated crucible, washed with the precipitant, dried, ignited, and weighed as magnesium oxide. When the amount of alkali salt originally present is large, the precipitate may be freed from traces of the alkali salt by pouring off the supernatant liquid through the prepared asbestos filter, dissolving the precipitate, and precipitating ammonium magnesium carbonate as at first. This second precipitate, collected upon the filter originally used, leaves upon ignition practically pure magnesium oxide.—*American Journal of Science*, xxv., p. 444.

THE DETERMINATION OF BENZENE IN ILLUMINATING GAS.*

By L. M. DENNIS and ELLEN S. McCARTHY.

I. *The Absorption of Benzene by Ammoniacal Nickel Nitrate.*

In 1903 Dennis and O'Neill described an absorption method for the determination of benzene in illuminating gas (*Journ. Am. Chem. Soc.*, xxv., 503). The absorbent there recommended was an ammoniacal solution of nickel nitrate, the use of such a solution for the determination of benzene having been suggested by the statement of Hofmann and Küspert (*Zeit. Anorg. Chem.*, 1897, xv., 204), that when illuminating gas acts upon a mixture of nickel hydroxide and ammonia, there is formed a compound of nickel cyanide with ammonia and benzene, $Ni(CN)_2.NH_3.C_6H_6$.

In practice, this method for the determination of benzene in some localities has given most excellent results, while in other quarters it has been far from satisfactory. Morton recently demonstrated that when mixtures of *benzene and air* are analysed with the use of the reagent (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1728), the results are scarcely better than might be obtained with water alone, and that, moreover, the efficiency of the absorbent steadily decreases as the amount of benzene that it has taken up increases. These statements of Morton have been substantiated in this laboratory, and the only explanation of the excellence of the results in the analyses of mixtures of air and benzene as published by Dennis and O'Neill would seem to lie in the fact that but few absorptions of benzene were made, and that, consequently, the reagent had not taken up sufficient benzene to render the loss in its absorbing power noticeable.

Confronting the facts adduced by Morton, however, were arrayed statements from several University and technical laboratories testifying to the satisfactory character of the method and the uniformity of results obtained by it in analyses of illuminating gas. In seeking for explanation of these variations in the reports of different chemists it occurred to the authors of the present paper that those samples of illuminating gas on which the method gave good results might have contained cyanogen compounds necessary to the formation of the compound that Hofmann and Küspert described, while the poor results on other samples of illuminating gas might be caused by the absence of cyanogen compounds from the gas. To test the validity of this assumption, the ammoniacal nickel nitrate solution recommended by Dennis and O'Neill was used in a series of analyses of a gas mixture containing benzene, hydrocyanic acid, and air.

The hydrocyanic acid gas for these analyses was prepared by filling a Hempel nitrometer with mercury, then introducing from five to ten cubic centimetres of a concentrated solution of potassium cyanide, and adding gradually through the side arm about the same volume of hydrochloric acid (one part of acid to one part of water). The gas set free by this reaction was completely absorbable by caustic potash. It probably contained small amounts of cyanogen and carbon dioxide, but it will be referred to below as "hydrocyanic acid." A mixture of this gas with benzene and air was obtained by measuring off a volume of air, then passing this into a Hempel simple gas pipette containing liquid benzene, drawing the gas back into the burette and noting the increase in volume, and finally drawing into the burette the hydrocyanic acid gas that had been evolved in the nitrometer, and again measuring the volume. The measurements were made in a jacketed Hempel gas burette with mercury as the confining liquid. Several mixtures prepared in this manner were analysed by the Dennis and O'Neill method. The same sample of ammoniacal nickel nitrate was employed for all of the absorptions listed in Tables I., II., and III.

* From the *Journal of the American Chemical Society*, xxx., No. 2.

Table I. gives the results obtained with the mixture of air, benzene, and hydrocyanic acid. The completeness of the absorption may be seen by comparing the volume of air taken with the volume of gas remaining after absorption. It will be noted that the agreement is practically exact in every case except the fourth.

TABLE I.

No. of experiment.	Air taken.	Benzene taken.	Hydrocyanic acid gas taken.	Volume remaining after absorption by ammoniacal nickel nitrate.
	Cc.	Cc.	Cc.	Cc.
1.	56·2	1·0	3·2	56·2
2.	56·4	0·6	2·4	56·5
3.	56·5	1·9	2·4	56·5
4.	56·8	3·4	5·5	57·1
5.	57·7	1·5	1·2	57·7
6.	58·1	1·4	1·5	58·1
7.	58·2	2·1	6·1	58·3
8.	59·1	0·8	1·3	59·1

While the above table demonstrates that, in the presence cyanogen compounds, ammoniacal nickel nitrate quantitatively absorbs benzene vapour, the accurate results obtained by some analysts with the reagent could even yet not be explained, if these cyanogen compounds in a gas mixture are completely removed by potassium hydroxide, the reagent that precedes the ammoniacal nickel nitrate in the analysis of illuminating gas. To ascertain whether any of the cyanogen compounds are left in the gas mixture after it has been passed into the potassium hydroxide pipette, the analyses given in Table II. were made. In each analysis the gas mixture was allowed to remain in the potassium hydroxide pipette for such a length of time as had been found to suffice for the absorption of all of the hydrocyanic acid when that was mixed with air alone. The results show that when hydrocyanic acid, benzene, and air are present together, potassium hydroxide does not remove all of the hydrocyanic acid, the benzene appearing to exert a deterrent effect upon the absorption. It will be noted that the ammoniacal nickel nitrate quantitatively removed the benzene and the residual hydrocyanic acid in nearly every case.

TABLE II.

No. of expt.	Air taken.	Benzene taken.	Hydrocyanic acid gas taken.	Volume absorbed by potassium hydroxide.	Volume absorbed by ammoniacal nickel nitrate.	Volume remaining after absorption by ammoniacal nickel nitrate.
	Cc.	Cc.	Cc.	Cc.	Cc.	Cc.
9.	59·4	1·4	7·2	6·9	1·7	59·4
10.	59·9	0·5	8·6	8·4	0·5	60·1
11.	60·2	1·1	3·1	3·0	1·1	60·3
12.	56·1	0·9	5·5	4·8	1·6	56·1
13.	56·4	0·9	1·7	1·6	1·0	56·4
14.	56·7	1·3	2·0	1·8	1·5	56·7
15.	57·0	0·7	14·3	13·1	1·8	57·1
16.	57·8	1·7	1·9	1·9	1·7	57·8

If, from the results in the above table, we are justified in assuming that after treatment with caustic potash some cyanogen compounds still remain in illuminating gas, it at once becomes evident why the Dennis and O'Neill method gave satisfactory results with such samples of illuminating gas as contained cyanogen compounds.

After the first three determinations in Table II. had been made, it was thought possible that the ammoniacal nickel nitrate had then taken up sufficient hydrocyanic acid to enable it to absorb benzene vapour without the addition of further hydrocyanic acid gas to the mixture. This assumption seems also to be borne out by the fact that in Derminations 11 and 13 the absorption of benzene was complete even when only 1/10 of a cubic centimetre of "hydrocyanic acid" gas was present with the benzene vapour. The results of these analyses are given in Table III.

TABLE III.

No. of experiment.	Air taken.	Benzene taken.	Volume absorbed by ammoniacal nickel nitrate.
	Cc.	Cc.	Cc.
17.	60·5	1·5	1·5
18.	60·5	1·9	1·8
19.	60·9	0·9	0·7
20.	60·8	1·4	1·4
21.	61·2	0·7	0·7

The results, Nos. 12 to 21 inclusive, demonstrate that after the ammoniacal nickel nitrate has taken up some cyanogen it is able quantitatively to absorb fairly large amounts of benzene vapour, and that if cyanogen compounds are present in illuminating gas, the benzene content may accurately be determined by the method of Dennis and O'Neill. If, however, the reagent contains no cyanogen compounds, and if none are present in the gas that is being analysed, the method will not give accurate results.

II. *The Absorption of Benzene by Ammoniacal Nickel Cyanide.*

The foregoing experiments having demonstrated that a solution of ammoniacal nickel nitrate cannot be relied upon for the absorption of benzene from all samples of illuminating gas, the necessity arose for such modification of the method as would render it uniformly accurate.

It is apparent that to insure complete absorption of the benzene from all gas mixtures through the formation of the ammonia benzene nickel cyanide, cyanogen must be present in every case. This led to the use of an ammoniacal solution of nickel cyanide as an absorbent in place of the ammoniacal solution of nickel nitrate (see also Hofmann and Arnoldi, *Ber.*, 1906, xxxix., 339).

Preparation of the Ammoniacal Solution of Nickel Cyanide.—To 50 grms. of nickel sulphate ($NiSO_4.7H_2O$), dissolved in 75 cc. of water, are added 25 grms. of potassium cyanide dissolved in 40 cc. of water. After the addition of 125 cc. of ammonium hydroxide (sp. gr. 0·91) the mixture is shaken until the nickel cyanide has completely dissolved, and is then allowed to stand at a temperature of 0° for twenty minutes. The clear liquid is decanted from the crystals of potassium sulphate that have been precipitated, and is treated with a solution prepared by dissolving 18 grms. of crystallised citric acid in 10 cc. of water. After the mixture has stood again at 0° for ten minutes, the greenish blue supernatant solution is decanted and is introduced into a gas pipette. Two drops of liquid benzene are now added to the reagent through the large tube of the pipette, and the pipette is shaken until the benzene has combined with the reagent. This is effected in two or three minutes. This addition of benzene to the reagent is made because it was found that at times a freshly prepared solution of the ammoniacal nickel cyanide did not quantitatively remove benzene vapour until it had been used for four or five determinations and had absorbed some of the substance. Hofmann and Arnoldi used acetic acid in the preparation of the absorbent. This we have replaced by citric acid because of the appreciable vapour tension of acetic acid at ordinary temperatures.

Apparatus Employed.—The reagent was placed in a Hempel gas pipette of the form used for the absorption of heavy hydrocarbons by means of fuming sulphuric acid, the upper bulb that is filled with broken glass being, however, 4·6 cm. in diameter, which is somewhat larger than in the usual Hempel pipette. The measurements of the gas volumes were made in a Hempel gas burette provided with a water jacket, and if changes of temperatures occurred corrections were made for them. Numerous experiments showed that satisfactory results may be obtained with either water or mercury as the confining liquid in the burette.

Analytical Procedure.—After the sample of gas has been measured in the burette, the burette is connected by means of the usual capillary tube with a pipette containing the ammoniacal nickel cyanide solution, and the gas mixture is repeatedly passed over into the pipette and drawn back into the burette for a period of about two minutes. The pipette is then disconnected and the gas is passed into a "fuming sulphuric acid" Hempel gas pipette containing a 5 per cent solution of sulphuric acid, this being done to remove the ammonia that enters the gas mixture from the reagent. The ammonia is not easily absorbed by the dilute sulphuric acid, and the gas mixture must, consequently, be passed into and withdrawn from the pipette repeatedly for about two minutes to effect its complete removal.

Experimental Results.—The experiments that were made to ascertain the applicability of the reagent to the absorption of benzene and the accuracy of the method may be classified under the following heads:—

(1) Determination of Benzene in Known Mixtures of Benzene and Air;

(2) Study of the Behaviour of an Ammoniacal Solution of Nickel Cyanide toward Known Mixtures of Ethylene and Air;

(3) The Determination of Benzene in Coal Gas;

(4) The Determination of the "Analytical Absorbing Power" of the Ammoniacal Solution of Nickel Cyanide;

(5) The Determination of Benzene in Coal Gas that had been Freed from the Benzene that it originally contained and had been Mixed with Known Volumes of Benzene Vapour; and

(6) The Determination of the Vapour Tension (with reference to Benzene) of the Partially Exhausted Reagent.

(1) *The Determination of Benzene in Known Mixtures of Benzene and Air.*—Air was drawn into the gas burette and measured. It was next passed into a gas pipette containing mercury and a few cubic centimetres of liquid benzene, and was then drawn back into the burette and the increase in volume was noted. The percentage of benzene was then determined by absorption with the ammoniacal solution of nickel cyanide with the subsequent removal of the ammonia by dilute sulphuric acid in the manner described above. A large number of these analyses was made. The few results in Table IV. illustrate the average efficiency of the method.

TABLE IV.

No. of experiment	Benzene taken. Per cent.	Benzene found. Per cent.
22.	2·3	2·3
23.	2·6	2·6
24.	1·2	1·3
25.	4·9	4·9
26.	5·1	5·1
27.	2·7	2·7
28.	1·6	1·6
29.	1·8	1·8
30.	1·8	1·7
31.	5·2	5·1
32.	2·7	2·7

(2) *A Study of the Behaviour of an Ammoniacal Solution of Nickel Cyanide towards Known Mixtures of Ethylene and Air.*—Ethylene was prepared by reducing an alcoholic solution of pure ethylene bromide with a zinc-copper couple. The ethylene employed in the first experiments was made in a flask and the resulting gas was found to contain about 90 per cent of ethylene. In later experiments the preparation was carried on in a Hempel nitrometer, and the resulting ethylene was then found to be completely absorbable by 20 per cent fuming sulphuric acid. Mixtures of ethylene and air were prepared and passed over into the ammoniacal nickel cyanide. In no case was any absorption of ethylene noted after the reagent had been shaken once with the gas mixture and thus saturated with it. The data of two experiments are given as illustrative of the results here obtained: Per cent of ethylene taken 4·3, found 0·0; again, ethylene taken 10·4, found 0·0.

(To be continued).

MERCHANT VENTURERS' TECHNICAL COLLEGE.

The New Chemical Department in the Restored Building.

This department will occupy the top floor of the building, and will comprise the Chemical Lecture Theatre, the Preparation Room, the Advanced Chemical Laboratory, the Elementary Chemical Laboratory, the Balance Room, the Combustion Room, the Store Room, and the Dark Room; it will be practically isolated from the lower parts of the building, and will have a special separate ventilating and heating system.

Great care will be taken to ensure an ample supply of fresh air, and to prevent the accumulation of any fumes. The ventilation will be effected by a combination of the plenum and exhaust systems, air being driven into the rooms through heating chambers in winter and through cooling chambers in summer; it will be extracted by means of the exhaust flues placed on the benches and in the fume chambers.

The two laboratories will provide bench accommodation for sixty-six students with several auxiliary benches. Each student's place will be fitted with draught-hoods, bottle-racks, gas and water supply, and waste receptacles; the lockers, cupboards, and drawers will be so arranged that both day and evening students will have on their benches the means of locking up apparatus or materials needed for future experiments.

Three types of students' benches will be provided, one for elementary work, one for advanced work, and one suited for electro-chemical and organic work. The bench space which will be allotted to each student varies from 5 feet to 3 feet six inches.

Each laboratory will be fitted with steam-ovens and a still, also with lead-covered benches with draught-hoods suited for steam and vacuum work.

Ample fume chamber accommodation will be provided by building out from the windows on special balconies so that the whole room space may be left free. Special arrangements will be made for sulphuretted hydrogen closets in the shape of two small rooms separated from the laboratories by means of doors which will act as air locks.

Electric currents will be available, either direct or alternating, and of any desired voltage, as the department will be served directly from the machines and batteries in the electrical engineering department of the college.

The rooms and apparatus will be arranged so as to reduce the amount of moving on the part of the students to a minimum; thus the Lecture Theatre, Preparation Room, and Elementary Chemical Laboratory will form one suite, while the Balance Room, Combustion Room, and Advanced Laboratory will form another.

The Combustion Room will be fitted for blowpipe, furnace, and metallurgical work.

Although the department will be at the top of the building it will be easily reached by either of the stairways, and also by an excellent electric passenger lift.

It is impossible to give in a short space a detailed account of the fittings and apparatus, but they will include the modern details which have proved successful in recently built laboratories, as well as a considerable number of novel developments in addition to these. It is hoped that the Chemical Department will compare very favourably in every way with the most modern laboratories to be found in any of the universities or technical colleges in the United Kingdom.

PROCEEDINGS OF SOCIETIES

PHYSICAL SOCIETY.

Special General Meeting, May 22nd, 1908.

Dr. CHARLES CHREE, F.R.S., President, in the Chair.

A SPECIAL General Meeting was held to consider the proposed alterations in the Articles of Association. The principal changes were described by the Secretary, and on the motion of the CHAIRMAN, seconded by Mr. MATHER, a resolution was passed in favour of the alteration.

An Ordinary Meeting was then held.

Mr. F. P. SEXTON read a paper "*On the Spectrum Top.*"

The author explains in the paper the coloured bands which are seen when a Benham top is rotated. The best effects are obtained when the top rotates about six times per second, when the colours from the centre are purple, dull orange, yellow-green, and violet-blue for an anticlockwise rotation. When the direction of rotation is reversed the order of the colours is also reversed. The effect depends upon the position of the sector lines and on a contrast. The author assumes that the rates of growth of the colour sensations are in the order red, green, and blue where red is the greatest, and that the rates of decay are in the inverse order. Considering the inner ring with an anticlockwise rotation, the author explains the colour observed as follows:—As the black disappears the first impression will be black lines on a red ground, but this red impression will have somewhat passed to white when the sector lines disappear. Their disappearance also gives a red impression, which in this case is increased by a contrast. Finally, the disappearance of the white will give a bluish impression, not reinforced by contrast. Thus the eye will see red lines on a white ground. In the case of the second ring, the sector lines coming into view give a blue impression, depending on the amount of white preceding. When these lines pass from view they are followed by a red impression, depending on the amount of white succeeding. These two impressions combine to give a resultant orange effect. The third and outer rings are explained in a similar way.

Mr. F. E. SMITH asked if the author had viewed the top when illuminated with lights of different colours, and if so with what result.

The AUTHOR replied that experiments had not been tried in different coloured lights, as there was difficulty at the time of obtaining a coloured illumination of sufficient strength. The bands were visible in sodium light; but this did not affect the theory, because sodium light, although practically monochromatic, affects the three colour sensations.

A paper "*On the Coefficient of Diffusion*" was read by Mr. B. W. CLACK.

This paper deals with experiments which have been undertaken to test the practicability of a new method for the determination of the coefficient of diffusion of salts through water, and to find how this coefficient varies with the concentration of the solutions.

The apparatus consists of a special kind of flask of about 450 cc. capacity, fitted with a vertical glass tube of known dimensions. In the earlier experiments this was filled with distilled water and suspended by means of a fine wire in the salt solution under investigation, at the temperature of 0° C., from the arm of a chemical balance. Later, this arrangement was reversed, and the flask, filled with the salt solution, was suspended in cooled distilled water. In both methods the apparatus was so designed that one end of the vertical tube was maintained in contact with a salt solution of constant concentration, while the other end was kept in contact with distilled water. As the salt diffuses through the tube the weight of the flask varies, and an expression was deduced by which it is possible to find the value of the coefficient of diffusion from this rate of change in weight, which was automatically recorded. The accuracy in weighing was found to be greatly increased by covering the free surface of the liquid by a film of Fleuss pump-oil. As the method is complicated by the change in volume which is produced in a liquid when salt is added to it, it was found necessary to experimentally determine the value of this change in volume.

The salts experimented upon were NaCl, KCl, and KNO_3, and a large number of experiments were carried out in order to find the best relative sizes of the various parts of the apparatus and the best dimensions for the diffusion tubes.

The general conclusions may be summarised as follows:

1. The method referred to above, of filling the apparatus with the salt solution and suspending it in cooled distilled water, is much more satisfactory than the earlier method from a practical point of view. It enables greater control to be maintained over the working details, and is much simpler in operation.

2. The volume of the liquid in which the suspended apparatus is hung must be considerable. A volume of 7 litres was found to be too small, and in these experiments 13 litres was used. This was found to be sufficient.

3. With these precautions the method gives satisfactory results with a consistency of usually less than 1 per cent.

4. For a diffusion tube of 4 cm. length, no end correction need be applied, even for the widest tubes employed (1·5 cm.).

5. The coefficient for NaCl and KCl decreases as the concentration of the solution decreases.

6. For KNO_3 the opposite phenomenon is exhibited.

7. The most trustworthy results, obtained with the precautions mentioned above, for the coefficient of diffusion at 0° C., are:—

KNO_3	10 per cent	$0{\cdot}844 \times 10^{-5}$	C.G.S. unit
	5 ,,	0·870	,,
KCl	20 ,,	0·972	,,
	10 ,,	0·954	,,

Dr. A. GRIFFITHS congratulated the author upon his paper, and referred to the importance of keeping the temperature constant during the experiments. The effects of temperature changes were very marked. The importance of a deep outer vessel was also surprising, and Dr. Griffiths pointed out how it was possible to place a superior limit to the error introduced by the passage of the salt into the outer vessel. He also suggested the use of a differential method, using two glass vessels, to overcome some of the difficulties encountered in the experiments.

Prof. C. H. LEES said that all who had experience with diffusion experiments would congratulate the author. The idea of using a balance was an old one, but the author had made an old method a thoroughly reliable one. The question was still to be solved whether an increase of concentration increased or decreased the diffusion constant, and he hoped the author would be able to carry on his experiments and settle this point.

Mr. B. S. COHEN read a paper on "*The Production of Small Variable Frequency Alternating Currents suitable for Telephonic and other Measurements.*"

As an introduction a summary of the methods used by the author for such currents is given. A new method for producing these currents is then described; this consists of a form of vibrating wire interrupter which operates a make and break contact. This is used to put a source of potential on and off a resonating circuit tuned to any desired frequency. The alternating current is taken from a small transformer in the resonating circuit. A series of damped wave-trains of any frequency can be produced by this means, the trains following each other with the frequency of the wire vibrations. Several forms of circuit are described, one of which gives a train of oscillations at each break of the supply circuit. Other circuits give damped waves both on the break and on the make contact,

and by a suitable combination of two oscillating circuits worked from one mercury cup and contact it is shown that continuous and fairly uniform oscillations can be produced. The theory of action of the various circuits is briefly entered into, and the paper concludes with some applications of the waves produced to both telephonic and general electrical measurements. The wave forms given by the various circuits were shown at the meeting by means of a Duddell oscillograph.

Mr. A. Campbell mentioned that with his vibrating-bar microphone hummer he had found it easy to obtain more than one frequency from the same bar by altering the supports to suitable nodal points, and tuning the magnet circuit with a condenser. Harmonics of the fundamental frequency are thus produced. He asked if any of the composite wave forms shown gave vowel sounds in the telephone.

Dr. Russell congratulated the author on his interesting and valuable paper, and thanked him for the instructive demonstration he had given of methods of producing high-frequency currents suitable for telephonic and other measurements. He understood that the author's main object was not the obtaining of currents of excessively high frequency, but obtaining currents having frequencies varying between 100 and 5000 which followed the harmonic law. Some of the methods described, in particular the author's "double action circuit" method, seemed well adapted for this end. In some of these circuits there are two free periods of vibration, and it was exceedingly interesting to see the accuracy with which the oscillograph gave the resultant of two slightly damped trains of high-frequency waves of different periods. Tuning for resonance the author obtains a very perfect sine wave. He thought that the thanks of the meeting were also due to the National Telephone Company for the facilities they had afforded Mr. Cohen.

Mr. Cohen expressed his interest in Mr. Campbell's statement, that it was easy to get more than one frequency from his vibrating bar hummer. The currents shown, when passed through a telephone receiver, did not produce vowel sounds.

SOCIETY OF CHEMICAL INDUSTRY.
(London Section).

Ordinary Meeting, June 1st, 1908.

Dr. Lewkowitsch in the Chair.

"*Some Modern Chemical Plant.*" By Oscar Guttmann, M.Inst.C.E., F.I.C.

After discoursing on the general trend towards economy and high production per unit volume in sulphuric acid chambers, necessitated by the invention of the contact process, the author shows how greatly the yield of chambers is improved by increasing the height in proportion to the length, in fact turning the old type of chamber through 90°. Chambers are now built 48 feet square and 80 feet high, giving a capacity of about 178,000 cubic feet. The author also showed a novel method of hanging these chambers from the roof by means of vertical rods and straps.

Glover towers in Volvic lava built up in sections and held together by lead-covered iron hooks, were shown, and mention made of the feeding arrangements for Gay-Lussac towers, the best filling material for them, and the results obtained.

Next a nitric acid still holding 5 tons of nitrate of soda was described, and it was mentioned that such holding 10 tons, or fifty times as large as used twenty years ago, were already at work.

A large kiln for the manufacture of wood charcoal was of great interest, as illustrating to what extent the primitive charcoal burner's process has developed. This kiln is capable of taking 7000 cubic feet of cut wood in one charge, giving off 10,000 gallons of liquor and about 14,000,000 cubic feet of gas fuel, which latter is sufficient not only for primarily heating the kiln, but also for the whole factory.

Acid and alkali proof castings and iron-clad earthenware fans for hot acid gases were next discussed, and in conclusion the author warns against the practice of obtaining complete plans and estimates for chemical factories from engineering firms who may only make a few parts of the whole, and can have but little experience of the manufacture.

"*Explosions and the Buildings of Explosive Works.*" By Oscar Guttmann, M.Inst.C.E., F.I.C.

Very little has been done in the way of modifying the construction of buildings in explosive factories since the Explosive Act of 1875, in consequence of which it became customary to make some arrangement to minimise the destructive effect of an explosion. This was attempted in various ways; the most usual being to make light wooden huts, and to surround them by earth mounds, the buildings being spaced sufficiently far apart to prevent the explosion from becoming general.

The effect of an explosion, especially with modern high power explosives, is manifested in a variety of ways, and gives rise to very curious effects.

Apart from the usual dangerous shower of heavy and burning pieces of wreckage and *débris*, the concussion, both above ground and through the ground, must be considered. The former may cause disaster by penetrating or setting fire to other buildings, while the latter manifests itself by causing the collapse and destruction of buildings by what was usually considered a suction effect. The author proposes that buildings in explosive works should be constructed in ferro-concrete with fine river gravel.

Such a structure, being practically a solid mass, would not be liable to collapse; it would be fire and lightning proof, and should an explosion take place would be so pulverised that particles could not be projected to any considerable distance.

To prevent heavy pieces of machinery and the like penetrating the roof, this is made with a double ferro-concrete skin, a layer of sand about a foot thick being interposed, which latter effectually deadens and distributes the shock. By the use of wire glass the dangerous splintering of ordinary window-panes is avoided.

The whole structure being kept relatively low, and the skin of the mounds enclosing it being also in ferro-concrete, there is a large economy effected in the amount of material and space required.

This method of construction having been favourably considered by authorities and experts, the author has thought it his duty to bring it at once before the public.

The paper was illustrated by diagrams and a large number of lantern slides illustrating the effect of explosions on surrounding buildings.

"*The Autolysator; an Apparatus for the Automatic Estimation of Carbon Dioxide.*" By Charles A. Keane, M.Sc., Ph.D., and Harry Burrows, A.R.C.S., Ph.D.

The "Autolysator" is an apparatus devised by Strache, Johoda, and Genzkin for the automatic estimation of carbon dioxide in furnace gases, producer gas, and similar products. It differs from other forms of apparatus for automatic analysis in giving a continuous instead of an intermittent record of the carbon dioxide content of the gases examined.

Results obtained on the laboratory scale with a gas furnace showed that the records of the instrument agree with those obtained by the ordinary analytical methods within 0·3 per cent, and that it responds very efficiently to changes in the percentages of carbon dioxide present in the gas. Experiments were also conducted on the furnace gases from boilers, and the conditions of working examined, more especially in regard to the methods of withdrawing the sample and the life of the absorbent employed.

"*The Estimation of Orcinol in Orchella Weed.*" By Henry Edgar Watt, M.Sc., A.I.C. (Assistant Chemist, Scientific and Technical Department, Imperial Institute).

In this paper the author shows that the published processes for the estimation of colour-yielding substance in lichens of the genus *Roccella* are open to criticism, and proposes a modified method based upon the reaction which takes place between orcinol, $CH_3.C_6H_3.(OH)_2.1.3.5$, and a solution of sodium hypochlorite. Four samples of orchella weed, received at the Imperial Institute from the Seychelles, were assayed, and particulars of the results obtained recorded.

NOTICES OF BOOKS.

Thermodynamics of Technical Gas-Reactions. By Dr. F. HABER. Translated by ARTHUR B. LAMB, Ph.D. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

THIS book is a translation of a course of seven lectures delivered at the Technische Hochschule, Carlsruhe, in February, 1905, dealing with the latent heat of chemical reaction and its relation to reaction energy. After deducing the general relationships the lecturer proceeded to apply them first to the case of reactions, in which there is no change in the total number of molecules, and then to those in which the number of molecules is altered during the reaction. A very interesting chapter deals with the determination of the specific heats of gases both by direct and indirect methods, and finally the investigation of gaseous equilibria, especially at high temperatures, is discussed. The lectures dealt with a branch of thermodynamics which has not been adequately treated in any similar book, and introduced questions of great interest and technical importance, and the English translation can be recommended to chemists, both to those who are engaged in prosecuting research in technical physical chemistry and those who are teaching the elements of the same subject.

The Metallurgy of Iron. By THOMAS TURNER. Third Edition. London: Charles Griffin and Company, Limited. 1908.

THE third edition of this work contains a new chapter dealing with the gaseous products of the blast-furnace, in which the application of the surplus furnace gases for driving gas-engines is described, and an account is given of the recovery of tar and ammonia from blast-furnace gases. In addition the important recent advances in pyrometry and in the use of the microscope are treated fully, and valuable microphotographs illustrate the chapter on the structure of cast-iron. Methods of handling and transporting ores have recently undergone considerable modifications, which are described in this new edition, and the development of American iron mines, which has led to such an enormously increased production of pig-iron, is discussed, the Lake Superior ores being treated in a special section.

Leather Trades Chemistry. By S. R. TROTMAN, M.A., F.I.C. London: Charles Griffin and Company, Limited. 1908.

THE official and some of the more commonly employed non-official methods of analysing all materials used in the leather industry, including water and soaps, are described in this book. Both qualitative and quantitative processes are given, and the author's wide experience in leather chemistry enables him to offer to his readers valuable advice on the choice of analytical methods; he has, moreover, carefully collected from periodical and other literature examples of typical processes. Full tables are given, for instance, for the qualitative recognition of tannins, from Professor H. R. Procter's publications. The plates of the micro-photographs of the cuticles of different plants are excellently reproduced from the *Journal of the Society of Chemical Industry*. An outline of the classification and identification of dye-stuffs gives very clear schemes and tables, which, if they are carefully followed, should enable the chemist to detect any common dye comparatively easily. As a work of reference the book can be recommended, but there are objections to its use as a text-book for students, the chief being the order adopted; for example, the estimation of nitrogen by Kjeldahl's method, involving the use of standard solutions, precedes the chapter dealing with the preparation of such solutions.

Analysis of Mixed Paints, Colour Pigments, and Varnishes. By CLIFFORD DYER HOLLEY, M.S., Ph.D., and E. F. LADD, B.S. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1908.

WITH the aid of this book the chemist of ordinary education and experience will find little difficulty in performing an analysis of a mixed paint. The book opens with some notes on the general characteristics of the commoner mixed paints, in which some methods of adulteration are pointed out. The preparation of a sample and the separation of the vehicle and pigment are next considered, and the analysis of the former is then taken up. Special methods of oil analysis are treated in one chapter, and the methods of identifying the vehicle are made clear. The analysis of the pigments, grouped according to colour, by various systems is described fully, and examples to show the separation of the constituents from one another are included. One chapter on colour mixing contains hints for some exercises in colour-making, and an outline is given of the most satisfactory methods of analysing varnishes, both by chemical and physical and by practical tests.

Process Cost Accounts. By H. STANLEY GARRY, C.A. London: Gee and Co. 1908.

THIS volume of the "Accountants' Library" explains the outlines of the most satisfactory and correct methods of keeping accounts in relation to chemical industries. Problems which are more especially likely to occur in such trades are discussed, and typical results and examples are given to illustrate different kinds of Forms of Works Returns. The book will be found to provide accountants with considerable assistance in grasping how best to acquire a sufficient working knowledge of the technicalities of the more important processes, how to group various costs together, and finally how to represent statements and returns by charts and diagrams.

A Systematic Introduction to Analytical Chemistry. By A. F. WALDEN, M.A., and B. LAMBERT, M.A. Oxford: Joseph Thornton and Son. London: Simpkin, Marshall, Hamilton, Kent, and Co., Limited. 1908.

A USEFUL course of analytical chemistry is given in this book, and as it is now being recognised that students who have been taught by the heuristic method may gain much by a careful study of qualitative analysis, a text-book on the subject in which new ideas are incorporated should have a successful future before it. The book differs from the older type of practical chemistry book in many respects. No tables are given, the authors believing that the construction of them by the student himself forms a most instructive exercise. The metals are grouped in the familiar five groups, and the general characteristics of each group are discussed, but separation tables for mixtures of simple salts are not given. The free use of different type emphasises the most important reactions of the metals treated, and will be an assistance to the student in the laboratory, while the explanations of obscure reactions, inserted in smaller print, will repay careful reading in the study. The acid radicles are classified according to their behaviour on treatment with hydrochloric acid and concentrated sulphuric acid, and also with silver nitrate and barium chloride, and are on the whole well treated;

insoluble substances are also included, and analysis by the dry method is discussed particularly fully. The ionic nomenclature and notation are adopted, and in the case of each metal its chief properties, the action of air and water upon it, and the reactions of its salts in aqueous solutions, are systematically studied.

Modern Pigments and their Vehicles. By FREDERICK MAIRE. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1908.

PAINTERS and dealers in paints and paint vehicles will be able to glean a good deal of useful information about pigments and their applications for various purposes from this little book. It gives a brightly written account of the properties and uses of some important pigments, and if the author is a trifle verbose he may be forgiven for the sake of the unconventionality of his style, which is of exactly the right nature to appeal to the special class of readers for whom he writes. The lists of pigments given are exceptionally full, and a good working acquaintance with the nature (but not the chemistry) of each substance may be acquired from the book; the only omission of importance among common pigments is that of lithopone, which is coming into extensive use for many purposes; the paranitraniline reds are, moreover, rapidly taking the place of quicksilver vermilion, which has now been so far superseded that it hardly deserves the space devoted to it. Some notes on the compounding of pigments and the making of the principal tints conclude a book which is of considerable value to the practical painter.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 19, May 11, 1908.

Thorium Oxyfluoride and Fluoride.—Ed. Chauvenet.—When thorium nitrate is precipitated with silver fluoride a gelatinous precipitate of the hydrated fluoride is obtained. It retains four molecules of water when dried to constant weight in a vacuum. When heated to 800° in a current of anhydrous hydrofluoric acid, a white oxyfluoride, $ThOF_2$, is obtained. The same compound can be prepared by decomposing in a slow current of hydrogen the fluosilicate of thorium obtained by precipitating a solution of thorium nitrate with hydrofluosilicic acid. Gaseous hydrofluoric acid reacts on the anhydrous bromide or iodide of thorium, giving the pure fluoride, ThF_4. Thus prepared the fluoride is amorphous, and is not attacked by sulphuric acid.

Compounds of Silver Selenide with the Selenides of Arsenic, Antimony, and Bismuth.—H. Pélabon.—The solidification point of liquid silver selenide is considerably lowered by the addition of a small quantity of Bi_2Se_3, Sb_2Se_3, or As_2Se_3. The fusion curve consists at first of an almost rectilinear part, starting from the fusion-point of Ag_2Se. This part is practically the same for all three selenides. For Bi_2Se_3 the straight line stops at 670°, which corresponds to the eutectic mixture, $Ag_2Se.\frac{1}{4}Bi_2Se_3$ or $Ag_2Se.\frac{1}{3}Bi_2Se_3$; the temperature of solidification then rises, reaches a maximum at 773° for the compound $3Ag_2Se.4Bi_2Se_3$, and then diminishes to 692°, the solidification-point of the second eutectic. The curve then becomes a straight line. In the case of antimony the first eutectic solidifies at 540°, the maximum temperature of solidification is 650° for the compound $3Ag_2Se.4Sb_2Se_3$, and the second eutectic solidifies at 573°. The second eutectic cannot be observed in the case of arsenic selenide. The fusion curves of silver selenide with the compounds $SbSe$, Sb_3Se_4, and Sb_4Se_5 have the same general form as those of the mixtures of silver selenide with the selenides of bismuth, arsenic, and antimony.

Origin of Ozone in the Atmosphere and the Causes of the Variations of the Carbon Dioxide in the Air.—H. Henriet and M. Bonyssy.—The ozone in the air is formed at the expense of the oxygen of the upper regions of the air under the influence of the ultra-violet radiations emanating from the sun. The ozone is brought down to the lower layers of the air by winds and by rain. When the weather is calm and the atmosphere is transparent the solar radiations act on the lower layers of air and increase the proportion of ozone. All the variations in the carbon dioxide below the normal values are due to the air of the upper regions. The variations in the carbon dioxide above the normal originate in local phenomena; for example, the respiration of men and animals in the streets of large towns, &c.

Properties of Metallic Thiosulphocarbamates.—Marcel Delépine.—The thiosulphocarbamates of nickel, cobalt, copper, sodium, barium, zinc, silver, lead, iron, which the author has prepared, exhibit the following general properties:—They tend to crystallise with their solvents. The salts of the alkalis and alkaline earths and of zinc are colourless, while those of copper, nickel, cobalt, and iron are coloured. The nickel, cobalt, iron, and copper salts, $[(C_4H_9)_2N.CS_2]_2Ni$, $[(C_4H_9)_2N.CS_2]_3Co$—Fe, are not ionised in organic solvents, and hence the salts behave indifferently towards ordinary reagents.

Amide Derivatives of *o*-Dibenzoylbenzene.—A. Guyot and P. Piquet.—Tetramethyldiamido-*o*-benzoylbenzylbenzene,—

$$(CH_3)_2N—C_6H_4—CO—C_6H_4—CH_2—C_6H_4—N(CH_3)_2,$$

may be prepared by the condensation of dimethylaniline with the chloride of dimethylamidobenzylbenzoic acid in presence of aluminium chloride. When reduced with sodium amalgam it yields tetramethyldiamido-*o*-benzhydrylbenzylbenzene,—

$$(CH_3)_2N—C_6H_4—CHOH—C_6H_4—CH_2—C_6H_4—N(CH_3)_2,$$

which, on treatment with zinc and hydrochloric acid, undergoes a further reduction to tetramethyldiamido-*o*-dibenzylbenzene,—

$$(CH_3)_2N—C_6H_4—CH_2—C_6H_4—CH_2—C_6H_4—N(CH_3)_2.$$

The benzhydrylbenzylbenzene undergoes anthracene condensation in contact with concentrated sulphuric acid in the cold. When the dimethylaniline in the preceding compounds is replaced by diethylaniline, diethyldimethyldiamido-*o*-benzoylbenzylbenzene is obtained:—

$$(C_2H_5)_2N—C_6H_4—CO—C_6H_4—CH_2—C_6H_4—N(CH_3)_2.$$

This undergoes the same reactions as the tetramethyl compound, yielding the corresponding diethyl derivatives.

MEETINGS FOR THE WEEK.

WEDNESDAY, 17th.—Microscopical, 8. "On Cycloloculina, a New Generic Type of the Foraminifera," by E. Heron-Allen. "Illuminating Apparatus for the Microscope," by J. W. Gordon. Exhibition of a New Lens for High-power Microscopy, by Mr. Gordon and Mr. H. Fletcher Moulton. Exhibition of Micro-slides, "The Development of the Chick," by A. Flatters.

THURSDAY, 18th.—Chemical, 8.30. "The Thermal Decomposition of Hydrocarbons—Part I., Methane, Ethane, Ethylene, and Acetylene," by W. A. Bone and H. F. Coward. "Rusting of Iron," by W. A. Tilden. "Studies on Elementary Zirconium," by E. Wedekind and S. J. Lewis. "Constituents of Canadian Hemp—Part I., Apocynin," and "A New Synthesis of Apocynin," by H. Finnemore. "Constitution of the Diazonium Perbromides," by F. D. Chattaway. "Cholestenone," by C. Doreé and J. A. Gardner. "A New Form of Potash Bulb," by A. E. Hill. "Solubility of Silver Chloride in Mercuric Nitrate Solutions," by B. H. Buttle and J. T. Hewitt.

THE CHEMICAL NEWS.

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ON THE UTILISATION OF THE ATMOSPHERIC NITROGEN IN THE PRODUCTION OF CALCIUM CYANAMIDE, AND ITS USE IN AGRICULTURE AND CHEMISTRY.*

By Dr. ALBERT FRANK.

WHEN Liebig, about the middle of last century, laid down the scientific basis of the natural laws of agriculture and the cultivation of plants, he showed that the essential condition for ensuring the soil against loss of plant-food, and thereby enabling it to maintain its fertility, was the supply of such *mineral* foods as the plants require for their growth. These mineral foods are continually being withdrawn from the soil, where they are by no means over-abundant in available form, by the crops. Among such foods Liebig placed phosphates and salts of potassium in the front rank, and thus founded his theory of *mineral manure*. As regards bodies like oxygen, hydrogen, carbon, and nitrogen, which are used for building up of the intrinsic organic plant substances, Liebig maintained, in opposition to the supporters of the vegetable theory, which was believed in up till then, that the requirements of vegetation were continually and adequately supplied by the atmosphere, and that the effect of the nitrogen contained in certain bodies widely known in practice as efficacious manures, such as bone-ash and guano, was of less importance than that of the other inorganic plant foods. Technical chemists adopted Liebig's suggestion with enthusiasm and success. After the discovery of the rich mineral phosphate deposits, the conversion of these into the higher phosphates by treatment with sulphuric acid was utilised with much success. The author's father, Professor A. Frank, of Charlottenburg, succeeded, after the Stassfurt deposits were discovered, in placing at the disposal of agriculturists, the world over, an inexhaustible supply of the much needed potassium salts. As a result of the successes achieved in agriculture by Liebig's *mineral* theory, observant investigators, and amongst the first of these Liebig himself, could not in the long run ignore the fact that, by the addition of bodies containing nitrogen to the mineral manures, an essential requirement of plant life was met, and, at the same time, an improvement in the financial condition of the manure trade must ensue. In consequence an immediate demand for manures containing nitrogen, most of them of organic origin—*e.g.*, bones, blood, offal, and fish guano—arose. These, however, only partially supplied requirements, while at the same time the Peruvian deposits of animal guanos were being very rapidly depleted by an ever increasing demand. It became necessary, therefore, to turn to those inorganic compounds of nitrogen which had definitely been proved by scientific research to be suitable for plant food. Of these the two most important were the salts of ammonia, especially ammonium sulphate, the manufacture of which on a large scale from the gas liquors was first carried out in England in the early sixties, and the nitrates, of which an extensive deposit in the form of sodium nitrate, was discovered on the rainless plateaus of Peru and Chili as early as 1830. Their application to agriculture, however, dates from 1860. Since ammonium salts have up till now only been profitably obtained as a by-product in the manufacture of coal-gas and coke, their production, in spite of the great increase from 10,000 tons in 1860 to about 600,000 tons last year (of which England uses up some 316,000 tons), is limited and dependent on other factors than agricultural demand.

* A Paper read before the Faraday Society, June 9, 1908.

Output of Ammonium Sulphate in England.

Year.	Total production (tons).	Average price per ton.	Total home consumption (tons).
1898	196,500	9 2 7½	65,000
1899	208,000	11 5 9½	58,500
1900	210,000	11 2 0	65,000
1901	228,500	10 11 4	68,297
1902	229,000	11 16 3	68,700
1903	234,000	12 9 3	70,200
1904	245,000	12 3 8	71,200
1905	268,500	12 10 9	75,400
1906	289,000	12 0 9	78,000
1907	316,000	11 15 3	87,500

NOTE.—The amount used in agriculture may be anything between 90 to 75 per cent of the total home consumption, the balance being absorbed in arts and manufacture.

Output of Ammonium Sulphate in Germany.

Year.	Total (tons).	From coke (tons)	From gas works (tons).
1897	84,000	70,000	14,000
1898	98,000	84,000	14,000
1899	100,000	84,500	15,500
1900	106,500	88,500	18,000
1901	133,000	113,000	20,000
1902	140,000	117,000	23,000
1903	146,000	120,000	26,000
1904	182,000	152,000	30,000
1905	203,000	168,000	35,000
1906	235,000	197,000	38,000

It was these circumstances which placed sodium nitrate in the front rank of nitrogenous manures, and which caused the world's demand for these substances to rise from 935 tons in 1830 to about 1,740,000 in 1907 (see Fig. 1).

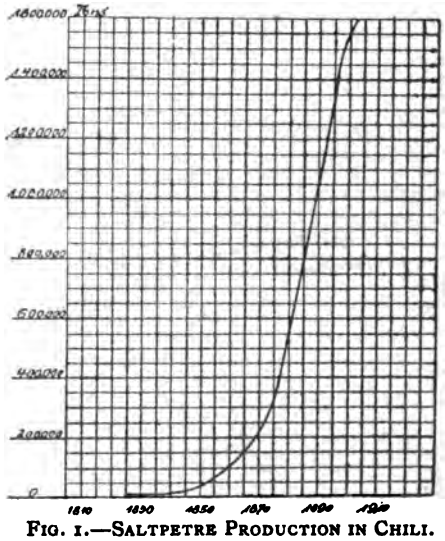


FIG. 1.—SALTPETRE PRODUCTION IN CHILI.

Of this amount Europe absorbs about 340,000 tons, 20—25 per cent of this being employed in the manufacture of chemicals and explosives, while the rest is used for agricultural purposes. Germany, which on account of the uncertain climate of its northern provinces, and because of its extensive beet-sugar industries, specially needs manures, is the largest consumer, importing over 500,000 tons yearly, about 400,000 of which are utilised in agriculture. The guano deposits which at first were considered inexhaustible

have now practically come to an end, and the same remark applies to the strictly limited nitrate deposits in the rainless region of Western South America. Agriculturists and political economists naturally regard with considerable anxiety the approaching disappearance of the deposits, while the demand for nitrates is steadily increasing year by year. Whether the date of exhaustion will be twenty or forty years hence is, on account of the vast importance of the question, of little consequence, seeing that even last year the price of sodium nitrate rose 35 to 40 per cent (in Germany), an increase due less to speculators than to higher working expenses and growing difficulty of production. It is also manifest that the chemical industries can afford to pay for the nitrate—which they consume in the production of nitrogenous compounds, nitric acid, and explosives—higher prices than the agriculturist is able to give. The price of sodium nitrate reveals, in addition, the state of the market for other nitrogenous manures. Ammonia and ammonium salts have likewise shown a marked advance, and agriculturists who have urgent need of these manures, not only for producing their present average crops, but also for securing the increased output made necessary by the growth of population, an urgent necessity pointed out some years ago by Sir William Crookes, were threatened with a serious nitrogen famine.

It is well known to all that the atmosphere surrounding our earth contains a diffused and practically inexhaustible supply of nitrogen, totalling about 4,041,200,000,000,000 tons. This works out at 31,000 tons of nitrogen over each acre of the surface of the globe, or the still air over every nine acres contains about 280,000 tons—*i.e.*, the same amount which is contained in the 1,740,000 tons of Chile saltpetre exported from that country in 1907. We know, further, that uncultivated plants, partly through certain organs which exist in them, as well as in leguminous plants, and partly by the aid of bacteria inhabiting the soil, are able to absorb the nitrogen they require from the air diffused through the soil. Furthermore, in 1775 Priestley showed that atmospheric nitrogen under the influence of the electric spark combined with atmospheric oxygen to form nitric acid, the latter being conveyed by moisture to the soil and then to the plants. But all this accumulated experimental knowledge, important though its results undoubtedly were, did not afford any clue to the possibility of producing nitrogen compounds in considerable masses, nor was it freely at the disposal of agriculturist or chemist. The method devised by Townes and Young last century, and experimentally applied by Bunsen and Playfair, showed that by passing atmospheric nitrogen over carbon and the alkalis or alkaline earths, the carbon compound cyanogen could be formed from which by further treatment ammonia could be obtained. This method, in spite of its extensive application and the many improvements which Marguerite and Sourdeval, and later Ludwig Mond, introduced in its technical details, produced no practical result, on account of the difficulty of attaining the requisite temperature. It was further complicated by the fact that the construction and maintenance of the apparatus, owing to the materials used in the furnaces, gave rise to what were then insuperable difficulties. The first successful advance was made through the discovery and application of the dynamo, which rendered it possible for electricity to be supplied in considerable quantities. By this means a hitherto unattainable temperature could be produced in quite a restricted space. Up to this time, now some few years ago, the necessary energy had to be obtained, except in so far as it was produced by reaction from the molecular energy of the elements, by means of the chemical process of "combustion." With the application of the dynamo and the invention of the electric furnace by Siemens, this process was greatly modified, as by means of electric energy thus applied heat could be produced by means of the electric arc or of an electrical resistance, and could be brought to bear directly on to the chemically reacting mixture.

With these improved means at their disposal, investigators endeavoured once more to find a solution, as already stated, of the all important question of the fixation of nitrogen.

Subsequent to 1894, when Thomas L. Willson and Moissan carried on the manufacture of carbide on a large scale in the electric furnace, the author's father, Professor Adolph Frank, in a paper published in February, 1895 ("Uber Gewinnung von Acetylen und dessen Verwendung zur Herstellung von Alkohol, &c.," *Verhandlungen des Vereins zur Beförderung des Gewerbfleisses*, No. 2, February, 1895), opposed Moissan's views as regards the possible use of this carbide combined with atmospheric nitrogen, for the preparation of cyanides and amides. Tests carried out in conjunction with Dr. N. Caro on this point established the truth of his hypotheses and further led to the invention of a method for the preparation of cyanides, cyanamides, ammonia, and other nitrogen compounds. It is on the technical and industrial manufacture of these and their value that the author has this evening to speak to you.

The other way of fixing nitrogen, on which much successful work has been accomplished, by oxidising it and turning it into nitric and nitrous acid by means of the electric spark, was soon established on practical lines, firstly with unsatisfactory technical results at Niagara Falls by Bradeley and Lovejoy, and then by the magnificent discovery of Birkeland and Eyde, as well as by the improvements which are now being perfected due to Schönbein and the Badische Anilin und Soda Fabrik. Prof. Birkeland made some highly interesting remarks on the oxidation of atmospheric nitrogen in this room in July, 1906, which you will all remember. In amplification of these the author may add that the production of calcium nitrate by the Birkeland-Eyde process seems to be developing exceedingly well in Norway, and that the factory mentioned by Prof. Birkeland is actually established at Notodden and is producing this substance. It should, however, be noticed that this industry has not made much progress in any other land save Norway, but it should not be forgotten that it is only in this northern clime that electrical energy can be as cheaply obtained on account of its unrivalled resources of water power. It would therefore seem probable that Norwegian saltpetre is destined to remain the only direct competitor of the Chilian variety.

As will be seen later on in my paper, the two methods of nitrogen fixation differ greatly as regards their chemistry. Physically they are similar; for, properly speaking, they are not electrical, but should be considered purely thermal processes. They do, however, differ in that the fixation of nitrogen by carbide is an exothermic process, in which heat is given out, while the combination of oxygen and nitrogen is endothermic—*i.e.*, it absorbs a large amount of heat, and for the fixation of an equal quantity of nitrogen requires at least three times the energy that the former process calls for.

The researches instituted, as mentioned above, by Frank and Caro in 1895 were first carried out on calcium carbide mixed with sodium carbonate. But as the yield of cyanide obtained in this way proved unsatisfactory, they soon substituted carbide of barium therefor, a substance which at that time could be more easily obtained, and this they found absorbed nitrogen isolated from the air with great avidity at a temperature of between 700° and 800° C. Frank and Caro were then contemplating the transformation of barium cyanide by treatment with carbonate of sodium or potassium into cyanide of potassium, which at that time commanded a very high price, with a considerably increasing demand. The first experimental plant was constructed with the object of perfecting as far as possible the process for obtaining cyanide of potassium and yellow prussiate. They soon found that the nitrogen absorbed by barium carbide was not merely in the form of cyanide, $Ba(CN)_2$, but that it was also present in the form of a more complex compound. The latter was found, on examination, to be cyanamide of barium, $BaCN_2$, from

which they inferred that the reaction had taken place according to the equation $BaC_2+2N=BaCN_2+C$.

Thus it appeared that in the reaction of carbide on nitrogen half of the carbon contained in the carbide had been set free. The proportion of cyanide and cyanamide of barium in the reacting mass was on an average as two to three, the product containing 30 per cent of barium cyanide and 45 per cent of barium cyanamide, the remainder consisting of barium oxide and carbon.

The transformation of the barium cyanamide into barium cyanide could be easily brought about by melting the mass containing both cyanamide and cyanide with a flux such as potash or soda, according to the equation $Ba(CN)_2+BaCN_2+C+2K_2CO_3=4KCN+2BaCO_3$. The great progress which had meanwhile been made in manufacturing carbide of calcium on an industrial scale gave rise to a renewed attempt to again try the method of treating carbide of calcium with nitrogen, which had been previously abandoned owing to the difficulties which it offered at first starting.

It was then discovered that the small yield of cyanide obtained in using carbide of calcium without an additional flux could be further reduced, and that no cyanide need be formed at all, but that the reaction would proceed in accordance with the equation $CaC_2+2N=CaCN_2+C$, and result in the formation of cyanamide of calcium alone, whilst, as has been seen, in using carbide of barium the corresponding cyanide was also formed.

About this time the patentees, Messrs. Frank and Caro, together with the well-known electrical firm Siemens and Halske, and the Deutsche Bank of Berlin, founded the Cyanid Gesellschaft of Berlin, for the further development of the process. The primary object of the new Company in taking up these inventions was to turn cyanamide of calcium into cyanide of potassium, for which there was an extensive and increasing demand for the purposes of gold extraction in South Africa and the United States. It is common knowledge that this object was successfully accomplished.

The low atomic weight of calcium carbide compared with barium carbide, owing to which 64 parts in weight of calcium carbide sufficed to bind about 28 parts of nitrogen, seemed to point to the conclusion that by using calcium carbide it might prove feasible to produce those nitrogenous compounds also in which the nitrogen would only command a low price, such as fertilisers, &c. Further research in this direction was starting with calcium cyanamide as the raw material for producing ammonia, especially when it turned out that the total nitrogen contents of the calcium cyanamide could by treatment with hot water be turned into ammonia without any difficulty or loss. The process is effected according to the equation $CaCN_2+3H_2O=CaCO_3+2(NH_3)$. In spite of the fact that this reaction requires an excess of water and a high temperature, and that acknowledged authorities on agricultural subjects passed unfavourable opinions in view of the presence of the poisonous cyanide group in the product, in consequence of a proposal made by me, an attempt was made to utilise crude calcium cyanamide directly as a fertiliser, burying it in the ground like any other manure. These experiments were first carried out in pots only. The results were satisfactory enough to indicate that the doubts entertained as to the applicability of the product as a fertiliser were groundless. Thereupon field experiments were arranged on an adequate scale at a large number of agricultural experimental stations, in most countries possessing agricultural interests, and in connection with almost every class of agricultural produce, and these have been continued for the last six years without intermission.

As has been the case with many other artificial manures, a great outcry was, and still is, made warning farmers against the use of calcium cyanamide, popularly known as nitrolim, or at least advising that it should be employed with the utmost caution. This outcry originated in the fact that not only farmers but even agriculturists are saturated with intense conservatism, and that initial failures did here and there occur when first using calcium cyanamide. It is, however, certain that manufacturers must in the first instance determine the most suitable form for every new manure, as a string of well-known instances in the case of other manures abundantly proves. Fifty years ago, when the author's father proposed the use of the potassium salts in the Stassfurt deposits, the chlorine compounds of potassium were not only considered as of doubtful value, but even as harmful, while to-day three million tons per annum are used in agriculture all the world over. In the same way there was a time when the use of Chili saltpetre was directly forbidden by the contracts of beet-sugar manufacturers, while to-day it is considered absolutely infallible by *all* agriculturists, and in certain processes quite indispensable. The storm raised against calcium cyanamide has been lulled in the same way, and recently Professor Wagner of Darmstadt, one of the greatest authorities on agricultural chemistry, summed up his exhaustive researches on the nitrogenous manuring of plants with Chili saltpetre, salts of ammonia, and calcium cyanamide as follows:—"The prospects for an advantageous use of calcium cyanamide are very bright, especially as regards its use for winter fruits. Calcium cyanamide can only be harmful in agricultural practice when it is submitted to abnormal decomposition through *unfavourable* circumstances. Such conditions are especially present in the cultivation of poor lands, such as high moorland and sandy soils which are inclined to be acid, and though rich in vegetable properties are poor in lime. It is, however, well known that this *soil behaves in an abnormal manner to other nitrogenous manures.* In order to prevent the unsuitable conditions of acid soil previous liming is necessary."

It was, besides, only natural that the manufacturers who were not in a position to turn out manure in bulk complying with all these demands should not have been very favourable. To-day, however, things are very different. A product is actually manufactured containing 20 per cent and upwards of nitrogen—that is, considerably more than did the earlier products—which recently has further been submitted to a successful dust removing process, is packed in air-tight sacks, and its efficacy appreciably increased thereby; there can be no longer any doubt that calcium cyanamide is in a position to compete industrially with any other nitrogenous manure. In this connection the question of price is of the highest importance. Now, as the cyanamide industry has been perfected in the course of the last few years, it must be considered to form, on the basis of the percentage of available nitrogen, the cheapest, and therefore for agriculturists the most economical, manure of the present time. When the first consignments of calcium cyanamide were placed on the market the question of packing and storing was not fully understood. The result was that the product absorbed a large amount of free lime, which under the influence of atmospheric moisture was naturally converted into calcium hydrate. This caused such a large increase in the volume of the material that the jute sacks containing it burst. The theoretical proportion of nitrogen showed a decrease which was not ascribed, as it should have been, to the increase in total weight, but was thought to be due to the fact that nitrolim lost nitrogen in some form or other when stored. Scientific research has shown conclusively, however, that calcium cyanamide may be kept stable for years without losing its nitrogen. The technical authorities have also taken notice of this fault, as mentioned above, and calcium cyanamide is now supplied by the manufacturers practically free from the influence of atmospheric moisture, and packed in double paper and jute sacks.

It has a further merit which is of great importance in agricultural operations where elaborate appliances are wanting: calcium cyanamide can be mixed with most widely different manures without loss. For instance, mixed manures of cyanamide and potassium salts, basic slag, &c., may be mentioned which have been found eminently successful in practice. Some difficulty is m

in mixing cyanamide with superphosphate, as the free phosphoric acid combines with the free lime of the cyanamide, and is changed from the water soluble to the citric soluble form. To a certain extent this is not preventable, but the interesting and exhaustive work of Professor Hall, the well-known agricultural chemist and director of the Rothamsted agricultural farm, on this subject has proved that, by observing certain conditions, the mixing of superphosphate with cyanamide can be easily accomplished, and is both successful and economical.

What makes cyanamide especially valuable as a manure is its after effects. It is generally decomposed by the chemical and bacteriological constituents of the soil into ammonia, which becomes fixed by the vegetable mould, and is not, as with Chili saltpetre, liable to be washed into the drains and so practically lost. For this reason cyanamide which has not been used during the *first* harvest is always available for the *second*. Researches on this subject show that the after effects of cyanamide can be very considerable according to circumstances, a property possessed by no other nitrogenous manure. As regards the economy effected by cyanamide manuring, the author will shortly describe the great number of tests which have been carried out for more than six years at agricultural research stations, and by users in all parts of the world, and render the operation of cyanamide apparent by the help of photographs.

(To be continued).

THE GRAVIMETRIC DETERMINATION OF TELLURIUM.

By VICTOR LENHER and A. W. HOMBERGER.

Of all the methods proposed for the precipitation of tellurium perhaps the one which is most used is a modification of the original method of Berzelius. He used sulphurous acid as a precipitating agent.

The method of procedure as commonly carried out consists in adding to the hydrochloric acid solution of tellurium a strong aqueous solution of sulphur dioxide, and allowing this mixture to remain in a warm place for a few days in order to effect a complete precipitation. It has been shown by Schroetter (CHEMICAL NEWS, lxxxvii., 17), Brauner (*Journ. Chem. Soc.*, lv., 392), Norris and Fay (*Am. Chem. Journ.*, xx., 278), Crane (*Am. Chem. Journ.*, xxiii., 408), Frerichs (*Journ. Prakt. Chem.*, lxvi., 261), and others that the precipitation by means of sulphur dioxide is far from satisfactory. Brauner has pointed out that part of the precipitated tellurium undergoes oxidation in the liquid, becoming converted into the tetrachloride, in which form it remains in solution. Crane has suggested that the main cause of the incomplete precipitation by means of sulphur dioxide is the very rapid increase in the ratio of the acids to the unprecipitated tellurium in solution, two-thirds of this being due to the hydrochloric acid set free and one-third to the sulphuric acid formed. He thought if these could be removed the reduction would be complete. The hydrochloric acid could be eliminated by evaporation, but the continuous increase in sulphuric acid would soon interrupt the reaction. This might, however, be kept under control by the addition of sodium or potassium hydroxide.

Whitehead has suggested a remedy in the use of acid sodium sulphite. He advises a moderately concentrated solution of the sulphite, and that the quantity added to the tellurium solution be sufficient only to just neutralise the acids present and that formed during the reaction. When the solution is thoroughly agitated and then allowed to stand in a warm place, the precipitate will form and settle evenly. He states that "while acid sodium sulphite does not completely remove all of the tellurium from the solution in the cold, that if not used in great excess, and the mixed solutions be raised to the boiling-point, toward the end of the action the precipitation will be perfect, and the tellurium will be obtained in a state of aggregation favourable to easy filtration."

Frerichs has worked on the basis that hydriodic acid and sulphur dioxide cause immediate and complete separation of tellurium from a tellurous solution even in the cold, and McIvor has confirmed this method (CHEMICAL NEWS, lxxxvii., 163).

Norris and Fay (*Am. Chem. Journ.*, xx., 278) have demonstrated that, under ordinary working conditions, precipitated tellurium increases in weight about 0·5 per cent, owing to oxidation, and that this increase is balanced by the quantity of the elements left behind as tellurium tetrachloride in the strongly acid solution in which the precipitate is formed by sulphur dioxide. They believe that it is more accurate to weigh tellurium dioxide than to weigh tellurium in the elementary state.

McIvor (CHEMICAL NEWS, lxxxvii., 163) and Donath (*Zeit. Angew. Chem.*, 1890, 214) have studied the precipitation of tellurium by hydrosulphurous acid. This method possesses the disadvantage of a precipitate of tellurium contaminated by more or less sulphur. The method hardly possesses any advantages over the sulphurous acid precipitation.

Stolba in 1873 (*Zeit. Anal. Chem.*, xi., 437), and later Kastner (*Zeit. Anal. Chem.*, xiii., 142). have proposed the precipitation of tellurium from an alkaline solution by means of grape-sugar.

Later, Gutbier described the precipitation of tellurium by means of hydrazine as a method for its determination (*Ber.*, xxxiv., 2724). His method of procedure is to dissolve telluric acid in warm water in a porcelain dish covered with a glass cover, and add by means of a pipette a 10 to 20 per cent solution of hydrazine hydrate. A dark blue almost black colour is noted, and after heating a short time, elementary tellurium is precipitated in a flocculent condition, the liquid becoming colourless. He continues the addition of hydrazine hydrate until the fluid is no longer coloured by further addition of the reagent.

Experimental.

Precipitation by Hydrazine.—In our hands the method of Gutbier gave fairly good results. The fact should be noted, however, that the addition of an excess of the hydrazine does not at once precipitate all of the tellurium. It is preferable to add a small amount of the precipitating agent from time to time. This necessitates several hours for complete precipitation. The following results were obtained by Gutbier's method in hydrochloric acid solution :—

TeO_2 (grm.)	0·2247	0·1988	0·2006	0·2056
Te required (grm.). ..	0·1795	0·1588	0·1603	0·1643
Te obtained (grm.) ..	0·1790	0·1577	0·1596	0·1637

Precipitation by Sodium Acid Sulphite.—In order to completely precipitate the tellurium by this reagent from a hydrochloric acid solution of a tellurous compound, the solution must contain excess of the reagent, and must be allowed to stand in a warm place for twenty-four hours. In the following experiments, the sodium acid sulphite was prepared freshly for this purpose by passing sulphur dioxide into a solution of sodium carbonate. It has been our experience that when acid sodium sulphite which has not been freshly prepared is used for the precipitation of tellurium, the precipitated element frequently contains sulphur.

That it is necessary for the solution to stand a considerable length of time is apparent from the following experiments, all of which experiments were made under exactly the same conditions. The solution of the dioxide in hydrochloric acid was brought to boiling, a saturated solution of acid sodium sulphite was added, the solution allowed to stand the requisite length of time, then brought on a Gooch platinum filter, washed with water until the filtrate no longer showed chlorides, after which it was washed with 15 cc. of alcohol, and dried at 105°.

Solution allowed to stand two hours—

Te requred (grm.) . .	0·1609	0·1609	0·1767
Te obtained (grm.) . .	0·1586	0·1590	0·1744
Error (grm.)	−0·0023	−0·0019	−0·0023

Allowed to stand six hours—

Te required (grm.)	0·1609	0·1609	0·1374	0·1527
Te obtained (grm.)	0·1600	0·1603	0·1366	0·1517
Error (grm.)	−0·0009	−0·0006	0·0008	−0·0010

Allowed to stand twenty-four hours—

Te required (grm.)	0·1609	0·1609	0·1726	0·1286
Te obtained (grm.)	0·1615	0·1618	0·1730	0·1289
Error (grm.)	+0·0006	+0·0009	+0·0004	+0·0003

After tellurium, which has been precipitated by means of sodium sulphite and hydrochloric acid, has been washed thoroughly with water and alcohol, it oxidises very slowly when heated as high as 200°, as evidenced by the following data :—

Length of time of heating.	Temperature.	Te(1).	Te(2).
15 minutes . .	105°	0·1619	0·1620
15 „ . .	105°	0·1619	0·1620
1 hour	120—130°	0·1620	0·1622
1 „	200°	0·1620	0·1623

Precipitation by means of Sulphur Dioxide.—By the treatment of tellurium dioxide dissolved in hydrochloric acid with a freshly saturated solution of sulphur dioxide, and allowing to stand for twenty-four hours, the following results were obtained :—

Te required (grm.) . .	0·1607	0·1609	0·1609	0·1609
Te obtained (grm.) . .	0·1617	0·1613	0·1615	0·1613

Unless the acidity in this precipitation is 10 per cent, the tellurium is not likely to be completely precipitated, or it will be precipitated in a very fine state of division. The solution should also be hot in order to secure satisfactory precipitation.

Simultaneous Precipitation by means of Sulphur Dioxide and Hydrazine.—By bringing both sulphur dioxide and hydrazine into a tellurium solution the whole of the element is thrown out of the solution almost instantaneously. The solution should have an acidity of 5 to 10 per cent, and it is desirable to have the solution in a high degree of concentration. The solution is brought to boiling, and 15 cc. of a saturated solution of sulphur dioxide is added, then 10 cc. of a 15 per cent solution of hydrazine hydrochloride, and again 25 cc. of the sulphur dioxide solution. The solution is boiled for a few minutes, when the elementary tellurium will settle in such a way that it can be rapidly washed. The precipitate is then transferred to a platinum Gooch filter, and washed, first, with hot water until all of the chlorine is removed, and then with 15 cc. of alcohol. The crucible and contents are then dried at 100—105°, and finally weighed.

The following results were obtained by the process as outlined above, using 10 cc. of solutions of hydrazine hydrochloride of different strengths with sulphur dioxide. Tellurium dioxide was used for the analysis :—

Strength of hydrazine hydrochloride, 20 per cent—

Te required (grm.)	0·1731	0·2065	0·1638	0·1608
Te obtained (grm.)	0·1735	0·2068	0·1641	0·1608
Error (grm.)	+0·0004	+0·0003	+0·0003	—

Strength of hydrazine hydrochloride, 15 per cent—

Te required (grm.)	0·2212	0·1435	0·1605	0·1072
Te obtained (grm.)	0·2210	0·1434	0·1607	0·1070
Error (grm.)	−0·0002	−0·0001	+0·0002	−0·0002

Strength of hydrazine hydrochloride, 10 per cent—

Te required (grm.)	0·1658	0·1642	0·1268	0·1422
Te obtained (grm.)	0·1656	0·1637	0·1264	0·1420
Error (grm.)	−0·0002	−0·0005	−0·0004	−0·0002

That hydrazine must be there in sufficient quantity is evidenced by the following series of tests in which a 6 per cent solution was used along with sulphur dioxide, and the solution boiled only a few minutes, other conditions being exactly the same as in the preceding series of experiments.

Te required (grm.) . .	0·1508	0·1701	0·1608	0·1521	0·1903
Te obtained (grm.) . .	0·1374	0·1443	0·1535	0·1140	0·1781
Error (grm.)	−0·0134	−0·0258	−0·0073	−0·0381	−0·0122

The following two experiments were made with a large excess of sulphur dioxide water along with a 6 per cent solution of hydrazine and the solution heated six hours.

Te required (grm.)	0·1680	0·1516
Te obtained (grm.)	0·1545	0·1416
Error (grm.)	−0·0135	−0·0100

The method which has been used in the laboratory of the University of Wisconsin for a number of years, and which has proven the most satisfactory for the gravimetric determination of tellurium is as follows :—The tellurium, either as derivative of the dioxide or as a tellurate, should be present in a solution which has an acidity of approximately 10 per cent of hydrochloric acid, and it is preferable to have the solution sufficiently concentrated, otherwise the fine state of division of the precipitate will render it unsatisfactory for washing. The solution is heated to boiling, and 15 cc. of a saturated solution of sulphur dioxide added, then 10 cc. of a 15 per cent solution of hydrazine hydrochloride, and, again, 25 cc. of a saturated solution of sulphur dioxide. The boiling is continued until the precipitate settles in such a way that it can be easily washed. This boiling should not take more than five minutes. The precipitated tellurium, after being allowed to settle, is washed with hot water on a Gooch filter until all of the chlorine is removed, after which the water is displaced by alcohol, and the crucible and contents dried at 105°.—*Journal of the American Chemical Society*, xxx., No. 2.

THE DETERMINATION OF BENZENE IN ILLUMINATING GAS.*

By L. M. DENNIS and ELLEN S. McCARTHY.

(Concluded from p. 284).

II. *The Absorption of Benzene by Ammoniacal Nickel Cyanide* (continued).

(3) *The Determination of Benzene in Coal-gas.*—A large number of determinations of the benzene naturally occurring in coal-gas was made by the above method and the results are given in Table V. It is perhaps unnecessary to state that here, as in all other absorption methods in gas analysis, freshly prepared reagents should first be shaken with the sample of the gas to be analysed in order to saturate the reagent with the slightly soluble constituents of the gas mixture. Moreover, the same sample of reagent should not be used for the analysis of gas mixtures of markedly different compositions.

The results given in Table V. demonstrate that an ammoniacal solution of nickel cyanide completely removes the benzene from coal-gas in two minutes. It should be understood that the gas mixture is repeatedly passed into and drawn out of the gas pipette during this time.

(4) *The Determination of the "Analytical Absorbing Power" of the Ammoniacal Solution of Nickel Cyanide.*—The term "analytical absorbing power" was introduced by Hempel and means one-fourth of the total volume of the gas that one cubic centimetre of the reagent is able to

* From the *Journal of the American Chemical Society*, xxx., No. 2.

TABLE V.

No. of experiment.	Date.	Time of contact with reagent. Minutes.	Benzene found. Per cent.
33.	Jan. 7	4	0·8
34.	7	2	0·8
35.	7	2	0·8
		4 more	0·8
36.	Feb. 13	2	0·7
37.	13	2	0·7
38.	13	4	0·7
39.	13	2	0·7
40.	15	6	0·6
41.	15	4	0·6
42.	15	2	0·6
43.	18	2	0·8
44.	18	2	0·8
		2 more	0·8
45.	18	6	0·8
46.	19	2	0·5
47.	19	2	0·5
		2 more	0·5
48.	June 3	2	1·2
49.	3	2	1·2
50.	3	2	1·3
51.	3	2	1·2
52.	3	4	1·2
53.	3	4	1·2
54.	3	2	1·2
		2 more	1·2
		2 more	1·2

absorb (see Hempel, "Methods of Gas Analysis," Translated from 3rd German Edition by Dennis, p. 145). Theoretically, one cubic centimetre of the ammoniacal solution of nickel cyanide will absorb about 20 cc. of benzene vapour measured under ordinary conditions of temperature and pressure. This corresponds to an "analytical absorbing power" of 5 cc. of benzene vapour, and inasmuch as the gas pipette holds 200 cc. of the reagent, this volume should suffice for the absorption of 1000 cc. of benzene vapour. The compound that is formed, $Ni(CN)_2.NH_3.C_6H_6$, exhibits, according to the experiments of Hofmann, no measurable vapour tension.

To ascertain whether this theoretical "analytical absorbing power" was in accord with actual results, the reagent that had been used in Experiments 48 to 53 inclusive, was shaken with 2 cc. of liquid benzene (equivalent to about 500 cc. of benzene vapour) until this was completely absorbed. This reagent was then employed in Experiment 54 and in Experiments 68 to 72 inclusive. The completeness of the absorption obtained in each case shows conclusively that the limit of the absorbing power of the reagent had not yet been reached even when one filling of the pipette had taken up over 500 cc. of the benzene vapour. Further examination of the absorbing power demonstrated that even after a pipetteful of the reagent had absorbed 800 cc. of the benzene vapour, quantitative results could still be obtained. Since, however, the compound of benzene with the reagent separates as a precipitate, it is advisable, in order to avoid the clogging of the pipette, to filter the reagent after it has taken up fairly large amounts (from 200 to 400 cc.) of benzene vapour.

(5) *The Determination of Benzene in Known Mixtures of Coal-gas and Benzene.*—These determinations were carried out to ascertain whether benzene can be determined accurately in the presence of the other gases that are usually found in coal-gas. The sample of coal-gas was first freed from benzene by treatment with the ammoniacal nickel cyanide and then known amounts of benzene were added to it in the manner above described.

In Experiments 64 to 67 inclusive, one sample of coal-gas was employed, and to this successive portions of benzene vapour were added, and were then removed by absorption with the reagent. The fact that the volume of the gas residue remained constant throughout these analyses demonstrates that the constituents of ordinary coal-gas other than benzene (with the exception of those gases absorbed by a concentrated solution of potassium hydroxide) are not absorbed by the reagent. This conclusion is corroborated by the fact that in Experiments 57, 58, and 61, a prolongation of the contact between the gas and reagent did not cause further appreciable diminution in the volume of the gas residue.

TABLE VI.

No. of experiment.	Time of contact with reagent. Minutes.	Benzene taken. Per cent.	Benzene found. Per cent.
55.	2	1·1	1·1
56.	2	2·8	2·8
57.	4	0·8	0·7
58.	8	0·8	0·8
59.	2	4·3	4·3
60.	2	2·7	2·7
61.	12	2·7	2·8
62.	2	0·9	0·9
63.	2	0·7	0·7
64.	2	0·9	0·9
65.	2	1·1	1·1
66.	2	1·3	1·4
67.	2	1·3	1·3
68.	2	1·4	1·4
69.	2	1·2	1·2
70.	2	1·0	1·0
71.	2	2·6	2·7
72.	2	3.6	3·6

(6) *The Determination of the Vapour Tension (with reference to Benzene) of the Partially Exhausted Reagent.*—Although Hofmann states that the ammonia benzene nickel cyanide exhibits no appreciable vapour tension, it was still deemed desirable to ascertain whether the reagent, after somewhat extended use, would show a measurable benzene vapour tension. To this end a measured sample of air was brought into contact with a pipetteful of the reagent that had previously absorbed about 800 cc. of benzene vapour. The sample of air was then drawn back into the burette, was passed into a pipette containing dilute sulphuric acid, and was then drawn back into the burette and measured. The results were as follows:—

Volume air taken (cc.)	60·7	61·4	74·8	89·2	83·1	73·9
Volume air after contact with reagent (cc.)	60·7	61·3	74·8	89·3	81·1	73·9

From these experiments it appears that the benzene vapour tension of the partially exhausted reagent is so slight as to be negligible.

Dennis and O'Neill (*loc. cit.*, p. 507) determined experimentally that benzene is not taken up by the concentrated solution of potassium hydroxide that is employed in the Hempel method for the determination of carbon dioxide, and that consequently absorption of carbon dioxide may properly precede the determination of benzene. This point has been examined further by the authors of the present paper, who also have found that potassium hydroxide solution does not absorb benzene from mixtures of benzene vapour and air. The order of procedure then in the analysis of coal-gas should be that recommended by Dennis and O'Neill (*loc. cit.*, p. 511), the absorption of benzene being effected by the ammoniacal solution of nickel cyanide in place of the solution of ammoniacal nickel nitrate which they there suggested.

III. *The Morton Method for the Determination of Benzene in Illuminating Gas.*

D. A. Morton has recently described (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1732) a simple method for the determination of benzene by absorption with concentrated sulphuric acid (sp. gr. 1·84), and before leaving this work it was thought advisable to examine Morton's method with

a view to ascertaining the accuracy of the results that can be obtained through its use. It is self-evident that for the determination of benzene in coal-gas, there must be employed an absorbent that does not remove ethylene. Morton states that the effect due to the absorption of ethylene by concentrated sulphuric acid is insignificant. This statement is somewhat surprising, for inasmuch as both benzene and ethylene are quantitatively absorbed by fuming sulphuric acid, it would seem reasonable to suppose that concentrated sulphuric acid would also take up ethylene, and that, although it might absorb this gas in smaller amounts than did the fuming sulphuric acid, the percentages of ethylene removed by it would yet be appreciable. Further, it was deemed possible that the apparently correct results in the separation of benzene and ethylene obtained by Morton might be ascribed to an accidental balancing of errors in the removal of the two gases in question. In looking up the literature of the subject it was found that Frankland and Thorne (*Journ. Chem. Soc.*, 1878, xxxiii., 89), in working upon "The Luminosity of Benzol" found "that ordinary sulphuric acid absorbs benzol vapour rather rapidly, and may be used for its eudiometric determination." They were, however, separating benzene from hydrogen, carbon monoxide, and methane, and no ethylene was present in the gas mixture that was employed. Butlerow and Gorjainow found that concentrated sulphuric acid will completely absorb ethylene at a temperature of from 160° to 170° (*Ber.*, 1873, vi., 196). Berthelot (*Ann. Chim. Phys.*, 1855, [3], xliii., 385) states that when ethylene is shaken with concentrated sulphuric acid, 100 grms. of the acid absorb 6·7 litres (120 volumes) of ethylene, and further, that the ethylene that escapes absorption upon passage through a Liebig bulb containing fuming sulphuric acid is afterward absorbed by shaking it with ordinary sulphuric acid. In a paper by Faraday (*Phil. Trans.*, 1825, p. 448) it is stated that when ethylene was allowed to stand for eighteen days in contact with concentrated sulphuric acid one volume of the acid absorbed 84·7 volumes of the ethylene.

Experimental.

The Absorption of Ethylene by Sulphuric Acid (sp. gr. 1·84).—Ethylene was prepared in the manner above described. A mixture of air and ethylene containing 22·5 per cent of ethylene was made and was shaken for one minute with about 150 cc. of concentrated sulphuric acid contained in a Hempel simple gas pipette. It was then drawn back into the burette and the diminution in volume noted. It was passed back again into the pipette and shaken for another minute and measured. This was repeated several times and the results are given in Table VII. It will be noted that 18 cc. of the 22·5 of ethylene present in the gas mixture was absorbed in thirty minutes, the rate of absorption diminishing as the percentage of ethylene decreased.

TABLE VII.

No. of expt.	Ethylene present in 100 cc. of gas mixture.	Ethylene absorbed.	Length of each shaking with concentrated H_2SO_4.	Total length of contact with concentrated H_2SO_4.	Total volume ethylene absorbed.
	Cc.	Cc.	Minutes.	Minutes.	Cc.
73.	22·5	2·3	1	1	2·3
74.	20·2	1·9	1	2	4·2
75.	18·3	1·3	1	3	5·5
76.	17·0	1·3	1	4	6·8
77.	15·7	1·2	1	5	8·0
78.	14·5	1·2	1	6	9·2
79.	13·3	0·8	1	7	10·0
80.	12·5	0·8	1	8	10·8
81.	11·7	1·0	1	9	11·8
82.	10·7	1·0	1	10	12·8
83.	9·7	0·8	1	11	13·6
84.	8·9	4·4	19	30	18·0

The Action of Concentrated Sulphuric Acid upon a Mixture of Air, Ethylene, and Benzene.—A mixture of air, ethylene, and benzene containing 1·5 per cent benzene and 10 per cent ethylene was prepared and was shaken with concentrated sulphuric acid in the manner that Morton describes, except that in Analyses 89 and 91 the shaking was continued for two minutes instead of only one minute. The results are given in Table VIII. It will be seen that of a total of 11·5 cc. of hydrocarbons in 100 cc. of the gas mixture, 8·2 cc. were absorbed in nine minutes. There was but 1·5 per cent of benzene present in the original mixture and yet 4·3 per cent of the hydrocarbons was absorbed in the first minute of shaking with the sulphuric acid, demonstrating that at least 2·8 per cent of ethylene was removed by the reagent. If the analyst is to regard the absorption by sulphuric acid as indicative of the per cent of benzene present, the actual error in this case would be very large. By further shaking of this mixture with the concentrated sulphuric acid from 0·3 per cent to 0·7 per cent more of the hydrocarbons was absorbed per minute.

TABLE VIII.

No. of expt.	Hydrocarbons present in 100 cc. gas mixture.	Hydrocarbons absorbed.	Length of contact with concentrated H_2SO_4.	Total length of contact with concentrated H_2SO_4.	Total volume hydrocarbons absorbed.
	Cc.	Cc.	Minutes.	Minutes.	Cc.
85.	11·5	4·3	1	1	4·3
86.	7·2	0·7	1	2	5·0
87.	6·5	0·3	1	3	5·3
88.	6·2	0·5	1	4	5·8
89.	5·7	1·4	2	6	7·2
90.	4·3	0·3	1	7	7·5
91.	4·0	0·7	2	9	8·2

The Action of Concentrated Sulphuric Acid upon Mixtures of Air with varying amounts of Ethylene and Benzene.—In this series of experiments the gas mixture was first shaken for one minute with the concentrated sulphuric acid and was then passed into a pipette containing ammoniacal nickel cyanide solution, to ascertain whether all of the benzene originally present had been absorbed by the sulphuric acid. An examination of the results in Table IX. shows that the gas absorbed by the concentrated sulphuric acid is not benzene alone, for upon comparing the figures in the third and fourth columns it will be seen that in Experiments 96 to 111, with the exception of the 100th and 102nd, the volume of gas absorbed is greater than the volume of benzene taken, in many cases considerably greater. Moreover, the absorption of the benzene by the concentrated sulphuric acid is frequently

TABLE IX.

No. of expt.	Ethylene taken.	Benzene taken.	Hydrocarbons absorbed in one minute by concentrated sulphuric acid.	Hydrocarbons afterward absorbed by ammoniacal nickel cyanide solution.
	Per cent.	Per cent.	Per cent.	Per cent.
92.	0·3	10·8	9·9	1·2
93.	0·5	11·0	9·4	1·5
94.	0·7	7·2	6·9	0·3
95.	1·3	5·4	5·5	0·2
96.	1·3	2·7	3·0	0·2
97.	1·4	0·8	1·0	—
98.	2·1	2·1	2·5	—
99.	2·3	4·9	5·7	—
100.	2·3	2·3	2·1	0·2
101.	2·7	2·4	3·0	—
102.	2·8	5·6	5·2	0·4
103.	3·3	1·2	1·7	—
104.	3·7	1·7	2·4	0·5
105.	3·9	0·7	1·2	0·3
106.	4·2	0·7	1·2	0·1
107.	5·2	1·9	2·0	—
108.	5·2	0·9	1·3	—
109.	6·3	0·7	1·0	0·2
110.	12·6	2·9	3·3	—
111.	15·8	3·0	4·1	—

incomplete, as is demonstrated by the results in the last column. In some cases the measurements showed that the volume of gas absorbed by the sulphuric acid is greater than the volume of benzene added, and yet even in these cases not all of the benzene that had been added was removed by the sulphuric acid. (See, in particular, Experiments 96, 104, and 105). The results in Table IX. would further demonstrate that with so large and so irregular variations a correction factor for the absorption of ethylene as suggested by Morton would be of no value.

The Determination of Benzene in Coal-gas by means of Concentrated Sulphuric Acid.—A series of determinations (Table X.) of benzene in coal-gas was made by the Morton method. At the time when these analyses were made the coal-gas showed by the ammoniacal nickel cyanide method an average content of less than 1 per cent of benzene. The results by the Morton method are in every case much too high and furnish further proof that concentrated sulphuric acid removes other constituents than benzene.

Table X.

No. of experiment.	Date.	Length of contact with concentrated sulphuric acid.	Hydrocarbons absorbed.
		Minutes.	Per cent.
112.	Feb. 14	1	2·0
113.	14	1	1·9
114.	14	2	2·2
115.	14	4	2·8
116.	15	1	1·7
117.	15	1	1·9
118.	15	1	1·8
119.	15	2	2·1
120.	15	4	2·3

The Effect in the Morton Method of Varying the Speed of Shaking.—Morton directs that the gas be passed into the pipette containing the concentrated sulphuric acid and be shaken *vigorously* (twice per second) with this reagent for one minute. The experiments in Table XI. were made to ascertain whether the amount of absorption by the sulphuric acid would vary if the speed at which the pipette is shaken is varied. With acceleration of the shaking slightly higher results were obtained, but they can not be taken as conclusive upon the point at issue, because the concentrated sulphuric acid when shaken foams to so great an extent as to render it difficult to obtain correct measurements of the residual gas volume. Moreover, minute gas bubbles become suspended through the sulphuric acid and do not all of them rise to the surface of the reagent even after that has stood undisturbed for two minutes.

Table XI.

No. of expt.	Length of contact with reagent.	Number of shakes per second.	Hydrocarbons absorbed.
	Minutes.		Per cent.
121.	1	1	1·9
122.	1	1	1·8
123.	1	2	1·8
124.	1	2	2·0
125.	1	4	2·2
126.	1	4	2·3

To avoid the difficulty that results from the foaming of the reagent, due to shaking, the concentrated sulphuric acid was placed in a pipette of the type used for fuming sulphuric acid (see Hempel's "Gas Analysis," p. 229). In the first determination the sample of coal-gas was measured in the burette and was then passed into a pipette and drawn back and measured. In the second determination a fresh sample of the gas was taken and was passed into and drawn out from the pipette twice. In the next determination another sample was run into the pipette three times, and so on. The coal-gas used in Experiments 127 to 134 inclusive, was found to contain by the ammoniacal nickel cyanide method 0·8 per cent benzene. The sample of gas on the following day, February 19th, Experiments 135 to 141 inclusive, contained 0·5 per cent benzene.

Table XII.

No. of experiment.	Date	Number of times gas mixture passed into pipette.	Hydrocarbons absorbed.
			Per cent.
127.	Feb. 18	1	1·1
128.	18	2	1·2
129.	18	3	1·4
130.	18	3	1·0
131.	18	3	1·6
132.	18	4	1·5
133.	18	6	1·6
134.	18	10	2·0
135.	19	1	0·2
136.	19	2	0·4
137.	19	3	0·7
138.	19	4	1·0
139.	19	5	1·7
140.	19	8	2·0
141.	19	11	2·1

The results given in this table show wide variations in the apparent amount of benzene present and demonstrate that the method will not give accurate results even when the foaming is avoided by the use of the fuming sulphuric acid pipette.

Summary.

An ammoniacal solution of nickel cyanide prepared according to the directions given in this article will quantitatively absorb benzene from mixtures containing benzene and air and from ordinary coal-gas. It will not absorb measurable quantities of ethylene or of the other constituents of ordinary coal-gas, with the exception of those absorbable in potassium hydroxide solution.

The method proposed by Morton for absorbing benzene by means of sulphuric acid (sp. gr. 1·84) does not give constant results even when the conditions are the same, and yields widely varying results when the conditions are changed. Moreover, it absorbs both ethylene and benzene, and from mixtures containing both of these gases it does not quantitatively remove the benzene, but does remove an indeterminate amount of ethylene. Moreover, in the manipulation suggested by Morton, the reagent foams to such an extent as to make the accurate reading of the gas volumes well nigh impossible.

NOTICES OF BOOKS.

Exercises in Elementary Quantitative Analysis. By Azariah Thomas Lincoln, Ph.D., and James Henri Walton, Jun., Ph.D. New York: The Macmillan Company. 1907.

The methods of agricultural analysis as carried out in the laboratories of the American Experiment Stations are described in detail in this book. The first part deals with typical operations employed in pure quantitative analysis, and by working through this section the student will get a good acquaintance with general methods. Some important separations, as, for example, that of magnesium from calcium in a mixture of their carbonates, are described, and throughout references to larger or more specialised books are inserted in order that the student may extend his reading. The second part of the book describes the application of the general methods to agricultural products, including milk, feeding stuffs, fertilisers, and soils. In every case accuracy appears to have been placed before speed in deciding the choice of methods, and some conveniently rapid estimations are not included. Thus the Werner-Schmidt method of determining fat in milk is not described, although, in spite of its quickness, it is generally regarded as being capable of giving very accurate results when carefully performed. The last section gives a selection of

problems in stöchiometry, with answers; some of these are fairly complicated, but illustrative examples are carefully explained, and the section will give the analyst plenty of practice in working out the results of his determinations.

The Life and Work of George William Stow. By Robert B. Young, M.A., B.Sc., F.R.S.E., F.G.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. Cape Town: Darter Bros. and Co. 1908.

The geological and ethnological work of George William Stow in South Africa was of such importance that a biographical account of his work will be received with great interest. Not very much has been written of the spread of scientific investigation in the colony during the period in which Stow lived, which makes the little book all the more welcome, and as a record of enthusiastic pioneering work against great odds the description of Stow's labours would be hard to beat. His survey of the geology of South Africa, culminating from an industrial point of view in the discovery of the Vereeniging coalfield, and especially his "Notes on the Geology of Griqualand West," which were never published, show that he was entitled to rank high as a geologist, while his papers on the native races of South Africa were equally valuable as a contribution to ethnology.

Official Chemical Appointments. By Richard B. Pilcher, Second Edition. London: The Institute of Chemistry of Great Britain and Ireland. 1908.

The second edition of this useful reference book contains lists of the chief appointments held by chemists, including professors and teachers of chemistry, in Great Britain and Ireland, and also in India, Canada, Australia, &c. Particular care has been taken in the compilation to ensure accuracy and completeness, and in some cases notes are added upon the regulations and conditions governing the selection of candidates for important posts. A short abstract is given of certain Acts of Parliament bearing upon the chemical industries, such as the Alkali, &c., Works Regulation Act, 1906, and the duties of the officials appointed are described in outline. In addition the book contains a list of societies and institutions directly interested in the advancement of chemical science, together with some information as to their chief objects and the conditions of membership.

The Journal of the Board of Agriculture. Volume XV., No. 1, April, 1908. London: The Board of Agriculture and Fisheries.

The first number of the fifteenth volume of the *Journal of the Board of Agriculture*, published in April, exhibits many new features, which add very materially to its value for the agriculturist. The size of the journal has been considerably increased, and thus room has been made for the insertion every month of a review of the market prices of agricultural products during the preceding month, with notes on the tabular statements which have hitherto been printed at the end of each number without comment. The state of foreign crops and markets is also discussed, the trade in those commodities which compete with home-grown produce being specially considered. A new series of articles on weeds and pests opens with a description of the appearance and poisonous properties of the meadow saffron, which is illustrated by a clear and well-drawn plate, and the April number also contains the first of a series of papers on the creation of small holdings under the Act of 1907. The conditions which have enabled the existing holdings to be worked successfully will be carefully scrutinised, and it is hoped that those who are contemplating taking up holdings will be able to obtain information which may be of practical value to them.

Milk and its Relation to the Public Health. Washington: Government Printing Office. 1908.

This Bulletin, issued by the Hygienic Laboratory, contains detailed accounts written by various experts of all aspects of the relation of the milk supply to the public health. The list of authors includes many well-known American authorities who have taken a careful critical survey of every branch of the subject. The chemistry and bacteriology of milk are treated in detail, and such practical questions as the most satisfactory methods of ensuring the purity of milk by strict attention to the cleanliness of the utensils employed, of the animal itself and the milker are fully described. The importance of sanitary water supplies for farms and the best means of guarding against pollution of springs and wells is discussed in one paper, and another is devoted to the consideration of methods and results of the examination of water supplies of dairies in the district of Columbia. The tabular statements showing the epidemics of typhoid fever, scarlet fever, and diphtheria, which have been traced to the milk supply both in America and elsewhere, give a complete review of all available data relating to milk as a carrier of infection, and the diagrams illustrate very clearly the connection between milk routes and cases of infectious disease in various outbreaks.

A Laboratory Outline for Determinations in Quantitative Chemical Analysis. By Albert F. Gilman, S.B., A.M. Easton, Pa.: The Chemical Publishing Company. 1908.

In this little book the most accurate and convenient methods of determining the commoner metals and acid radicles are described fully and clearly. The details of every experiment are given so explicitly as to leave practically no possibility of doubt or misunderstanding, and questions are inserted bearing on the practical work which will force the student to think of the reasons for what he is doing and the specific purpose of the application of each reagent he uses. Most of the methods given are gravimetric, but some volumetric determinations, when they appear preferable, are also described. The electrolytic estimation of nickel is discussed rather too shortly for the student who has not had a good deal of practice and experience in electrical work. The book is interleaved with blank schemes, which can either be used as models of the entering of results of determinations into separate note-books, or else the weights obtained can be directly inserted into the book, which will then be a complete record of the student's analytical work.

Practical Methods for the Iron and Steel Works Chemist. By J. K. Heess, Ph.C. Easton, Pa.: The Chemical Publishing Co. 1908.

Although this book professes to describe practical methods of analysing iron ores, fuels, iron, steel, blast-furnace gases, &c., the explanations of the details of manipulation are so much contracted that it does not do much more than provide information as to the quantities of sample taken and reagents used. Hence the only value of the book is as a summary for the use of those chemists who are well acquainted with the processes they mean to apply, but cannot carry in their heads all the necessary numerical data. The citation of one example will be sufficient:—The analysis of gases by the Orsat apparatus (which appears as Orstat in the text) is frequently found to require some little practice and explanation, and it seems improbable that the chemist who had never used the apparatus would find that the few lines in which it is described would help him very much. So also for the colour method of determining carbon in steels, which is explained very shortly. On the other hand, one method only, and that, of course, the best in the author's estimation,

is described for the determination of each constituent, which means that the analyst has not to waste his time reading or working through various processes; he will, however, be justified in thinking that the author deserves censure for the omission of an index.

Thermoelemente und Thermosäulen. ("Thermoelements and Thermopiles"). By Professor Dr. Franz Peters. Halle-A.-S.: Wilhelm Knapp. 1908.

It is not improbable that in the future thermoelements and thermopiles may be more generally used than at present on a technical scale as sources of electrical energy, and this monograph will be found to give a clear account of their possibilities and of the directions in which our knowledge of them and their applications particularly needs extension. The theory of thermoelectricity and thermocurrents is touched upon only cursorily, and experiments of purely theoretical interest are altogether passed over. On the other hand, the history of the discovery and perfecting of thermoelements is recounted, and the preparation of thermoelements made of two metals or alloys and also those made of other substances, such as copper sulphide or lead sulphide, is described. The union of elements to form piles and their application is next treated, the last section giving a full list with short explanations of the various uses of thermoelements, more especially as instruments for conveniently and accurately measuring high temperatures.

CORRESPONDENCE.

OFFICIAL METHODS OF ANALYSIS.

To the Editor of the Chemical News.

Sir,—It is not, I believe, generally known to analysts that the Board of Agriculture have recently drafted a set of official methods which "shall be" adopted by those holding appointments as agricultural analysts under the Fertilisers Act. May I ask the use of your columns to make this fact known, and to raise a protest against a proposal which is quite new in England and opposed to the freedom which every Englishman cherishes? It is the thin edge of the wedge for the introduction of a system which will soon affect every analyst in the country, our teaching institutions, and the development of research.

So far as I am aware, there has not yet been a single case under the Fertilisers Act where analysts have differed so as to affect the question at issue. Hence there was no necessity for official methods. So much cannot be said for the analyses which have been made by public analysts under the Sale of Food and Drugs Act. It is well known that there have been wide differences in analyses, and once the principle of official methods is recognised and adopted it is certain to be applied under the Food and Drugs Act as under the Fertilisers Act.

I am strongly opposed to a hard and fast stereotyped method of analysis being adopted, and for many reasons.

First, it is well known that in the hands of competent well trained analysts the differences in results due to methods are insignificant. If they have been well trained and had experience they will know that methods in their hands can be relied upon to give concordant and accurate results. But no official method can take the place of, or do away with, the necessity for a thorough training and proper experience. It may help to turn out automatons, or analytical machines, but not analysts.

Secondly, I am opposed to them as they will hamper the educational work and chemical training which is being carried out in the country. Students will want to study only those methods. How can you expect students to take an interest, or endeavour to obtain proficiency in other methods which are not recognised, and which, when they go into laboratories as assistants, they will not be allowed to use? It will be useless for the teachers to argue that it is a good training. Unless students feel that the work they are doing will subsequently be utilised they take no interest in it.

Lastly, official methods are detrimental to all progress. What is the use of an analyst striving to perfect an old method or seeking after a new method when he knows that it cannot be adopted? Those who are acquainted with the conservatism and red tapeism of all Government departments know that it would be almost impossible to get these "official" methods changed. And for one reason, if for no other, a new method would have but little chance of adoption because, owing to the stress of work under official methods, the new method would not get the attention and trial which would enable it to be recognised as worthy of becoming official. In fact, such a body as the Society of Public Analysts, &c., might as well dissolve.

It may be argued, in opposition to my views, that official methods of analysis are in vogue both in Germany and the United States. That may be so, but I do not think that either country is very enamoured of them. Moreover, they differ essentially from those proposed by the Board of Agriculture. These latter are confined to one single method for each determination, with most minute details specified, such as add 20 cc. "drop by drop," and maintain at 70° C. "for fifteen minutes." But abroad "alternative" methods are recognised where such methods are known to give accurate results, so that the analyst has some latitude. But these so-called official methods abroad have grown up by degrees at the suggestion and by the wish of the profession to meet special requirements, and they have been and are annually discussed in public, so that all affected, as well as analysts, may be heard concerning their value and possible effects. Such a condition is very different to the publication and legalising of a series of methods by a Government department such as is now proposed by the Board of Agriculture.

The Fertilisers Act undoubtedly says the Board of Agriculture may make regulations as to the manner in which analyses are to be made. Presumably Parliament gave them this power thinking the Board would only exercise it if desirable.

I venture to think, Sir, that it is not desirable, and I trust that my brother analysts and those who are interested in the education of analysts, and in the future of chemical science, will help me to protest against the Board's unwise and unnecessary procedure.—I am, &c.,

Fredk. J. Lloyd,
Official Agricultural Analyst.

Muscovy House, E.C., June 9, 1908.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 20, May 18, 1908.

Time taken by Substances to Dissolve.—Gaston Gaillard.—As the quantity of solute increases the ratio of the time to the concentration is at first practically constant. In certain cases when the temperature is altered the curve of the reciprocal of the times resembles that of the solubility. Salts having similar coefficients may take very different times to dissolve, and the variation of the time with the temperature does not always follow that of the solubility.

Iodomercurates of Thorium and Aluminium.—A. Duboin.—The author prepared thorium iodide by decomposing thorium carbonate with hydriodic acid, and evaporating to dryness on the water-bath. Then the residue and mercuric iodide were dissolved together in water at a gentle heat. The liquid on cooling deposited, first, mercuric iodide, and then a crystalline mass which

consisted of the iodomercurate, $ThI_4.5HgI_2.18H_2O$. This salt is very easily decomposed by water. A saturated solution of mercuric iodide in a solution of aluminium iodide yields an oxyiodide in dry air. From the mother-liquor, when it is kept in a perfectly dry atmosphere, long deliquescent crystals are deposited. Analysis shows that they have the formula $AlI_3.HgI_2.8H_2O$.

Definite Compounds of Silicon and Palladium.—Paul Lebeau and Pierre Jolibois.—Silicon and palladium combine directly with evolution of enough heat to fuse the mass when they are heated together in a porcelain crucible. By this method it is possible to obtain two compounds of silicon and palladium, corresponding to the formulæ $SiPd_2$ and SiPd. Only the former of these has been isolated and analysed, but the existence of both compounds is proved by the perfect agreement observed in the metallographic examination and in the determination of the fusibility curve of the system silicon-palladium. The formulæ of these silicides are comparable with those of the silicides of platinum. The study of the cooling of the silicides of palladium containing less than 20 per cent of silicon has revealed a phenomenon of recalescence which seems to correspond to the crystallisation of a super-saturated solution.

Volumetric Method of Determining Tartaric Acid.—Em. Pozzi-Escot.—The raw material (tartar) is treated with a boiling solution of sodium or potassium carbonate. An integral part of the solution is acidified with hydrochloric acid, the carbon dioxide is boiled off, and ammonia is added till the liquid is alkaline. Then the tartaric acid is precipitated as barium tartrate by the addition of a known volume of a standard solution in barium bromide in alcohol. The excess of barium bromide in the filtered liquid is then determined by adding ammonium oxalate, barium oxalate being thus precipitated. It is decomposed by sulphuric acid, and the oxalic acid is estimated by titration with standard potassium permanganate.

Propargylcarbinol.—MM. Lespieau and Pariselle.—The ether, $CH_2Br—CHBr—CH_2—CH_2OCH_3$, when subjected to the action of hydrobromic acid, gives a colourless liquid tribromo-butane . 1 . 2 . 4, $CH_2Br—CHBr—CH_2—CH_2Br$. This tribromide yields with potash an ethylenic dibromide, $CH_2 : CBr—CH_2—CH_2Br$, from which the corresponding alcohol, $CH_2 = CBr—CH_2—CHOH$, can be prepared by the action of potassium acetate. This alcohol is attacked by an aqueous solution of potash, the product being butinol, $CH \equiv C—CH_2—CH_2OH$. Triiodobutenol is obtained by precipitating butinol with ammoniacal cuprous chloride, adding a solution of iodine in potassium iodide, and heating to 100°. The formula of the triiodide is $CI_2 = CI—CH_2—CH_2OH$.

Constitution of Compounds of Tetramethyldiaminobenzhydrol with some Methylenic Derivatives.—R. Fosse.—This alcohol unites equimolecularly with β-ketonic ethers, 1.3-diketones, and ethyl malonate, yielding one molecule of water and a series of substances which might be formed by the elimination of one molecule of water from two hydroxyl groups, thus:—

$$[(CH_3)_2N.C_6H_4]_2CH—OH + H—O—C(CH_3) = CH—CO_2.C_2H_5$$

$$= H_2O + [(CH_3)_2N.C_6H_4]_2CH—O—C(CH_3) = CH—CO_2.C_2H_5.$$

The author, however, has found that the compounds formed in a neutral or alkaline medium do not contain the separate oxygen atom, but the group CO. Thus the formula of the ethyl acetyl acetate is $[(CH_3)_2N.C_6H_4]_2CH—CH<^{CO.CH_3}_{CO_2.C_2H_5}$.

Mixed Trihaloid Derivatives of Methane.—V. Auger.—The author has prepared the hitherto unknown compounds chloroiodoform, HCI_2Cl; bromoiodoform, HCI_2Br; and iodobromoform, $HCIBr_2$. The first of these is formed when the raw product of the action of mercuric chloride on iodoform is distilled *in vacuo*, while the fractional distillation of a mixture of equal parts of mercuric bromide and iodoform yields iodobromoform as the first of the fractions, and in the final fractions bromoiodoform is found.

Orthobenzylated Dyes from Triphenylmethane.—A. Guyot and P. Pignet.—Ortho-substituting groups exercise a protective action on dyes of the type of malachite green making them exhibit a resistance towards alkalis which varies with the nature of the group, but is independent of its positive or negative character. It is supposed that these substituents impart a special stability to the quinonic complex to which the colouration is due. If this is the case, substituting radicles with high molecular weights should exercise a pronounced influence. To verify this the authors have prepared the tetra-alcoholated-diamido-*o*-benzoylbenzyl benzene, and benzhydrylbenzyl benzene, $C_6H_4<^{CO—C_6H_4—NR_2}_{CH_2—C_6H_4—NR_2}$ and $C_6H_4<^{CHOH—C_6H_4—NR_2}_{CH_2—C_6H_4—NR_2}$. They condense easily with amines, giving orthobenzylated malachite greens or their leuco-derivatives. The dyes thus prepared are remarkably stable towards alkalis, and the protective action of the orthobenzylated group seems to be of the same order of magnitude as that of the ortho-sulphonated group.

No. 21, May 25, 1908.

Oxidation Phenomena produced by Iodic and Bromic Acids.—H. Baubigny.—Silver bromide in ammoniacal solution is said to be oxidised at 100° by iodic acid, yielding silver iodide and ammonium bromate. The author has made a study of the action of iodic acid at different temperatures on a solution of ammonia in order to explain this reaction. He has found that a gas is evolved and ammonium iodide is formed. Apparently the iodic acid oxidises the ammonia, giving water, ammonium iodide, and nitrogen, $NH_4IO_3 + 2NH_3 = NH_4I + 3H_2O + N_2$. The ammonium iodide then acts on the silver bromide in solution, giving silver iodide which is only slightly soluble in the cold. Bromic acid acts in exactly the same way as iodic acid.

Volumetric Method of Determining Simultaneously the Carbonic Acid and other Acids in Atmospheric Air.—H. Henriet and M. Bouyssy.—The air is made to bubble through a solution of soda or potash, and the alkaline liquid is divided into two parts, One-half is titrated with acetic acid, using phenolphthalein as indicator, and the reading is multiplied by two to give the total carbon dioxide. To the other half of the solution barium chloride is added, and thus barium carbonate is precipitated by the alkaline carbonate present in the liquid. The free alkali can then be titrated with acetic acid, thus giving the total acids in the air. If R is the free alkali, *c* the carbon dioxide always present in this alkali, A the acids in the air other than carbon dioxide, C the atmospheric carbon dioxide, *n* the reading corresponding to the first method of determination, and *n'* the reading of the solution into which the air has bubbled, *p* the reading corresponding to the second method of determination with barium chloride, *p'* the reading of the carbonated solution, then in the first case $R + \frac{c}{2} = n$, $R + \frac{c}{2} - A - \frac{C}{2} = n'$. In the second case $R = p$, $R - A - C = p'$. Hence—

$$A = 2(n - n') - (p - p')$$
$$C = 2[(p - p') - (n - n')].$$

Determination of Tungstic Acid and its Separation from other Substances by a Mixture of Chlorine and Sulphur Chloride.—F. Bourion.—When a gaseous mixture of chlorine with a little sulphur chloride is allowed to act on compounds of tungstic acid in a porcelain or silver

boat at a temperature which is gradually raised from 180° to 500°, two volatile oxychlorides, $WOCl_4$ and WO_2Cl_2, are formed. These are received in water, and the acid liquids thus obtained, after addition of nitric acid, are evaporated to dryness. The residue is taken up with a solution of ammonium nitrate (which contains hydrochloric acid when iron is present), and the tungstic acid is separated by filtration. The weight of the residue in the porcelain boat gives the weight of the chloride of the base with which the tungstic acid is combined.

MISCELLANEOUS.

The Iron and Steel Institute.—The Autumn Meeting of the Iron and Steel Institute will be held at Middlesbrough on Monday, Tuesday, Wednesday, and Thursday, September 28th, 29th, and 30th, and October 1st, 1908. An influential Reception Committee has been formed, with the Worshipful the Mayor of Middlesbrough (Lieut.-Colonel T. G. Poole, V.D.) as Chairman, and Mr. John H. Amos (Queen's Terrace, Middlesbrough) as Hon. Secretary. The provisional programme of the meeting is as follows:—On Monday, September 28th, the members will arrive at Middlesbrough, and in the evening there will be a Conversazione and Concert by invitation of the Reception Committee, in the Town Hall, Middlesbrough. The mornings of Tuesday, Wednesday, and Thursday, September 29th, 30th, and October 1st, will be devoted to the reading and discussion of papers. On Tuesday luncheon will be provided by invitation of the Reception Committee; works will be visited in the afternoon; and in the evening there will be a special performance of light opera at the Middlesbrough Grand Opera House, by invitation of the Reception Committee. On Wednesday luncheon will be provided, and in the afternoon members will be invited to the official opening of Smith's Dry Docks on the Tees, and in the evening a banquet will be given by invitation of the Reception Committee. On Thursday, October 1st, the members will be invited to luncheon by the Cleveland Institution of Engineers, the members and ladies accompanying them afterwards proceeding to Rounton Grange, where a garden party will be given by Sir Hugh and Lady Bell. By the courtesy of the Caledonian, the Great Central, the Great Northern, the Great Western, the London and North Western, the Midland, the North Eastern, and other railway companies, return tickets to Middlesbrough at a single fare and a quarter, available from September 26th to October 2nd, will be issued from London and provincial towns on production of a voucher signed by the Secretary. The proprietors of the following hotels in and near Middlesbrough have intimated that they have accommodation available for Members of the Institute:—Middlesbrough—Corporation, Grand; Stockton-on-Tees (4 miles)—Royal, Queen's; Saltburn-by-the-Sea (13 miles)—Alexandra, Zetland; Redcar (8 miles)—Coatham; Darlington (15 miles)—King's Head, Imperial. Rooms should be booked as soon as possible, as already applications have been received by the hotels. A detailed programme will be issued when the arrangements are further advanced.

MEETINGS FOR THE WEEK.

Tuesday, 23rd.—Faraday Society, 7.45. Annual General Meeting. "Recent Developments of the Kjellin and Rochling-Rodenhauser Electric Induction Furnaces," by J. Harden. "New Applications of Electro-metallurgical Alloys," by A. Jouve.

Friday, 26th.—Physical, 3.30. (By kind invitation of Dr. R. T. Glazebrook, this meeting will be held at the National Physical Laboratory, Bushy House, Teddington). Demonstrations of work in progress in the Laboratory will be given.

THE CHEMICAL NEWS.

Vol. XCVII., No. 2535.

REFORM OF CHEMICAL AND PHYSICAL CALCULATIONS.

By C. J. T. HANSSEN.

Under this title was, in 1897, published in English, German, and Danish editions a book which, in a preface by Dr. G. Karsten, Professor of Physics on the University of Kiel, was warmly recommended, and fairly and gently noticed by scientific authorities of various nations. The Chemical News published (in vols. lxxi. and lxxii.) extracts from the manuscript, and Dr. Phil. Prof. Wilh. Foerster, Director of the Royal Observatory in Berlin, and Chairman of the International Committee of Metric Measures and Weights, wrote to the author:—

Berlin, Nov. 25, 1895.

"My opinion is that such chemical and physical investigations as developed in your 'Reform of Calculations,' apart from the ordinary course of research and study, not only now are of high importance, but ultimately may lead to very great and eminently practical simplifications of scientific work and study, and therefore are worthy of public acknowledgment and promotion.

(Signed) W. Foerster."

The Carlsberg Foundation in Copenhagen, an institution for the advancement of science, administrated by professors of the University, granted 2700 kronen (£150) to get the three editions of the book printed; many scientific journals and magazines reviewed and recommended the "Reform," and the success of the book seemed to be sure; but the author had in his "Reform" dared to protest against the "immensely accurate and absolute correct" determinations of atomic weights decreed by the *pro temp.* reigning "great masters" of chemical science and the heretical "Reform," and its author was, in the Leipzig *Zeitschrift fur Physikalische Chemie* (vol. xxv., p. 755, April 29, 1898), punished by a total and absolute condemnation.

This severe judgment, however, is now obliterated; the chemical research of the last ten years has found the errors of the atomic weights of 1898, and we know that previous to February, 1902, pure hydrogen was unknown (Chemical News, vol. lxxxv., pp. 85 and 97), and the atomic weight of many elements now expressed in plain figures show so clearly that elements combine in plain proportions, that also the plain proportion H = 1 : O = 16 must be a necessity.

This proportion has already been found by experiment in the synthesis of water. According to this proportion do 8 grms. of O combine with 1 grm. of H, producing 9 grms. of water (H_2O).

Dumas burnt 13·179 grms.	= 13179 mgrms.	O
Which combine with 13179/8 ..	= 1647⅜ „	H
Producing..	14826⅜ „	H_2O
The experiment produced	14827 „	H_2O

(Error + 1/23723).

Dumas burnt 45·887 grms.	= 45887 mgrms.	O
Which combine with 45887/8 ..	= 5735⅞ „	H
Producing..	51622⅞ „	H_2O
The experiment produced	51623 „	H_2O

(Error + 1/412983).

Erdmann and Marchand, 37·034 grms.	= 37034 mgrms.	O
Which combine with 37034/8 ..	= 4629⅜ „	H
Producing..	41663⅜ „	H_2O
The experiment produced	41664 „	H_2O

(Error + 1/55551).

The atomic weights of pure elements, consequently, are multiples of H = 1, or of Dr. G. Hinrich's pantogen = ½H. Until this proportion is finally settled may it be convenient to arrange the table of atomic weights as follows:—

Pantogen ..	½	And the still unsettled elements with their decimals.
H	1	
O	16	
N	14	
C	12	
Ag	108	
	&c.	

And thus, after a period of mistakes, we have found the harmonious simplicity which every true explorer of nature is searching for and hopes to find.

Upon this plain and solid foundation, and upon a few universally acknowledged laws of nature, has the author built his "Reform," and hopes that it may help to ease and simplify chemical and physical study and work, and the rational application of science to practical and useful purposes.

The author has found that at 41° 10′ geographic latitude, sea-level, mean atmosphere pressure, and the temperature of freezing water (± 0° C. = 273° C. absolute), 1 cubic metre oxygen weighs 1·4285714285 kg. = exactly 10/7 kg., and from this determined the figures given in the accompanying table.

1 cubic metre gas.		Kgrm.		Kgrm.		Cubic metre.	
Hydrogen	H	10/7 × 16	= 10/112 =	5/56	and 1 kgrm. gas	56/5	= 11·200
Oxygen	O	10/7	=	80/56	„ „	56/80	= 0·700
Nitrogen	N	14 × 5/56	=	70/56	„ „	56/70	= 0·800
Carbon	C	12 × 5/56	=	60/56	„ „	56/60	= 0·93333

The 41° 10′ latitude the author proposes to adopt as the circle of international gravity; to reduce all chemical and physical determinations of weights to this latitude, and to establish there—on the west coast of Italy—an international observatory and laboratory, similar to that by which the astronomers of all nations reduce their observations and determinations of time to the meridian of Greenwich.

By the very plain calculations given in the book, the author has found many thousands of numbers, values, and facts, which agree more nearly with the determinations of celebrated masters than those do amongst each other. The author hopes and wishes that his work may be investigated earnestly, and impartially judged.

Copenhagen V., Valdemarsgarde 3.
May, 1908.

Triboluminescence of Inorganic Substances.—Adrien Karl.—Triboluminescence appears to be a fairly common property of solids. Pure substances are not triboluminescent. A triboluminescent system preserves its property when it is subjected to various chemical transformations. Triboluminescence appears to be a property of solid solutions of a certain dilution, and thus resembles phosphorescence; it follows the same laws as this last phenomenon.—*Comptes Rendus*, cxlvi., No. 21.

THE POTENTIAL ENERGY OF THE ELEMENTS.

By DANIEL J. RANKIN.

The elements as known to us are the most simple forms of matter that can exist in our cosmic environment.

Matter is the phenomenon exhibited by energy when in a state of integration. The differences between any two forms of matter are determined by variations in quantity of energy.

An element is a system of energy. Under normal conditions the energy exists in two states or conditions. First, the static or intrinsic energy. This intrinsic energy is incapable of being freed, is inert, is uninfluenced by any ordinary extraneous energy whether chemical, thermal, or electric. Its intensity is so enormous as to be incalculable. The phenomena alone exhibited by radio-active bodies permit us a partial realisation of its intensity. Apart from this static or intrinsic form, energy also exists in an element in a free state. The amount of this free or potential energy permits of calculation in terms of thermal calories, and this I have done in the accompanying tables.

The intrinsic energy and the potential energy of every element are fixed values, and an element cannot exist in an uncombined state when their equilibrium is disturbed beyond definite limits.

The state of integration of an element is a function of its potential.

In thermo-chemical measurements the "heat of formation" is the value of that portion of the potential which is lost or integrated, and the resulting compound undergoes diminution or increase in volume in a fixed ratio to the loss or gain of potential. As an illustration let us consider the formation of the compound Al_2S_3.

From my table we find the potentials of the constituent elements are Al = 19463 K and S = 17120 K. These quantities of energy and heat refer to such quantities of the substances as amount to their formula weights in grms. Thus—

Al_2	= 38926
S_3	= 51360
	90286 K

That is, these quantities of the elements Al + S in a free state contain 90286 large calories of free energy or potential.

The chemical combination is attended with a loss of 1224 K (heat of formation). Therefore the potential of Al_2S_3 is 90286 K − 1224 K = 89062 K.

Now as mass or volume is simply the phenomenon exhibited by the integration of energy or change due to its loss or accretion, the loss of 1224 K of energy to the system must be evidenced in a correlated loss of mass or volume.

For most elements I have found that the ratio of loss of potential to loss of volume = 1 : 1.

The volumes of the constituent elements are—

	Cc.
Al_2 .. .. .. $\frac{54{\cdot}2}{2{\cdot}583}$	= 21·031
S_3 .. .. .. $\frac{96{\cdot}18}{2{\cdot}07}$	= 46·464
	67·495

The volume of $Al_2S_3 = \frac{150{\cdot}38}{2{\cdot}26} = 66{\cdot}540$ cc.

We find, therefore, that the ratios of potentials and ratios of volumes are equivalent—

90286 : 89062 :: 1 : 0·986

67·495 : 66·540 :: 1 : 0·986

The ratio 1 : 1 holds good generally for elements whose atomic weight is below 60, with the exception of the zinc, cadmium, mercury family, where the ratio is 1 : 0·76 nearly. In such elements as sodium, calcium, and potassium the ratio is 1 : 0·65 nearly.

The following applications of these values of potential are given as illustrations.

In calculating the reactions of energy in chemical combinations containing such gaseous elements as oxygen and chlorine it is necessary to know the density of these substances in a solid form as they exist in chemical compounds. This may be effected in the following way.

To find the density of solid oxygen, in a chemical compound, let us consider the compound Cu_2O (sp. gr. 5·85).

The potentials of the constituents are—

Cu_2	15458
O	38912
	54370 K
The potential of Cu_2 + O . ..	54370
Heat of formation	− 408
Potential of Cu_2O . ..	53962 K

The volume of $Cu_2O = \frac{143{\cdot}2}{5{\cdot}85} = 24{\cdot}478$ cc.

Ratio of potentials : 54370 : 53962 :: 1 : 0·992496.

Now, in this instance, the ratios of volume and potential are equivalent, *i.e.*, 1 : 0·992496. Therefore—

0·992496 : 1 :: 24·478 : 24·663 cc.,

i.e., the sum of the volumes of Cu_2 + O = 24·663 cc., but $Cu_2 = \frac{127{\cdot}2}{8{\cdot}945} = 14{\cdot}253$, and 24·663 − 14·253 leaves 10·410 cc. for the volume of 16 grms. of O.

$$\frac{16}{10{\cdot}410} = 1{\cdot}537 \text{ grms.},$$

the weight of 1 cc. of O under the conditions of integration in a chemical compound.

By a similar method the specific gravity of solid chlorine in chemical compounds may be deduced to be 2·0045.

To calculate the *heat of formation* of $PbCl_2$ (sp. gr. = 5·322) :—

From my table of potentials we find—

Pb	= 969
Cl_2	= 31202
Sum of potentials of Pb + Cl_2 ..	32171 K

Volume of $PbCl_2 = \frac{277{\cdot}8}{5{\cdot}322} = 52{\cdot}194$ cc.

The sum of volumes Pb + Cl_2 :—

	Cc.
Pb .. .. $\frac{206{\cdot}7}{11{\cdot}37}$	= 18·199
Cl_2 .. .. $\frac{70{\cdot}9}{2{\cdot}0045}$	= 35·374
	53·573

Ratio of volumes. .. 53·573 : 52·194 :: 1 : 0·97426

Ratio of potentials .. 1 : 0·97426 :: 32171 : 31343

Potential of Pb + Cl_2	= 32171
Potential of $PbCl_2$	= 31343
Loss of potential, or heat of formation..	828 K

POTENTIAL ENERGY OF THE ELEMENTS (in Large Calories).

Cu	7729	N . ..	39622	Li ..	75521	Ti ..	12380	C . ..	39050
Ag	3622	P . ..	17894	K . ..	13503	Zr ..	6568	Ru ..	3710
Au	954	As ..	7396	Rb ..	6183	Ce ..	3028	Os ..	951
Zn	7681	Sb ..	3636	Cs ..	2616	Th ..	465	B . ..	43199
Cd	3499	Er ..	1914	Im ..	1183	V . ..	11847	Rh ..	3712
Tb	1768	Bi ..	993	A . ..	14553	Nb ..	6453	Ir . ..	951
Hg	946	S . ..	17120	He ..	133743	Pr ..	3143	Be ..	52940
Al	19463	Se ..	6930	Na ..	23210	Ta ..	1590	Pd ..	3592
Ga	7535	Te ..	3228	Ca ..	13340	Cr ..	11813	Gd ..	1744
In	3675	Fl. ..	29096	Sr. ..	6107	Mo ..	6412	Pt. ..	953
Tl	965	Cl. ..	15601	Ba ..	2487	Nd ..	3125		
Si	19057	Br ..	6913	Mg ..	24124	W ..	1629		
Ge	7465	I.. ..	3210	Sc ..	13326	U . ..	437		
Sn	3559	Ne ..	28033	Y . ..	6603	Mn ..	11304		
Pb	969	Kr ..	6854	La ..	3010	Sm ..	3149		
		X . ..	3245	Yb ..	1747	O . ..	38912		
		H . ..	522564			Fe ..	11178		
						Co ..	10643		
						Ni ..	10642		

To calculate the specific gravity of a chemical compound, having given the heat of formation.

The heat of formation of Ag_2S = 33 K, to determine its specific gravity.

Potentials of constituents—

Ag_2 .. .. =	7244 K
S .. .. =	17120
	24364 K

Potential of Ag_2+S ..	24364
Heat of formation ..	−33
Potential of Ag_2S	24331 K

Ratio of potentials, Ag_2 + S : Ag_2S—

24364 : 24331 :: 1 : 0·99865.

Sum of volumes of constituents—

	Cc.
Ag_2 .. .. .. $\frac{215·86}{10·575}$ =	20·412
S .. .. .. $\frac{32·06}{2·07}$ =	15·488
	35·9

1 : 0·99865 :: 35·9 : 35·851 cc., volume of Ag_2S.

$\frac{247·92}{35·851}$ = 6·915, sp. gr. Ag_2S.

ON THE UTILISATION OF THE ATMOSPHERIC NITROGEN IN THE PRODUCTION OF CALCIUM CYANAMIDE, AND ITS USE IN AGRICULTURE AND CHEMISTRY.*

By Dr. ALBERT FRANK.

(Concluded from p. 292).

As regards the part which cyanamide or nitrolim plays in the soil various theories have been propounded. It appears that when brought in contact with the ground calcium cyanamide is first decomposed through the action of the moisture and of the carbonic acid in the soil into free cyanamide and carbonate of lime according to the formula $CaCN_2$—H_2O—$CO_2H_2CN_2$—$CaCO_3$.

The free cyanamide will then, by absorbing water, probably be further decomposed into urea, $H_2CN_2 + H_2O = CO\frac{NH_2}{NH_2}$.

The final product of this decomposition has been found to be ammonia, but later nitrate is produced through the nitrification of the ammonia. Special experiments have demonstrated that the process of transformation of calcium cyanamide or nitrolim is assisted by a host of microbes which are to be found in almost all cultivated soil. On this point very important and interesting investigation has been carried out quite recently by Dr. Löhnis and Sabashnikoff, of Leipzig ("Untersuchungen über Kalkstickstoff und Stickstoffkalk," von Dr. Alers Sabaschnikoff,

* A Paper read before the Faraday Society, June 9, 1908.

Berlin, 1908, Verlag von Paul Pavey), and Dr. R. Perotti, of Rome ("Dottore Renato Perotti, "Su i Bacteria della Diciandiamide," Roma Typographia Enriev Voghera, 1908).

It is, however, not only to the production of fertilisers that the scope of the new calcium cyanamide industry has been limited, for it has been also successfully extended to the production from nitrolim of a number of chemical substances to a great extent by utilising derivative forms of reaction long known to science. I am able to show you here some small samples of several of these derived products, all obtained from cyanamide of calcium. Although calcium cyanamide does not display the typical character of the cyanamides, it can, by melting with fluxes, be turned into calcium cyanide, which product can then be treated by well-known methods to yield pure cyanide of potassium or sodium. The molten mass obtained by melting nitrolim with a flux contains approximately an amount of cyanide corresponding to 25 per cent KCN, the cost of the said molten mixture, to which we have given the name of "surrogate," being much less than that of an equivalent amount of pure cyanide of potassium, and the material having been shown by the investigations of English experts to be of equal efficiency with pure cyanide of potassium for the extraction of gold and silver. It appears particularly suited to the requirements of the countries where gold and silver are mined, as it can be produced with difficulty at the mine itself where it is to be used.

The production of ammonia and ammoniacal salts from nitrogen, to which I have made reference previously, has also been further worked out and perfected on an industrial scale. You will readily understand that the ammonia obtained by heating $CaCN_2$ with water is very pure and free of empyreuma. It is therefore particularly suitable for the production of pure ammoniacal salts as well as liquid ammonia (see Fig. 2).

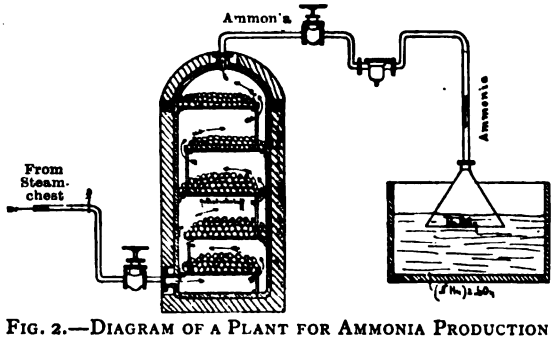


FIG. 2.—DIAGRAM OF A PLANT FOR AMMONIA PRODUCTION FROM LIME NITROGEN.

Further, the author would point out that a number of complex organic nitrogenous compounds have been derived from calcium cyanamide, and are already being produced on a manufacturing scale. Out of the great number of these I will only mention dicyandiamide, $CNNH_2$, $(—)_3$, for which there is an increasing demand in Germany for the manufacture of organic dyes, besides which there are urea, CONH, and sulphourea, $CSNH_2NH_2$.

The author would also mention that one of our German companies is producing from nitrolim the salts of guanidine, such as carbonate and nitrate of guanidine, nitro-guanidine, and other salts, all of which should now gradually come into use on an increasing scale in the industries of organic chemistry, as the cost of production will be considerably lower when starting from calcium cyanamide than by the methods of manufacture hitherto employed. Recently, attention has been paid to the use of nitrate of guanidine, nitro-guanidine, and dicyandiamide as a "deterrent" for reducing the temperature of combustion with explosives and gunpowder. In consequence of the high contents of inert nitrogen in dicyandiamide (66·6 per cent) it evolves a strong pressure when burnt in a gun, and in contradistinction to the other constituents of the explosive which contain more carbon and hydrogen, its decomposition produces but little heat. This peculiarity is of great importance in powder used with ordnance, such as cordite and filite, which, because of the high temperature of combustion, rapidly destroy the rifling of the barrels. With many powder mixtures the cooling action of dicyandiamide is shown by the disappearance of the flash at the muzzle, so that on discharge both powder-smoke and powder-flash are done away with.

The composition of the crude cyanamide of calcium made it appear likely that it would lend itself quite as well as yellow prussiate and potassium cyanide for use in case-hardening, and tempering of iron and steel. Tests carried out to this end have confirmed this impression. It has been shown that by adding certain fluxes to the crude cyanamide of calcium a very high hardening effect can be produced. This new hardening mixture, under the name "ferrodur," has been introduced on the market in Germany, England, and other countries, and its property of producing an extraordinary depth of the hardened surface without the material being at all deteriorated has already secured it a great number of friends.

If I may ask your indulgence for a few more minutes, I would like to give you a short description of the method by which the nitrolim is being produced in some of the factories, and to say also a few words on its position in the markets of the world. The carbide coming from the electric furnaces is ground, charged into retorts made of fire-proof material which are mounted in a furnace similar to gas-house furnaces (see Fig. 3). The nitrogen is then

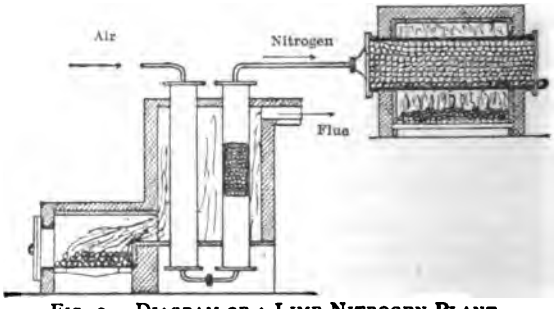


FIG. 3.—DIAGRAM OF A LIME NITROGEN PLANT.

passed over the carbide at a temperature of from 800° to 1000° C. The carbide used is of the same quality and percentage as that employed for lighting purposes, and the nitrogen consumed is obtained by fractional distillation of liquefied air by the Linde system, or the so-called "copper" process in which air has passed through heated copper particles. The copper takes up the oxygen and the free nitrogen passes to the furnaces. The resulting copper oxide is reduced in the same apparatus by treatment with reducing gases or vapours, and the copper which is recovered is then ready for a new cycle. In the Linde process the oxygen remaining after separation of the nitrogen may be utilised for any purposes. As soon as the carbide in the retorts is saturated with nitrogen, a fact which will be made apparent by the controlling gas-meter coming to a standstill, the calcium cyanamide is extracted from the retorts in the form of a hard cake, and cooled while the air is excluded. It is then ground into a fine powder, and is ready for use. During the last year a new electric furnace has been developed for treating carbide with nitrogen, and is being universally adopted by all the new cyanamide factories in preference to the older retorts. This process is cheaper to instal and to operate where the cost of power is lower than the retort furnaces just described; and notwithstanding that the average life of the retorts has been greatly prolonged, the new electric furnace is cheaper to maintain, possessing practically an unlimited life.

Crude nitrolim contains about 57 to 63 per cent of the pure cyanamide of calcium, so that its total contents in nitrogen will amount to roundly 20 to 22 per cent, the same as sulphate of ammonia. The material contains besides this about 20 per cent of calcium oxide, 7 to 8 per cent of silicious acid, iron oxide, and alumina, and 14 per cent of carbon, which imparts to the product its characteristic slate-black colour.

Most carbide works obtain at the present time a yield of two tons of carbide per kw. year, and two tons of carbide will combine with practically 500 kilogrms. of nitrogen in the form of nitrolim; a power of two kw., or 2½ horse-power, is required per year for fixing one ton of nitrogen by the Frank-Caro process. In addition thereto, about ½ horse-power is required for grinding and all other operations. If, therefore, it were proposed to substitute nitrolim for the nitrate of soda at present consumed in the world, it would require plants disposing of no less than 800,000 horse-power to do so.

It goes without saying that before the process of making nitrolim could be developed on an industrial scale, its value as a fertiliser had first to be ascertained. And as it naturally took a number of years to complete the exhaustive agricultural researches instituted for this purpose sufficiently to make them conclusive, it will not surprise you, gentlemen, that it was only about three years ago that the question of putting up industrial works was attacked.

About that time the Cyanid-Gesellschaft, in conjunction with two important Italian companies chiefly interested in the manufacture of calcium carbide, promoted, under the management of Cav. Morani, the founder of the Italian Carbide Industry, the Societa Generale per la Cianamide in Rome.

The first plant on a large industrial scale was started about two and a-half years ago at Piano d'Orta in Central Italy (see Fig. 3), near to the Adriatic Sea, for a yearly production of 4000 tons of lime nitrogen, and is just now being enlarged to a capacity of 10,000 tons. In addition to this, the Societa Generale is also about to appropriate a large water-power it owns in Italy for the erection of other works. One is ready to start in Terni in connection with the large carbide factories there, and another factory is in course of erection in San Michel in the Val d'Aosta.

There are at present in Austria-Hungary important cyanamide works in course of erection, all promoted by the Societa Generale of Rome. In Sebenico, in Dalmatia, at the carbide works one is being built for an initial yearly production of 4000 tons. At Fiume, in Istria, works are also in construction for a similar output.

At the present time a water-power installation of at least 50,000 horse-power is being erected at Almissa, also in Dalmatia, for the manufacture of this new artificial manure. The market for the products of these works will be the Balkans, Asia Minor, and Egypt, where, owing to the practice of irrigation, nitrolim will be of special value to agriculture.

In France, the Société Francaise des Produits Azotés installed works a few months ago at Nôtre Dame de Briançon (Haute Savoie), for the manufacture of cyanamide, with an output of about 4000 tons per annum. In the Rhone Valley in Switzerland the Société Suisse des Produits Azotés has just opened equally important works. In Germany, the works at Westeregeln and Brühl on the Rhine are manufacturing 10,000 tons of nitrolim annually. It is interesting to mention that the works at Brühl for the preparation of carbide do not employ water-power, but produce the power required in the works themselves, using cheap coal in large quantities for this purpose. Another installation is that of the Brandenburgischer Carbidwerke for the preparation of nitrolim with an output of 2500 tons per annum, near Bromberg, in North Germany, which is also completed, while the large works of the Cyanid Gesellschaft for an output of over 15,000 tons of nitrolim at Alz-Fluss, in Bavaria, are at present in construction. In the United States of North America the American Cyanamide Company has taken up the manufacture of nitrolim, and are constructing on the Canadian side of the Niagara Falls works of a present capacity of from 5000 to 6000 tons per annum, to be enlarged later to an output of 40,000 tons.

It is quite natural that English enterprise should have given this new artificial fertiliser considerable attention. The North-Western Cyanamide Co., Ltd., with a capital of £120,000, was incorporated in the middle of 1906 to acquire from the Societa Generale and work licences for the manufacture and sale of cyanamide in a vast territory comprising the United Kingdom, the Colonies, Protectorates and Dependencies (excepting Canada and Egypt), and a large portion of the North-West of Europe, viz., Norway, Sweden, and Belgium, with 30 per cent of the consumption of Denmark, Germany, and Holland. The Sun Gas Company, now widely known as the Alby United Carbide Factories, Ltd., and their able Board of Directors, Mr. Albert Vickers, Sir Vincent Caillard, Mr. A. E. Barton, and others, took a leading part, with the co-operation and assistance of the Societa Generale of Rome, in the promotion of the North-Western Cyanamide Co., the Alby Company undertaking the erection of a new factory adjoining to that of the North-Western Company to supply them with the requisite carbide. These works, erected at Odda, situated at the head of the beautiful Hardanjer Fjord, you will see in the picture, which shows the carbide works and the adjoining nitrolim works, the largest at present constructed. The capacity of the cyanamide works at present is 12,500 tons of nitrolim, and is laid out so as to be eventually enlarged to 50,000 tons. The nitrogen is produced by the largest Linde pump ever erected, with a capacity of 375 cubic metres per hour, and the latest electrical furnaces are there installed. The author wishes to point out here that the works at Odda, which produce 2500 tons of nitrogen, only employ from 5000 to 6000 kw., whereas from the statement of Mr. Eyde (extract from the "Archives of the Deutschen Landwirtschaffsrats," 31st year, 1908) it appears that in the works at Notodden, in Norway, for the preparation of an equivalent amount of nitrogen in the form of nitrate of calcium 25,000 kw. are required.

In order to complete the review which the author has made of the works already erected for the preparation of nitrogenous fertilisers, it should be stated that the British allies in the Far East, the Japanese, are erecting in the south of the Kinskzu Island a works capable of producing 4000 tons per annum, so that the manufacture of the new fertiliser will soon be localised all over the world.

At the end of the present year, works for a total production of over 45,000 tons of nitrogen will be in full swing, and in the course of next year there will be a correspondingly large increase in the means of production of this product.

Though these figures may appear relatively high, they are quite diminutive in comparison with the continual increase in the demand for nitrogenous food for our agriculture, which in Germany alone at the present time shows an annual increase of 15,000 tons of nitrogen.

It would be an error to assume that the competition of calcium cyanamide on the fertiliser market with Chili saltpetre, sulphate of ammonia, or Norwegian saltpetre can take on the character of a war of annihilation, as was the case with artificial indigo in respect to the natural product. On the contrary, Industry and Agriculture will welcome increasingly large supplies of nitrogen, tending to prevent the rising in the prices of the nitrogenous foods required for the development of plant life.

It will be an especial satisfaction to you, gentlemen, to be assured that just at the present juncture discoveries in the field of electrical chemistry have made it possible to succeed in the attempt to supply vegetation with its most valuable food, and that in the future the increasing demands for this form of nutrition by agriculturists can be satisfied, and mankind will, for the future, be able to manufacture unlimited bread and strength.

DISCUSSION.

Mr. HENRY COTTRELL pointed out that a great advantage of these artificial nitrogenous manures is that they are alkaline, whereas the native nitrates are acid and produce in time sickness in the soil. It was difficult to persuade the farmer, however, to use new manures.

Mr. WALTER REID, referring to some tests he had made on calcium cyanamide, drew attention to the moisture in the soil as having considerable effect on the results of such tests. With regard to the use of calcium cyanamide in smokeless powder, he had found it rather too efficient in slowing the explosion.

Dr. H. BORNS hoped the author would furnish some fuller details regarding the efficiency and construction of the electric furnaces in which combination of nitrogen with carbide took place.

Dr. J. H. VOELCKER said farmers could not be expected to use new manures until they were perfectly satisfied as to their cost and effect. There were, for example, at present certain disadvantages connected with the use of nitrolim which would have to be eliminated before it could become entirely satisfactory. Beyond that, the situation was determined entirely by price.

Mr. W. MURRAY MORRISON asked whether the cyanamide could not be made direct from limestone and coal in one operation.

Mr. J. L. F. VOGEL asked what fear there was of a charge of carbide not being completely nitrated.

The Chairman (Dr. F. MOLLWO PERKIN) drew attention to the use of cyanamide in synthesis, and hoped that some of the very interesting and important compounds that could be made from it would be manufactured in this country.

Dr. FRANK replied to the points raised by the various speakers. Cyanamide was 10 per cent cheaper than ammonium sulphate. Its stability was good; although the lime absorbed moisure, there was no loss of nitrogen. Up to the present its manufacture in one operation had not proved successful.

(For the woodcuts illustrating this article we are indebted to the courtesy of the Secretary of the Faraday Society).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 4th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Mr. J. GIBSON was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Thomas Aubertin, B.A., care of Messrs. George Anderson and Co., Ltd., Carnoustie, N.B.; John William Pearson, B.A., Buxton College, Buxton; Frank Perry, 63, Tunnel Street, Coseley, near Bilston, Staffs.; George O'Brien Power, Fatehpur, U.P. of Agra and Oudh, India; William Frothingham Roach, M.D., M.S., Royal Mersey Yacht Club, Rock Ferry, Cheshire.

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

*124. "*The Interaction of Copper and Nitric Acid in presence of Metallic Nitrates considered with reference to the Existence of Hydrates in Solution.*" By EDWARD HENRY RENNIE, ALFRED JAMES HIGGIN, and WILLIAM TENNANT COOKE.

The authors find that in most cases the addition of metallic nitrates greatly accelerates the dissolution of copper in nitric acid, but that nitrates, such as those of rubidium and cæsium, cause considerable retardation. They consider that these effects are due to the withdrawal by the salts of water or nitric acid from the solution, and the consequent concentration or dilution of the acid, and regard their results as confirmatory of the views now generally held that combination takes place between solvent and solute. They find, moreover, that the accelerations produced by the nitrates of any one group of metals decrease as the atomic weights of the metals increase. When copper nitrate is added to the nitric acid, the dissolution is greatly accelerated. Hence the view that the auto-acceleration always observed when copper is dissolved in nitric acid is due to nitrous acid requires to be modified, the accumulation of copper nitrate in the solution being an important factor in the progress of the change.

DISCUSSION.

Dr. VELEY remarked that the results obtained by the authors might in some cases be due, not to the nitrates *per se*, but also to the nitrous acid or nitrites formed therefrom. Thus, when the conditions are such that copper dissolves in nitric acid (containing nitrous acid), copper nitrite is initially formed, which is subsequently converted into the nitrate. It appeared to him that it would be of interest if the authors were to extend their investigations to metals other than copper, such as mercury, which dissolves initially as mercurous nitrite, yielding mercurous nitrate, and, finally, mercuric nitrate under certain conditions. Silver and bismuth behave generally as copper.

Mr. W. C. REYNOLDS pointed out that nitric acid, with or without the presence of nitrates, has no action whatever on metallic copper if it is freed from traces of nitrous acid, even in the case of much stronger acid than that referred to. This could be effected in a few seconds at the ordinary temperature by adding a trace of sodium peroxide to the acid solution—the addition of carbamide was not so effective.

The alkaloids, morphine, and especially brucine, afford colour tests for the presence of nitrous acid in such acid solutions, and the addition of either should cause no coloration for some hours in the absence of nitrous acid (Reynolds and Sutcliffe, *Journ. Soc. Chem. Ind.*, 1906, xxv., 512). He thought some of the apparently anomalous results obtained by the authors might be due to the varying amount of the "trace" present.

Prof. ARMSTRONG (who had given an account of the paper) said that, whilst he was in accord with the authors that salts exercised a "concentrating effect," he did not think that the acceleration observed was due to the direct withdrawal of water from the nitric acid; the acid used was too dilute and the proportion of salt too small to account, on such an assumption, for the effects produced. It was, however, well known that the dissolution of copper was dependent on the presence of nitrous compounds, and he was inclined to think that salts produced their effect by modifying the condition of these compounds in solution. From this point of view, the observations were most striking and valuable as throwing fresh light on the changes involved in the dissolution of metals in presence of nitric acid.

As to the influence of copper nitrate, it was to be remembered that the heat of dissolution of copper in nitric acid is a negative quantity, and that, from this point of view, copper nitrate is a more effective solvent of copper than the acid.

*125. "*The Triazo-group.* Part IV. *Allylazoimide.*" By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

Allylazoimide, $CH_2{:}CH{\cdot}CH_2{\cdot}N_3$, prepared with some difficulty from allyl chloride and sodium azide, is a mobile refractive liquid which boils at 76·5° under 760 mm. pressure; owing to subsidiary changes the yield is disappointing. The *dibromide*, $C_3H_5N_3Br_2$, is a heavy colourless liquid, boiling at 87° under 5 mm. pressure.

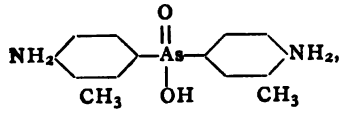
The diazoamino-*compound*, $C_3H_5N_3$, arises from allylazoimide by spontaneous isomeric change, crystallising from the liquid azoimide in colourless transparent lustrous prisms, which melt and decompose at 192°; the substance is bimolecular, and is remarkably sensitive towards dilute

acids, including acetic, which liberates two-thirds of the nitrogen in elemental form.

*126. "*Aromatic Arsonic and Arsinic Acids.*" By FRANK LEE PYMAN and WILLIAM COLEBROOK REYNOLDS.

In the preparation of *p*-aminophenylarsonic acid and 2-aminotolyl-5-arsonic acid, the corresponding bisamino-arylarsinic acids, which have been briefly alluded to by Benda and Kahn (*Ber.*, 1908, xli., 1672), were obtained. The isolation of these by-products was described, and the following new substances were characterised :—

Bis-2-aminotolyl-5-arsinic acid,—



forms highly refracting microscopic needles, melting and decomposing at 247—249°. The *sodium* salt forms large, hard, prismatic needles, which melt at 74—75°, and contain 7½ molecular proportions of water of crystallisation.

Bis-2-acetylaminotolyl-5-arsinic acid,—

$$C_{18}H_{21}O_4N_2As,\tfrac{3}{2}H_2O,$$

crystallises from water in highly refracting microscopic prisms, melting at 242—244°.

Its *sodium* salt forms radial clusters of silky needles, which melt at 106—107°, and contain 6 molecules of water of crystallisation.

Bis-p-aminophenylarsinic acid, $C_{12}H_{13}O_2N_2As$, forms matted needles melting at 248—249°. Its *sodium* salt crystallises in large monoclinic plates, containing between 5 and 6 molecular proportions of water of crystallisation; its *barium* salt forms large hard prisms containing 7½ molecular proportions of water of crystallisation.

Bis-p-acetylaminophenylarsinic acid,—

$$C_{16}H_{17}O_4N_2As,3H_2O,$$

crystallises from water in rosettes of needles, and melts at 275°. Its *sodium* salt forms prismatic needles containing 9 molecules of water of crystallisation.

DISCUSSION.

The PRESIDENT inquired whether, in view of the fact that antimony compounds appeared to be more effective than arsenic compounds as a remedy for sleeping sickness, any attempts had been successful to form similar compounds with antimonic acid?

Dr. PYMAN replied that no such attempts had as yet proved successful.

127. "*Condensation Products from Aminopinenedicarboxylic Acid.*" By WILLIAM GODDEN.

Condensation products of glycine and aspartic acid with aminopinenedicarboxylic acid have been obtained, and their copper salts prepared.

128. "*A Delicate Test for Bromides alone or in Solution with Chlorides.*" By JAMES SPRUNT JAMIESON.

The solution to be tested is heated to boiling with 1 or 2 cc. of dilute sulphuric acid and 1 or 2 cc. of potassium dichromate; it is then cooled, and shaken with chloroform. The chloroform layer is separated, washed two or three times with water, and finally shaken with a little dilute potassium iodide solution. In the presence of a bromide, the chloroform is coloured violet, due to the liberated iodine.

The following equation probably represents the reaction:

$$6NaBr + K_2Cr_2O_7 + 7H_2SO_4 = 3Na_2SO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Br_2.$$

The above reaction will detect 0·5 mgrm. of sodium or potassium bromide, either free or in presence of sodium chloride.

129. "*Experiments on the Synthesis of 1-Methylcyclohexylidene-4-acetic Acid*, $CHMe<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>C{:}CH\cdot CO_2H$." (Part I.). By WILLIAM HENRY PERKIN, jun., and WILLIAM JACKSON POPE.

The authors have continued the work of which a preliminary account has already appeared (*Proc.*, 1906, xxii., 107).

130. "*A Method for the Measurement of Rate of Change in Solid Alloys.*" (Preliminary Note). By GUY DUNSTAN BENGOUGH.

The method consists in heating portions of the metastable alloy at a selected temperature for various lengths of time. The portions are then quenched in water to stereotype as far as possible the phases present at the selected temperature. Photomicrographs are made at a magnification determined by the coarseness of the crystalline structure. From the entire negative, an enlargement is made on bromide paper, the degree of enlargement again depending on the coarseness of the structure. The relative proportions of the phases present may then be determined by cutting them out separately, and weighing. Curves are then plotted with axes representing time and percentages of any given constituent, showing the rate of change at the selected temperature.

Tests made on the uniformity of the bromide paper used for the enlargement and on the difference in weight between portions of the paper which printed black and white respectively have shown that the errors due to these causes are negligibly small when compared with some others inherent in the process.

Duplicate measurements of the percentage of one of the constituents in a copper-zinc alloy gave the following results :—

	Proportion of α-constituent.		Mean.
	i.	ii.	
Alloy—Cu, 60 per cent; Zn, 40 per cent	67·3	67·7	67·5
Another specimen of the same alloy	67·5	67·7	67·6
Another specimen annealed 7 hours at 540° and slowly cooled ..	89·2	89·3	89·25

By careful selection of typical portions of the alloy, and with crystalline structures suitable to the method, the limit of accuracy appears to be about ± 0·25 per cent.

Comparative tests have been made to ascertain how far planimetric measurements of the areas of the phases after enlargement agree with the results obtained by the method described :—

	Proportion of α-constituent.			
	By planimeter.		By weighing.	
Alloy—Cu, 60 per cent; Zn, 40 per cent	59·2	58·5	59·6	60·0
Mean	58·85		59·8	
Same, annealed at 640° and slowly cooled ..	64·6	64·2	65·3	64·6
Mean	64·4		64·95	

The planimeter gives the lower result in both cases, for a reason not yet ascertained. The actual proportions of the α-constituent in the above experiments have no significance; they depend on the rate of cooling adopted in the various experiments. The particular alloys used have merely been chosen to test the method of measurement proposed.

Huntington and Desch have very recently (April 28, 1908) read a paper before the Faraday Society on the "Planimetric Analysis of Alloys," and their work has come to the author's notice since his own results were obtained. They consider the planimetric measurement of the areas to be more accurate and preferable to weighing. The present author considers the weighing method to be preferable for many kinds of structure, and to be susceptible of considerable accuracy. The author is using it for the measurement of rate of change in copper-zinc alloys.

131. "*Viscosity Determinations at High Temperatures.*" By CHARLES EDWARD FAWSITT.

The viscosity of some fused salts and metals has been measured by the method recently described by the author (*Proc. Roy. Soc.*, 1908), lxxx., A, 290). The absolute viscosities of sodium nitrate, potassium nitrate, sodium chloride, potassium chloride, sodium bromide, potassium bromide, and lithium chloride have been determined over a considerable range of temperature. The best comparison of the viscosities of salts is obtained by choosing in all cases the values at the melting-points, or at temperatures easily equally distant from the melting-points. The viscosity of a sodium salt at its melting-point is very nearly the same as the viscosity of the corresponding potassium salt. The viscosity of the salts examined was in no case greater than 0·03 (C.G.S. units); as the viscosity of water at 20° is 0·01, the viscosity of these salts is really not so much greater, as might have been expected. The viscosity of a mixture of sodium and potassium nitrates shows a maximum value at the composition corresponding with the eutectic mixture, provided the comparison is made at temperatures equally distant from the melting-points. The viscosity of a salt decreases with rise of temperature. The temperature coefficients of these salts are proportional to their viscosities. Metals have also a small viscosity. Lead and tin at their melting-points are only about three times as viscous as water. Bismuth and mercury have only about twice the viscosity of water. When a molten metal is cooled to its solidfying-point, there is no abrupt or large increase in the viscosity to indicate the approach of the solid state. The change from the liquid to the solid state corresponds with a sudden and violent change in viscosity.

132. "*Dinitrodiphenylamine-o-sulphonic Acids.*" (Preliminary Note). By SAMUEL SMILES.

By heating 2-chloro-5-nitrobenzenesulphonic acid with the nitroanilines, the corresponding diphenylamine-*o*-sulphonic *acids* are formed. The acids may be isolated as the sparingly soluble, yellow *sodium* salts in a yield equal to about 20 to 25 per cent of the theoretical. These substances have been prepared with a view to effecting the synthesis of the diphenylamine sulphoxides.

133. "*The Study of the Absorption Spectra of the Hydrocarbons Isolated from the Products of the Action of Aluminium Chloride on Naphthalene.*" By ANNIE HOMER and JOHN EDWARD PURVIS.

In an investigation of the action of aluminium chloride on naphthalene, one of the authors isolated, besides Friedel and Crafts' $\beta\beta$-dinaphthyl, three new hydrocarbons, $C_{14}H_{16}$, $H_{26}H_{22}$, and $C_{40}H_{26}$ (*Trans.*, 1907, xci., 1103). In the hope of obtaining additional evidence as to the constitution of these substances, a comparative study of their absorption spectra with that of naphthalene has been made. The absorption spectrum of the hydrocarbon $C_{26}H_{22}$, which was supposed to be an alkyl derivative of dinaphthanthracene, $C_{22}H_{14}$, has also been compared with those of dinaphthanthracene and picene.

The absorption curves for these hydrocarbons show that:—

1. The hydrocarbon $C_{14}H_{16}$ is a naphthalene derivative.
2. The hydrocarbon $C_{40}H_{26}$ has a constitution similar to that of $\beta\beta$-dinaphthyl.
3. The isomeric hydrocarbons, picene and dinaphthanthracene, have markedly different absorption curves.
4. The hydrocarbon $C_{26}H_{22}$ is an alkyl derivative of picene and not of dinaphthanthracene, as had been previously suggested.

134. "*The Synthesis and Constitution of certain Pyranol Salts related to Brazilein and Hæmatein.*" By WILLIAM HENRY PERKIN, jun., ROBERT ROBINSON, and (in part) MAURICE RUSSELL TURNER.

The authors have continued the work of which a preliminary account has already appeared (*Proc.*, 1907, xxiii., 149).

135. "*Brazilin, Hæmatoxylin, and their Derivatives.* Part IX. *On Brazilein, Hæmatein, and their Derivatives.*" By PAUL ENGELS, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

The authors have continued the investigation of which a preliminary account has already appeared (*Proc.*, 1907, xxiii., 166, 291).

136. "*The Effect of Constitution on the Optical Activity of Nitrogen Compounds.*" By REGINALD W. EVERATT.

Three substituted ammonium iodides containing the *n*-butyl group, namely, phenylmethyl-*n*-butylallyl, *p*-bromophenylbenzylmethyl-*n*-butyl, and *p*-bromophenylmethyl-*n*-butylallylammonium iodides, and also *p*-bromophenylbenzylmethylallylammonium iodide, have been resolved. The first three were required to fill up gaps in the series already examined (Thomas and Jones, *Trans.*, 1906, lxxxix., 280; Jones and Hill, *Trans.*, 1908, xciii., 295), whilst the fourth was needed for purposes of comparison with the phenylbenzylmethylallylammonium iodide of Pope and Peachey (*Trans.*, 1899, lxxv., 1127). The camphorsulphonic acids failed to effect resolution in the case of the third compound mentioned, which was successfully accomplished by means of both camphoric and tartaric acids.

The values obtained for the ammonium salts containing the radicles named are as follows:—

	$[M]_D$ for basic ion.	$[M]_D$ for iodide in alcohol.	$[M]_D$ for iodide in chloroform.
Phenylmethyl-*n*-butylallyl	85·6°	105·1°	123·0°
p-Bromophenylmethyl-*n*-butylallyl	98·0°	114·3°	187·9°
p-Bromophenylbenzylmethyl-*n*-butyl ..	−308·7°	−354·2°	−481·5°
p-Bromophenylbenzylmethylallyl	−191·1°	−242·1°	−346·0°

In all the cases previously examined, the value of $[M]_D$ for the iodide in chloroform is greater than in alcohol; $[M]_D$ for the iodide in alcohol is greater than $[M]_D$ for the ion in water, and the chloroform solution becomes inactive, owing to racemisation.

These relations hold in the above cases, which were, however, peculiar in that the rapidity of racemisation in chloroform was much greater than usual, none of the above compounds requiring more than twenty-four hours, and some considerably less, for complete racemisation.

137. "*The Electrolytic Oxidation of some Hydroxybenzoic Acids.*" By ARTHUR GEORGE PERKIN and FREDERICK MOLLWO PERKIN.

Sodium purpurogallincarboxylate, $C_{11}H_7O_5\cdot CO_2Na,4H_2O$, obtained by the electrolytic oxidation of gallic acid, forms orange-brown leaflets, and this with potassium acetate gives the *potassium* salt, $C_{11}H_7O_5\cdot CO_2K,3H_2O$, crystallising in prismatic needles. The *barium* salt, $(C_{12}H_7O_7)_2Ba$, crystallises similarly.

Methyl tetramethylpurpurogallincarboxylate,—

$$C_{12}H_3O_7(CH_3)_5,$$

forms pale yellow needles, m. p. 120—121°, and on hydrolysis furnishes the *acid*, $C_{12}H_4O_7(CH_3)_4$, yellow needles, m. p. 182—183°. Purpurogallincarboxylic acid by boiling with concentrated potassium hydroxide solution is converted into *purpurogallonecarboxylic acid*, $C_{11}H_7O_5\cdot CO_2H$, yellow needles melting above 360°, which separate both in the anhydrous form and with two molecules of water. On acetylation, *acetylanhydropurpurogallonecarboxylic acid*, $C_{12}H_4O_6\cdot(C_2H_3O)_2$, is produced in colourless needles, m. p. 236—238°, which on hydrolysis is reconverted into purpurogallonecarboxylic acid.

Methyl tetramethylpurpurogallonecarboxylate,—

$$C_{11}H_3O(O\cdot CH_3)_4\cdot CO_2\cdot CH_3,$$

colourless prisms, m. p. 110—111°, and the corresponding *acid*, $C_{12}H_4O_7(CH_3)_4$, prisms, m. p. 166—167°, were described. By the electrolytic oxidation of gallic acid in

60 per cent sulphuric acid (compare D.R.-P. 85390), flavellagic acid, $C_{14}H_6O_9$ (*Trans.*, 1906, lxxxix., 251), is obtained, whereas protocatechuic acid gives catellagic acid, $C_{14}H_6O_6$ (*loc. cit.*), but the yields do not compare favourably with those previously obtained by means of persulphates. The best results with gallic acid were obtained by employing a platinum tube as anode and passing cold water through it, using a divided cell. A current density of 0·22 ampère per square centimetre at 7—8 volts was employed, and the yield of flavellagic acid varied from 35 to 40 per cent.

For the preparation of sodium purpurogallincarboxylate, the electrolyte employed was 15 per cent sodium acetate, and the best results were obtained without the employment of a divided cell. The solution was vigorously agitated during the electrolysis, the current density being 0·75 ampère per square dcm. and the E.M.F. 5 to 6 volts.

138. "*Note on Morindin.*" By ARTHUR GEORGE PERKIN.

Morindin (*Morinda citrifolia*) according to Oesterle and Tisza (*Arch. Pharm.*, 1907, ccxlv., 534) possesses the formula $C_{27}H_{30}O_{15}$, not $C_{26}H_{28}O_{14}$ as suggested by Thorpe and Greenall (*Trans.*, 1887, li., 52), and gives an acetate, $C_{27}H_{21}O_{15}(C_2H_3O)_9$, m. p. 236—237°, readily soluble in alcohol. An examination of morindin (*Morinda umbellata*) by the author gave results agreeing with the older formula, $C_{26}H_{28}O_{14}$ (found, C = 55·37; H = 5·14). The acetyl derivative, prepared by adding pyridine to the substance in acetic anhydride and boiling for three hours, forms pale yellow needles, m. p. 246—248°, very sparingly soluble in alcohol, and possessing the formula $C_{26}H_{20}O_{14}(C_2H_3O)_8$ (found, C = 56·01; H = 5·14, and, on hydrolysis, acetic acid = 53·60, morindone = 29·84, 29·99). The morindone thus produced was pure (found, C = 66·64; H = 3·90). Morindin acetate was unaltered by long digestion with acetic anhydride, and was also formed when the method given by Oesterle and Tisza (*loc. cit.*) was employed. The sugar obtained by hydrolysis of the glucoside gave an osazone, m. p. 202—203°, sparingly soluble in alcohol, whereas that described by Oesterle and Tisza is readily soluble, and melts at 197°. Independent analyses of morindin carried out for the author at the University, Manchester, gave C = 55·10, 55·10; H = 5·00, 5·20 per cent, and it thus seems likely that the morindin present in the *Morinda citrifolia* is not identical with that contained in the *Morinda umbellata*.

139. "*Some Esters of Arsenious Acid.*" By WILLIAM ROBERT LANG, JOHN FRANCIS MACKEY, and ROSS AITKEN GORTNER.

The authors have heated a number of alcohols and phenols in contact with arsenious oxide, using a reflux condenser with a Soxhlet attachment containing anhydrous copper sulphate to remove the water formed in the reaction $6ROH + As_2O_3 = 2R_3AsO_3 + 3H_2O$, otherwise a condition of equilibrium is set up at a point where only a small portion of ester has been formed. Anhydrous copper sulphate has also been employed mixed with the alcohol and arsenious oxide in the cold with good results. The following esters have been prepared in large quantities; they all decompose with water, and are capable of dissolving considerable amounts of the arsenious oxide:—

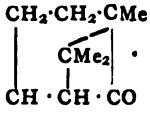
Percentage Yield with Anhydrous Copper Sulphate.

	In Soxhlet.	Mixed together cold.
Propyl arsenite	56·75	14·8
*iso*Butyl arsenite	56·25	15·8
Trimethylcarbinol arsenite ..	54·27	—
Amyl arsenite..	54·00	—
*iso*Amyl arsenite	58·62	17·2
Phenyl arsenite	60·00	—

Yields of 33·8 per cent and 4·5 per cent of methyl and ethyl arsenites respectively were obtained also, and it is found that ethyl alcohol has a much greater attraction for water than methyl or the higher alcohols, which accounts for the smallness of the yield in its case. In addition to those mentioned above, esters with the three cresols, naphthol, benzyl alcohol, the dihydric and trihydric phenols, and with methyl salicylate have all been prepared, but not quantitatively; the reaction takes place very readily. A method of analysis for the phenyl ester by titration with iodine and with dichromate was worked out and gives accurate results.

140. "*α-Methylcamphor and Fenchone.*" By WALTER HAMIS GLOVER.

The general chemical behaviour of α-methylcamphor has been contrasted with that of fenchone, and it is shown that the two substances are essentially different; thus, α-methylcamphor, unlike fenchone, is readily brominated, yielding α′-bromo-α-methylcamphor (Minguin, *Comptes Rendus*, 1903, cxxxvi., 751), and is also easily converted into a β-sulphonic acid. Fenchone, therefore, cannot possess the constitution assigned to it by Wallach (*Annalen*, 1898, ccc., 319); objections may also be raised to Semmler's formula (*Chem. Zeit.*, 1905, xxix., 1313). It is suggested that the following formula better represents the behaviour of fenchone:—



The following new derivatives of α-methylcamphor have been prepared; they are very similar to the corresponding derivatives of *d*-camphor.

α′-Bromomethyl-α-methylcamphor, $C_{10}H_{14}Br(CH_2Br)O$, crystallises in colourless, silky needles, m. p. 108—109°, $[\alpha]_D$ 20 +117·5° in benzene. *α-Methylcamphor-β-sulphonic acid*, $C_{10}H_{14}MeO\cdot SO_3H$, forms large, deliquescent, colourless prisms, m. p. 114—116° (decomp.), $[\alpha]_D$ 20 +18·7° in water; the *barium* salt, $(C_{11}H_{17}O_4S)_2Ba,6H_2O$, forms large, thick, transparent, hexagonal plates, m. p. 66°; the *sulphonyl chloride*, $C_{11}H_{17}O\cdot SO_2Cl$, crystallises in transparent, prismatic needles, m. p. 33°, $[\alpha]_D$ 20 +29·5° in benzene; the *sulphonamide*, $C_{11}H_{17}O\cdot SO_2\cdot NH_2$, crystallises in long, silky needles, m. p. 150°, $[\alpha]_D$ 20 −6·3° in chloroform; the *sulphonanhydramide*, $C_{11}H_{15}ONS$, is a fine, crystalline powder, m. p. 167·5°. *β-Bromo-α-methylcamphor*, $C_{11}H_{17}OBr$, crystallises in white, silky needles, m. p. 55°, $[\alpha]_D$ 25 +18·8° in ethyl alcohol. *α-Methylcamphoroxime*, $C_{11}H_{18}{:}NOH$, crystallises in long, slender needles, m. p. 55°, $[\alpha]_D$ 20 +30·3°; the *hydrochloride*, $C_{11}H_{19}ON,HCl$, forms silky needles, m. p. 138° (decomp.). *Methylcampholenonitrile* is an oil with a peppermint-like odour, b. p. 226—228°.

141. "*Ester Hydrolysis and Theories of Esterification.*" By ARTHUR LAPWORTH.

The author has recently pointed out (*Proc.*, 1908, xxiv., 101) that, whilst the initial velocity of hydrolysis of ethyl formate in acetone with hydrogen chloride as catalyst is roughly proportional to the respective concentrations of mineral acid and ester, it is hardly dependent on the amount of water present within a range of 4—20 per cent, and concluded that this afforded definite proof of the incorrectness of the theory advanced by Stieglitz, which demands a proportionality between the velocity and the concentration of the water. This conclusion was erroneous, because the possibility remains that the water so affects the medium (compare following Note) that the effects due to its possible depressing effect on the reaction velocity, to the altered ionisation of the mineral acid, and to its own increased concentration exactly neutralises one another. It must be noted that the striking coincidence must be assumed to apply in alcoholic solution within similar

limits as the results of Kistiatowski show (*Zeit. Phys. Chem.*, 1898, xxvii., 253 *et seq.*).

Reference must here be made to the experiments of Ostwald (*Journ. Prakt. Chem.*, 1883, [ii.], xxviii., 463), in which the effect of replacing some of the water by acetone during ester catalysis was found to be very small.

The observed increase on the velocity of catalysed esterification with increase of alcohol concentration in acetone and water (see following Note), as well as in water (van 't Hoff; Kistiatowski). makes it appear very probable that the suggestion of Acree and Johnson (*Am. Chem. Journ.*, 1907, xxxviii., 344), namely, that the alcohol and water enter into these reactions as neutral components in a complex ion formation, is correct; as an alternative it is possible (Stieglitz, *Ibid.*, 1908, xxxix., 60; Acree and Johnson, *loc. cit.*) that both ions of these compounds act simultaneously, but this seems less acceptable. It is not necessary, however, *a priori*, either for chemical or mathematical reasons, to suppose that during reactions in which carbonyl compounds take part under the influence of mineral acids it is the instantaneously formed oxonium ions which are directly concerned, and the fallacy in this assumption is obvious when it is remembered that the measured velocity of bromination of acetone (*Trans.*, 1904, lxxxv., 31 *et seq.*) is that of a change induced in the carbonyl compound itself by the mineral acid before the bromine enters into the reaction at all; something similar is not excluded in esterification.

142. "*Experiments on the Formation and Hydrolysis of Esters, Acetals, and Allied Compounds.*" (Preliminary Note). By EDWARD FITZGERALD and ARTHUR LAPWORTH.

At 18·2°, the initial velocity of hydrolysis of methyl acetate is nearly independent of the concentration of the water within the limits 4—30 per cent in acetone.

During esterification by ethyl alcohol in acetone or ether, the velocity for a short time is roughly proportional to the concentration of the alcohol. In acetone, which appears to take no part in the reaction, alcohol depresses the initial velocity of hydrolysis of methyl acetate, but the effect of water on the reverse reaction is much greater, and the speed of esterification of acetic acid is, very roughly, inversely proportional to the concentration of water within the limits 4—20 per cent. This appears to lend considerable support to the supposition that the velocity of hydrolysis of an ester is intrinsically proportional to the concentration of the water, but is proportionately depressed by its action on the medium and the ionisation of the hydrogen chloride, but this leaves no room for the depression which water might produce on the velocity of esterification by sharing the intermediate products with the alcohol. (Depression of the velocity of esterification by water was noticed by Goldschmidt, Kistiatowski, and others).

Methods of estimating the speed of hydrolysis of acetals and of ethyl orthoformate have been devised. The latter is hydrolysed by N/1000 hydrochloric acid at a speed which is too great to be followed, but in N/5000 hydrochloric acid (or in N/10 acetic acid to which an equivalent of sodium acetate has been added) the change into alcohol and ethyl formate can be traced; the velocity is more than 10,000 times as great as that of the hydrolysis of ethyl formate.

In all the above experiments, hydrogen chloride was used as catalyst, and the temperature was constant within 0·05°.

The equilibrium "constant" for esterification in acetone shows irregularities similar to those seen when acetone is absent, the proportion of ester being altered to an unexpectedly small extent by addition of excess of alcohol.

It is hoped that the ionisation factor of hydrogen chloride in the media employed having been ascertained, a further study of the reactions will throw some light on these questions.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 22, June 1, 1908.

Hydrates of Fatty Acids.—D. E. Tsakalotos.—The study of the coefficients of viscosity of binary systems provides a simple and very sensitive method of detecting the existence of molecular compounds in the liquid state, even when these compounds undergo partial dissociation. From experiments with formic acid it is found that, although pure formic acid has a higher coefficient of viscosity than its homologues, aqueous solutions of the acid have much lower coefficients than corresponding solutions of other acids of the fatty series. The coefficients of viscosity of the system HCOOH and H_2O are rather lower than those calculated by the law of mixtures, while other systems have much higher coefficients than the calculated values. The study of the coefficients shows that no compound of formic acid and water exists, while acetic, propionic, and butyric acids form molecular compounds: $CH_3COOH + H_2O$, $CH_3CH_2COOH + H_2O$, $CH_3CH_2CH_2COOH + H_2O$.

Action of Ammonia on Chlorphosphamide.—MM. Besson and Rosset.—Stokes has shown that a solution of ammonia acts on an ethereal solution of chlorphosphamide giving an amide derivative, $P_3N_3Cl_4(NH_2)_2$. When liquefied ammonia is used in absence of water the product has the formula PN_3H_4, and apparently the equation is $PNCl_2 + 4NH_3 = 2NH_4Cl + PN(NH_2)_2$. When $PN(NH_2)_2$ is heated to 220° for several days it loses NH_3. and its composition approaches that of Gerhardt's phosphamide, $PN(NH_2)_2 = NH_3 + PN_2H$. With gaseous ammonia in absence of water the substance obtained has the formula $P_2N_2Cl_3(NH_2)$ $2PNCl_2 + 2NH_3 = NH_4Cl + P_2N_2Cl_3(NH_2)$. When the raw product is extracted with carbon tetrachloride a white insoluble residue remains, which does not appear to be a definite compound but a mixture of NH_4Cl and $PN(NH_2)_2$. The reaction of gaseous ammonia upon phosphamide can be represented by the equation $(PNCl_2)_3 + 6NH_3 = \underset{\text{Soluble in } CCl_4.}{P_2N_2Cl_3NH_2} + 3NH_4Cl + \underset{\text{Both insoluble in } CCl_4.}{PN(NH_2)_2}$. The first substance is obtained at a low temperature in presence of a limited amount of NH_3 and the second with excess of the gas.

Phosphoric Acid Ethers of Guaiacol.—V. Auger and P. Dupuis.—The authors have obtained acid phosphates containing one or two molecules of guaiacol to one molecule of H_3PO_4 by three methods:—1. By boiling phosphorus oxychloride with guaiacol; according to the conditions of the reaction the product obtained is the dichloride of guaiacol phosphoryl, the chloride of diguaiacol phosphoryl, or the neutral phosphate of guaiacol. The hydrolysis of the chlorides gives the corresponding acids. 2. By allowing phosphorus oxychloride to react on a mixture of guaiacol and pyridine in the cold. The salt of pyridine obtained when decomposed by an alkali gives salts of the ether acids formed. 3. By saponifying with alcoholic soda the neutral phosphate of guaiacol.

Mechanism of Formation of Cyclic Compounds in Geranic Series. Synthesis and Structure of Dihydromyrcene.—M. Tiffeneau.—The condensation of methylheptanone in presence of zinc or magnesium, either with ethyl-α-bromopropionate or ethyl α-chloropropionate, gives the ethyl ether of oxydihydro-α-methyl geranic acid, which yields α-methyl geranic acid on saponification, $(CH_3)_3:C:CH.(CH_2)_2.CCH_3:C(CH_3).CO_2H$. When distilled slowly at the ordinary pressure the acid loses CO_2, and gives dihydromyrcene, $(CH_3)_2:C:CH(CH_2)_2.C(CH_3):CH.CH_3$. This hydrocarbon is identical with Enklaar's dihydroocimene. This synthesis

confirms Enklaar's conclusions on the nature of the terminal chain, $(CH_3)_2C=$, and shows that the dehydration of oxydihydromethyl geranic acid is effected at the expense of the neighbouring carbon atom.

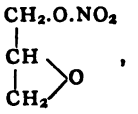
Berichte der Deutschen Chemischen Gesellschaft.
Vol. xli., No. 7, 1908.

Action of Dimethylsulphate on Alkaline Polysulphides.—W. Strecker.—Dimethylsulphate reacts very energetically with alkaline polysulphides, and when sodium pentasulphide is used an oil is obtained which contains approximately the amount of sulphur shown by the formula $(CH_3)_2S_5$. If the raw product is distilled under diminished pressure both from preparations derived from sodium penta- and tetrasulphides, methyltrisulphide is obtained.

Glycerin Nitrates.—W. Will.—When dinitroglycerin is prepared by Mikolajczak's method the resulting oil is a mixture of the two stereo-isomers :—

$$\begin{matrix}CH_2.O.NO_2\\ CH.OH\\ CH_2.O.NO_2\end{matrix} \quad \text{and} \quad \begin{matrix}CH_2.O.NO_2\\ CH.O.NO_2\\ CH_2.OH\end{matrix}.$$

They may be separated as follows:—The oil is allowed to absorb water from the air, and is then mixed with kieselguhr, and cooled. After some time crystallisation ensues. If traces of this solidified mixture are introduced into dinitroglycerin which has been exposed to the air, large clear prismatic crystals are at once formed. Small quantities of an oil remain, and the author has shown that the crystallising portion consists of one of the isomers and the oil of the other; he calls the former "Dinitroglycerin K" and the latter "Dinitroglycerin F." Both forms yield trinitroglycerin when nitrated, and from both of them the same mononitroglycide,—



can be obtained. Similarly, mononitroglycerin exists in two stereoisomeric forms, of which β-form yields only dinitroglycerin F when cautiously nitrated. The α-form fuses at 58° and the β-form at 54°. From the results of the author's experiments it is evident that the mononitrate fusing at 58° has the formula—

$$\begin{matrix}CH_2.O.NO_2\\ CH.OH\\ CH_2.OH\end{matrix},$$

while the β-form (melting-point, 54°) is—

$$\begin{matrix}CH_2.OH\\ CH.O.NO_2,\\ CH_2.OH\end{matrix}$$

The dinitrate, which does not crystallise, is—

$$\begin{matrix}CH_2.O.NO_2\\ CH.O.NO_2\\ CH_2.OH\end{matrix},$$

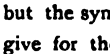
and the crystallising dinitrate is—

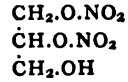
$$\begin{matrix}CH_2.O.NO_2\\ CH.OH\\ CH_2.O.NO_2\end{matrix}.$$

The following table shows the chief properties of glycerin and its nitrates :—

Glycerin—	
Specific gravity (15°)	1·27
Melting-point	17°
Boiling-point (15 mm.)	150—160°
Solubility in water at 15°	Unlimited.
Heat of combustion (H_2O liquid)	4317 cals.
Mononitrate—	
Specific gravity (15°)	1·40
Melting-point: α-Nitrate	58°
Melting-point: β-Nitrate	54°
Boiling-point (15 mm.), both isomers	155—160°
Solubility in water at 15°	70 per cent
Heat of combustion (H_2O liquid), α-nitrate	2812 cals.
Dinitrate—	
Specific gravity (15°)	1·47
Melting-point: α-Hydrate	26°
Melting-point: β-Hydrate	Liquid.
Boiling-point (15 mm.), both isomers	About 145°
Solubility in water at 15°	7·7 per cent
Heat of combustion (H_2O liquid): K, dried	2088 cals.
Heat of combustion (H_2O liquid): K, cryst.	1986 "
Heat of combustion (H_2O liquid): F	2055 "
Trinitrate—	
Specific gravity (15°)	1·60
Melting-point: Labile modification	2·2°
Melting-point: Stable modification	12·2°
Boiling-point (15 mm.)	Evaporates rapidly at 160° without boiling.
Solubility in water at 15°	0·16 per cent.
Heat of combustion (H_2O liquid)	1570 cals.

Constitution of Carbon Suboxide.—Otto Diels and Paul Blumberg.—The authors believe that the constitutional formula of carbon suboxide is not that ascribed to it by Michael,—

but the symmetrical formula  . The reasons they give for their opinion are as follows:—1. The boiling-point of the compound is 7°. 2. The compound resembles the metallic carbonyls. 3. The values of the molecular refraction and dispersion are high. 4. The compound shows great resemblances to ketenes. 5. Four atoms of bromine readily add themselves on, and the compound can be prepared from dibrommalonylbromide. 6. It is very improbable that a β-lactone with a triple bond exists. 7. The addition of water gives only malonic acid.

New Synthesis of Isoxazoles.—Julius Schmidt and Karl Th. Widmann.—By the action of red fuming nitric acid on β-diacetosuccinic acid ethyl ester at a temperature of from 0° to 5°, a fairly good yield of a compound with the empirical formula $C_{10}H_{13}NO_5$ is obtained. This is found to be α-methyl β-isoxazole γ-dicarbonic acid ethyl ester,  . The ester can be saponified by shaking with caustic soda solution, yielding α-methyl β-isoxazole γ-dicarbonic acid, from which the α-methyl isoxazole,  , can with difficulty be isolated by distillation.

Decomposition of Antimony Hydride.—Alfred Stock, Eusebio Echeandia, and Paul R. Voigt.—The investigation of the decomposition of antimony hydride at 0°, 25°, 50°, and 75° shows that at all four temperatures the variation in the velocity of the reaction is given by the equation $\Lambda = \frac{1}{Cx-p}$, where C is the concentration of the hydride in the space containing the gas and p is a constant.

The coefficient p increases as the temperature rises. All the phenomena observed agree with the assumption that the decomposition of the hydride occurs only in the layer adsorbed on the surface of the antimony.

Decomposition of Arsenic Hydride.—Alfred Stock, Eusebio Echeandia, and Paul R. Voigt.—The investigation of the decomposition of arsenic hydride is difficult, because the compound is split up only at comparatively high temperatures. Nevertheless, the authors have succeeded in showing that as the concentration of arsenic hydride falls the velocity of decomposition increases. This result agrees with the assumption that the reaction occurs only in the adsorbed layer.

Reactions of Pyridine.—Hans Th. Bucherer and Julius Schenkel.—When pyridine is subjected to the action of sodium bisulphite very labile derivatives are formed, which appear to be sulphurous acid esters. These are soluble in water and are not volatile in steam. They are characterised by the ease with which they are attacked by alkalis, which split off all the nitrogen in the form of ammonia in the cold. The authors have not yet completed the investigation of the action of bisulphite solutions on the homologues and isomers of the pyridine series. If a mixture of different homologues and isomers of pyridine bases is treated with excess of bisulphite solution, the product consists of soluble addition products and of insoluble or difficultly soluble pyridine bases; it may then be treated with water vapour, ether, or benzene to separate the original mixture into two different parts.

Reaction between Indigotin and Potassium Permanganate.—O. Miller and J. Smirnoff.—Mohr found that when indigotin is oxidised with potassium permanganate, 316·2 parts of permanganate oxidise 750 parts of indigotin, whereas the amount of the latter theoretically oxidised is 655 parts. The authors have repeated the titrations, using specially purified natural and synthetic indigo from which to obtain the indigotin, and they have arrived at a result which agrees with Mohr's, viz., that the oxygen used up is a constant amount (12·6 per cent) too small. The cause of this phenomenon does not lie in the composition of the indigotin. The authors have observed that when indigotin is sulphated no sulphurous acid is evolved, nor is the oxygen of the air taken up by the product of the reaction.

Red Phosphorus.—G. Linck and P. Möller.—When purified dried red phosphorus is sublimed at the melting-point of lead in an exhausted glass tube a black brittle mass, which shows no trace of crystallisation, is obtained. In thin fragments it appears red, and it contains 99·4 per cent of phosphorus. The specific gravity determinations gave results which varied from 2·145 to 2·192 at 18—20°, and this agrees almost exactly with that of commercial red phosphorus. By prolonged heating in a closed tube both forms can be converted into the crystalline form, the powder becoming a light red. From this it appears that a modification of phosphorus exists which is labile as regards the densest known form, and which possibly forms the isotropic amorphous phase, corresponding to red crystalline phosphorus. Mixtures of arsenic and phosphorus can readily be obtained if red phosphorus and metallic arsenic are sublimed together; the product of the sublimation exhibits a conchoidal fracture and a black metallic lustre, and in very thin splinters appears brown in transmitted light. The specific gravity varies between fairly wide limits according to the percentage composition.

Reduction with Platinum and Hydrogen at the Ordinary Temperature.—Richard Willstätter and Erwin W. Mayer.—Substances which are not volatile enough, or are too easily decomposed to be led over nickel, can readily be reduced by hydrogen in presence of platinum. This method can be applied to compounds containing the difficultly reducible ethylene bond. From phytene the saturated hydrocarbon phytane, $C_{20}H_{42}$, is obtained. Benzoic acid slowly takes up hydrogen in ethereal solution, and the hexahydro-compound is formed. Unsaturated alcohols, *e.g.*, erucyl alcohol, give saturated alcohols, or, as in the case of genaniol, a mixture of saturated alcohol and saturated hydrocarbon.

Hexathiocyanate Salts of Molybdenum.—Johanna Maas and J. Sand.—When a solution of ammonium molybdate and ammonium thiocyanate in hydrochloric acid is reduced electrolytically with platinum cathodes, from the reduced solution after a time yellow crystals separate out in the cold. These have the formula—

$$\overset{IV}{Mo}(SCN)_6 \begin{matrix} NH_3H \\ NH_3H \\ NH_3 \\ OHH \end{matrix} + 3H_2O.$$

The ammonium salt forms a very characteristic acetate, $[\overset{IV}{Mo}(SCN)_6(NH_3)_3HOH\,{}^{H_2}_{CH_3.COOH}$. By the electrolytic reduction of hydrochloric acid solutions of potassium molybdate-potassium thiocyanate a very pure potassium salt can be isolated, containing the group $Mo(SCN)_6R_3$. Besides loosely bound water of crystallisation the salt contains a firmly bound oxygen atom for each molybdenum atom. Hence it might be supposed that trivalent molybdenum is present and one aquo molecule is contained in the complex, *i.e.*, the formula is $[\overset{III}{Mo}(SCN)_6H_2O\ K_3 + 4H_2O$. If a hydrochloric acid green solution of pure molybdenum trichloride is used as the starting-point, only traces of the salts of the yellow series are formed. Hence tetravalent molybdenum is undoubtedly present, and the structural formula is—

$$\begin{matrix} R{-}SCN & \cdots & IV. & \cdots & SCN \\ R{-}SCN & \cdots & Mo & \cdots & SCN \\ R{-}SCN & \cdots & | & \cdots & SCN \\ & & OH & & \end{matrix} + 4H_2O.$$

In all the derivatives of the yellow series the hydroxyl group can be detected, and thus apparently the hexathiocyanate compounds belong to the class of hydroxo-salts; possibly they are allied to Werner's "*ol*" salts. This hydroxyl, however, does not possess the well marked basic properties of the hydroxyl in the typical hydroxo-salts of cobalt. The hydrohexathiocyanate salts, especially the ammonium and potassium salts, give with acids addition products, which are split up into their components in aqueous solution. The co-ordination number of tetravalent molybdenum appears to be 8. The formula of the potassium salt-acetate is given in the original paper.

MISCELLANEOUS.

Albert Medal of the Royal Society of Arts.—The Albert Medal of the Royal Society of Arts for the present year has been awarded, with the approval of His Royal Highness the President, to Sir James Dewar, M.A., D.Sc., LL.D., F.R.S., "For his investigations into the liquefaction of gases and the properties of matter at low temperatures, investigations which have resulted in the production of the lowest temperatures yet reached, the use of vacuum vessels for thermal isolation, and the application of cooled charcoal to the separation of gaseous mixtures and to the production of high vacua."

NOTES AND QUERIES.

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

Carbon Tetrachloride.—A correspondent would be glad to know who are the makers of carbon tetrachloride.

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END OF VOLUME XCVII.