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No. 1936.—JANUARY 1, 1897.

SEA-WATER MICROBES IN HIGH LATITUDES.

By E. FRANKLAND, D.C.L., F.R.S.,
and W. T. BURGESS, F.I.C.

THE bacteriology of sea-water is beginning to receive deserved attention from biologists, for it lies at the very foundation of the marine flora and fauna, as bacteria doubtless form the initial food of higher marine organisms; unless indeed there be a still more minute world of living matter too small for discovery by our present modes of investigation.

In the year 1892, Mr. H. L. Russell examined at the biological station in Naples, a number of samples of sea-water collected at various depths in the Bay of Naples. The water at or near the surface was found to contain a number of colonies per c.c., varying from 64 at four kilometres from land, to six at fifteen kilometres. There was, however, no constant relation between the numbers of bacteria and the distance from land; thus, at eleven kilometres from land 78 per c.c. were found. On the other hand, Sanfelice and de Giaxa found a rapid reduction on receding from the shore, but only within a distance of three kilometres.

In 1894 M. Cassedebat studied the action of sea-water upon pathogenic organisms, and found that in sterilised sea-water *Staphylococcus aureus* died in twenty-two to twenty four days, *Citreus* in nineteen to twenty-two days, *B. Friedländer* in thirty-five to forty days, *B. Anthracis* in twenty-one to twenty four days, *B.* of green diarrhæa in sixteen to twenty days, *Spirillum Deneke* in twenty-two to twenty-five days, *Proteus vulgaris* in twenty-three to twenty-six days. The cholera bacillus lived more than thirty-five days, but the typhoid bacillus died in forty-eight hours.

The most complete bacteriological investigation of sea-water hitherto undertaken was made by Drs. Bernhard Fischer and E. Bassenge, and the results are published in the *Centralblatt für Bacteriologie*, 1894, xv., 657. They include microbe determinations in the waters of the Atlantic, English Channel, the Baltic, and the North Sea. The places where the samples were taken range from 8° S. Lat. to 60° N., and were collected at various seasons during the celebrated Plankton expedition, and on a voyage to and from the West Indies. The plate cultures were made with gelatin containing 2 per cent of agar-agar dissolved in a little sterilised sea-water, and the final investigation of the pure cultures was made in the Bacteriological Institute at Kiel.

The maximum number of microbes found at the surface was 29,400, the minimum 0, and the mean in 175 samples 1083. The mean was only surpassed 26 times; seven samples developed no organisms, fifty-seven developed from one to twenty-five colonies, seventeen from twenty-six to fifty, and fourteen from fifty-one to one hundred colonies per c.c. The highest numbers were found near land, thus confirming, in this respect, the observations of Sanfelice and de Giaxa in the Bay of Naples. It was also found that sunshine affected the number of bacteria at the surface.

During the recent solar eclipse expedition to Vadsö, we were able to extend these observations up to 71° N. lat., Captain Eilertsen, of the Bergen Company's steamer *Neptun* kindly stopping the ship whilst we took the samples. The water for bacteriological examination was collected at about 2 feet from the surface in glass tubes (previously exhausted, sealed, and sterilised) by means of the apparatus devised by one of us and described in the CHEM. NEWS, lxx., p. 54. The colonies were counted after about five days incubation at 20° C.

Sample No. 1: Vest Fjord, five miles from land, lat. 68° N., at 6 a.m. Aug. 5, 1896; No. of colonies, mean of two cultivations, 51 per c.c.

Sample No. 2: Off Loppen, about three miles from land, lat. 70° 12′ N., at 10 a.m. August 6, 1896. Unfortunately, the note of the number of colonies counted, in duplicate cultivations of this and of the following sample, has been lost; but the average number in each case did not differ materially from that obtained from the Vest Fjord water.

Sample No. 3: Off the North Cape, about two miles from land, lat. 71° 10′ N., temperature of sea 7·8° C., 1 a.m. August 7, 1896. A blank culture plate, similarly treated in every way, did not yield a single colony.

No sample was taken in the Väranger Fjord on account of proximity to land and the towns of Vardö and Vadsö. The temperature of the sea in the Fjord at 7 a.m. on August 8 off Vadsö was 9·0° C.

We have to apologise for this very fragmentary record of bacterial life in the Arctic Ocean, but we trust that it may have the effect of directing the attention of arctic and antarctic voyagers to the subject; for, in view of the important relations existing between microbes and animal life in the arctic regions, it is very desirable thut these observations should be carried on up to higher latitudes, especially where the temperature of the sea does not rise above 0° C.

ON THE SPECTRA OF COPPER, SILVER, AND GOLD.*

By J. M. EDER and E. VALENTA.

Our former preliminary research had shown that the elements copper, silver, and gold give continually new results on the variable spectra of the elements, for these elements yield spark-spectra extremely rich in lines for surpassing the corresponding arc-spectra in number and sharpness. These researches were commenced two years ago, but could not then be completed, as the spectrograph with a quartz prism at the disposal of the authors had too slight a dispersion in the less refrangible regions, and the spectrograph with a compound glass prism supplied this deficiency in the blue and the violet as far as the beginning of the ultra-violet, but was not sufficiently effective in the visible part.

We obtained two excellent Rowland's concave gratings with a very short focus, giving an admirable definition if the light was very strong. We selected one which produced the spectra of the first, second, and third order with great clearness. The spectra on both sides of the grating never show a pefectly equal brightness.

The ultra-violet of the first order, of $\lambda = 3900$, at about 2500 is moderately bright, but from λ 2500 very faint. The spectrum of the second order is decidedly darker on the red, the yellow, and the green than the spectrum of the first order, which is in this region three times brighter than the latter. On the contrary, the brightness of the spectrum of the second order is very great. From λ 2800 to λ 1900 we worked with the quartz spectrograph with one prism, which in these regions is far superior to the grating spectrograph in brightness and in resolving power. The spectrum of the third order is with our grating very bright; in the ultra-violet of λ 2200 it is about equal in brightness to the ultra-violet of the second order, perhaps somewhat brighter. Consequently the spectrum of the second order is intersected by very luminous lines of the third order, which require to be separated out and identified, and then furnish an exceedingly sharp control for the measurements of the spectrum of the second order. The violet and ultra-violet near the Fraünhofer line H come up so strongly in the spectrum of the third order as even to penetrate light yellow glass, and can be eliminated only by dark yellow glasses or concentrated strata of picric acid. The spectrum of the fourth order was plainly visible in the grating which we used, but its brightness is small.

The authors reproduce an important illustration from Ames's memoir, "The Concave Grating in Theory and Practice," taken from the *Johns Hopkins University Circular*, No. 273, 1889.

As a source of error in working with the grating-spectrograph are mentioned the so-called ghostly lines, which sometimes appear as rather sharp lines at almost equal distances, or sometimes as a unilateral expansion of very intense lines.

1. The copper lines 5782, 5218, and 5105 correspond to the lowest temperature prevailing in the Bunsen flame.
2. The same lines with an accession of Cu $\lambda = 5700$, 5292, 5153, 4704, 4651, and 4275, pertain to the rather higher temperature of the faint sparks springing on between electrodes saturated with copper chloride.
3. All the lines occur in the arc-spectrum, and at the highest temperatures of the arc-spectrum, and must consequently be considered as constant lines peculiar to copper at the most variable temperatures.
4. In the arc-spectrum there occur far more lines than in the cases described under 1 and 2, which holds good especially for the more strongly refrangible lines. As especially characteristic lines, in addition to those mentioned under 1 and 2, we mention $\lambda = 4062$, 3308, 3275, 3247, 2392.
5. In the spark-spectrum all the main lines mentioned under 1, 2, and 3 occur also as principal lines. In addition there appear many very intense new lines which are wanting in the arc- and the flame-spectra, whilst some strong Cu lines of the arc-spectra recede or disappear at the high temperature of the spark of the Leyden jar.

As regards these phenomena, the Cu-spectrum must be regarded as very variable according to the temperature.

Silver, even in the strongest Leyden jar spark, is less luminous than copper or gold. When the Ruhmkorff spark strikes over, the atmospheric lines come up very strongly, so that we were compelled to work in an atmosphere of hydrogen. But even in this case the subordinate rays of the Ag-spectrum were but feebly luminous. A number of the silver lines in the green part of the spectrum are extended into bands, but there are many sharp lines, and in the more refrangible part of the spectrum sharp lines predominate.

The spectrum of silver must be considered as variable, since it becomes extremely rich in lines by the accession of intense silver lines in the hot Leyden spark. The moderately bright lines of the arc-spectrum are mostly retained, but are often surpassed in intensity and sharpness by the new lines of the spark-spectrum.

The spectrum of gold is less known than the spectra of copper and silver. The lines of Lecoq, $\lambda = 5601$, 5230, 5210, 4437, 4338, and 4064, do not belong to gold. 5601 and 5210 belong to palladium, 5228 and 4442 to platinum, and 4355 to air (nitrogen).

Krüss was in error in ascribing the line 4064 (more correctly 4065) to nitrogen, since it appears distinctly in an atmosphere of pure hydrogen.

The authors have observed 660 lines in the spark-spectrum of gold, 50 of which are common to the spark and arc spectra, but more than 500 are new lines.

CALCIUM CARBIDE: A NEW REDUCING AGENT.

By H. N. WARREN, Principal, Liverpool Research Laboratory.

Since the introduction of this remarkable substance, it is significant that scientific men have been content to allow the product to rank solely as a water decomposer, and thus regard the production of acetylene the only available product.

Researches of a somewhat lengthy description, which have lately been carried out at the above laboratory, involve the use of calcium carbide as a metallurgical reducing agent.

In the first instance an excess of litharge was heated to redness in contact with the carbide, in a clay crucible, the reaction being accompanied by vivid incandescence, resulting in the formation of metallic lead and calcium oxide, CaO.

A further portion was now selected, in which the proportion of carbide excelled that of the litharge; this was further subdivided into various smaller portions, each portion being exposed to various temperatures, resulting in a regulus of calcium and lead of varying percentage, together with the expulsion of CO_2.

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* An especial reprint from the *Transactions of the Mathematical and Natural Science Class of the Imperial Academy of Sciences, Vienna*, 1896.

The alloys thus formed are all more or less brittle, and to a certain extent sonorous when struck, their melting-point ranking below that of pure lead, and are slowly, but completely, decomposed in contact with aqueous vapour, the reaction being much less energetic than that afforded by alloys of lead with the alkaline metals. Stannic oxide, cupric oxide, and also ferric oxide, at corresponding higher temperatures, were readily reduced, yielding results of no practical value; in the case of the cupric alloys those samples containing under 1 per cent of calcium being rendered cold-short and breaking under very small strain, whilst, on the other hand, iron containing calcium approaches in appearance that of ferro-manganese, being even more brittle, and very oxidisable in contact with water.

In a further operation, oxides of manganese, nickel, cobalt, and even chromium, molybdenum, and tungsten, were readily reduced, yielding calcium alloys. Results of experiments, comprising the reductive action of the carbide upon the earthy chlorides and their haloids, will be shortly to hand. The already partial success of these reactions seem to point most conclusively towards a new and powerful reducing agent, which at the same time, considering the market value of the carbide in question, could not fail to replace both sodium and potassium.

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THE MANUFACTURE OF CALCIUM CARBIDE.*

By J. T. MOREHEAD and G. de CHALMOT.

So universal is the interest in acetylene gas and so different the estimates and opinions as to the cost of calcium carbide as a source of the cheap production of acetylene gas, that we have thought it desirable to place on record the data from our actual experience in the production of calcium carbide in quantities. The works of the Willson Aluminium Company have been running night and day since May 1st, 1895, producing calcium carbide. These works are daily duplicating the results here given and can expand indefinitely. Each individual step, except water power, as taken at Spray, N. C., is capable of being changed in the direction of reducing the cost of the output, as these efforts have been attended with the clumsiness, lack of adaptability, and excessive cost that is incident to all efforts along an untrodden path. Still we can produce calcium carbide at less than 25 dols. per ton, including wear and tear and interest on capital.

Beyond looking after the dynamos, no special training is necessary, as neither metallurgical nor chemical skill is required in the operations. We grind and mix coke and lime, start the water wheel, see that the arc is formed, shovel in the mixture of lime and coke, and the volt- and ammeter show when to lower or raise the carbon pencils, which is done by means of a screw located in the dynamo room, away from the furnace. We can measure with an ordinary yard stick on this screw the height of the piece of carbide in the furnace. We stop when we have raised the carbon pencils 33 inches, switch the current off to another furnace and repeat the operation. The carbide in the former furnace, as soon as cooled and brought in contact with water, is all ready to do perfect work in generating acetylene gas; it will proceed with this work without help and will make room therefor in spite even of bands of steel.

Water power costs us 6 dols. per horse power. Water in the raceways ready for the water wheels is now offered in enormous quantities to the Willson Aluminium Company at the rate of 5 dols. per horse power per year. These powers are located at different places, where coke and lime can be had cheaply, and also cheap transportation for the carbide to the market.

The technical description of our process which follows herewith was written by G. de Chalmot, who has had for some time personal supervision of the operations of the Willson Aluminium Company.

In the year 1888 Mr. T. L. Willson started a series of experiments with a view of reducing refractory ores in the electric furnace, and among other valuable things he made calcium carbide.*

We will first give a short description of the furnace and a general outline of the process, then enlarge somewhat on the details. The furnace used in Spray, N. C., is built of ordinary brick (a sectional front view is given in Fig. 1). The front side is formed by four iron doors, the one above the other. The upper two remain closed usually. The chimney is attached near the top of the furnace, and commences with a flue, *m*, in the corner. The furnace measures at the bottom inside 2½ by 3 feet. The electric current enters at the bottom and top. The bottom electrode is an iron plate, *a*, covered with 8 inches of carbon, *b*. For this covering we use pieces of carbon pencils or a mixture of coke and coal tar. Sixteen copper cables of 0·75 inch in diameter, *c*, convey the electricity from the dynamos to the bottom electrode.

Sixteen other cables are connected with the top electrode, *d*. The top electrode is composed of six carbon pencils, *e*, each 4 inches square and 36 inches long. Six pencils are arranged in three pairs behind each other, and are cut out at the top so as to fit in the carbon holder, *f*. They are enveloped together by a sheet of iron, *g*, which is shown in the right-handed furnace of Fig. 1. They really form one pencil. The carbon holder is screwed to a copper bar, *h*, which is three inches square, and to which the copper cables are connected. This bar is fastened by a chain that runs over two pulleys to a long upright screw, *i*. On this screw is a nut which forms the centre of a wheel, *k*. By turning the wheel the screw can be raised or lowered. The man who attends to the wheel has the volt- and ammeter before him. The electric current is generated in two dynamos to which transformers are connected, and which can give a current of from 50 to 100 volts. The power is furnished by a water wheel of 300 horse power under 28 feet fall.

Two of the furnaces have been working for twelve months, and they have given satisfaction, except for working not sufficiently economically. In the furnaces built for the Niagara Falls Carbide plant many changes which we suggested have been adopted, looking to economy of production. We give here a short description of these furnaces (Figs. 2 and 3).

In Spray it is necessary to allow the furnace to cool before emptying it. In order to use one and the same furnace continuously, the bottom of the furnace is replaced by an iron car, *a*, which runs on a track, and in which carbide is formed. When the car is filled the pencils, *b*, have been lifted entirely out of it. The current is then shut off, door *c* is opened, the full car is run out and replaced by an empty car. The pencils are lowered again to the bottom of the car and a new run is commenced.

The bottom of the car is covered with from 4 to 8 inches of carbon. When the contents of the car have sufficiently cooled outside the furnace, which will take from six to twelve hours, the body of the car is lifted from the track by the trunnions, *d*, and turned over. The con-

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* Read Sept. 3rd before the Springfield meeting of the A.A.A.S. by one of us (M). We have made since then several additions, so as to make the article complete up to the present time. From the *Journal of the American Chemical Society*, April, 1896.

* We will note here that Moissan, who discovered this process for making carbide, independently of Mr. Willson, communicated incidentally, at the meeting of the French Academy of December 12th, 1892 (*Compt. Rend.*, 115, 1033) that a carbide of calcium is formed if calcium oxide is heated in an electric furnace with carbon electrodes. He investigated the compound much later (*Compt. Rend.*, 118, 50). Mr. Willson, who sent, during the summer of 1892, samples of carbide, for examination, to Lord Kelvin, of the Glasgow University, clearly antedates Moissan. See *Journal of Franklin Institute* of 1895, page 333.—Note.

tents are dropped on a grate formed of iron bars, on which the piece of carbide remains, while the unreduced material falls through into a lower room, where it is collected to be used again for the formation of carbide. The mixture of lime and coke is fed into the car through the flues, *e*, which extend along the whole length of the car. The rods, *f*, which bear four blades, extend through the whole breadth of the feeding flues. These rods are turned automatically, and the faster they turn the more material is fed into the car. In order to stoke the furnace automatically, the car is attached to an iron bar, *g*, by two hangers and a coupling in front of the car. Bar *g* extends through the back wall of the furnace, and is automatically moved forward and backward for about 2 inches and about twenty times per minute. The car is thus also rolled backward and forward on the track for about 2 inches each time. Every time that the car stops or starts it gets a little jerk which is sufficient to fill up the holes made by the escaping gases in the loose material. This motion of the car further prevents the arc being located for a longer time at one point, for which the arc has always a great tendency. This will materially increase the efficient use of the heat of the arc. Under the track of the car is the bin, *h*, in which the unreduced material is collected that will fall from the car when this is taken out. This material can from time to time be taken out through the door *i*. The carbon holder is more complicated than in the Spray furnace. Twelve carbons are used, and the holder is therefore about twice as heavy. It is not advisable to suspend this carbon holder from a copper bar, which moreover becomes rather hot in this closed furnace. The carbon holder is therefore attached to a rod, *l*, which is composed of three slabs. The inner one is of copper, and measures 6 by 1½ inches, and the outer ones are of iron and are 6 inches by 1. Since it is not practical to attach the twelve carbons in their iron casing to the carbon holder in the furnace, the holder itself is composed of two pieces, *m* and *n*, which slide into each other. The aggregate of pencils is connected to piece *n* outside the furnace, and the whole is placed in the car *a*. Rod *l* is so far lowered that piece *m* will easily slide into piece *n*, and the connection can easily be effected. Iron plates, *o*,

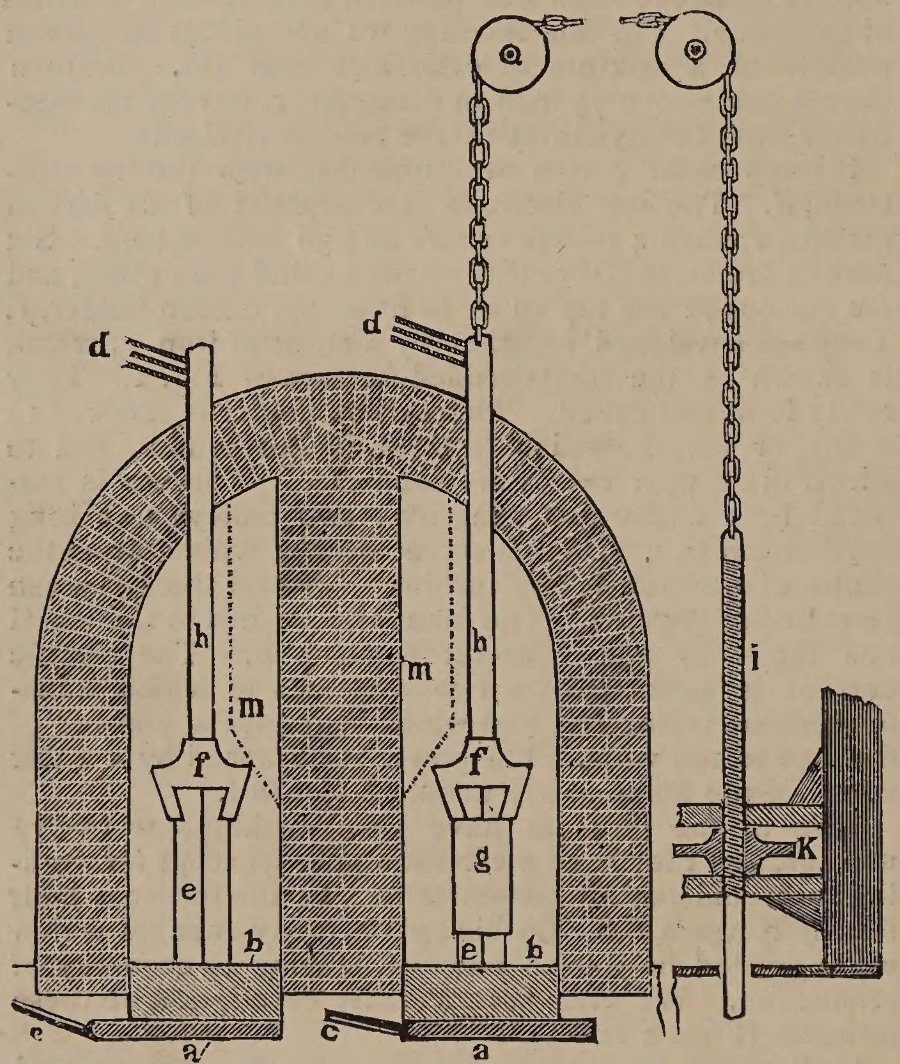


Fig. 1.

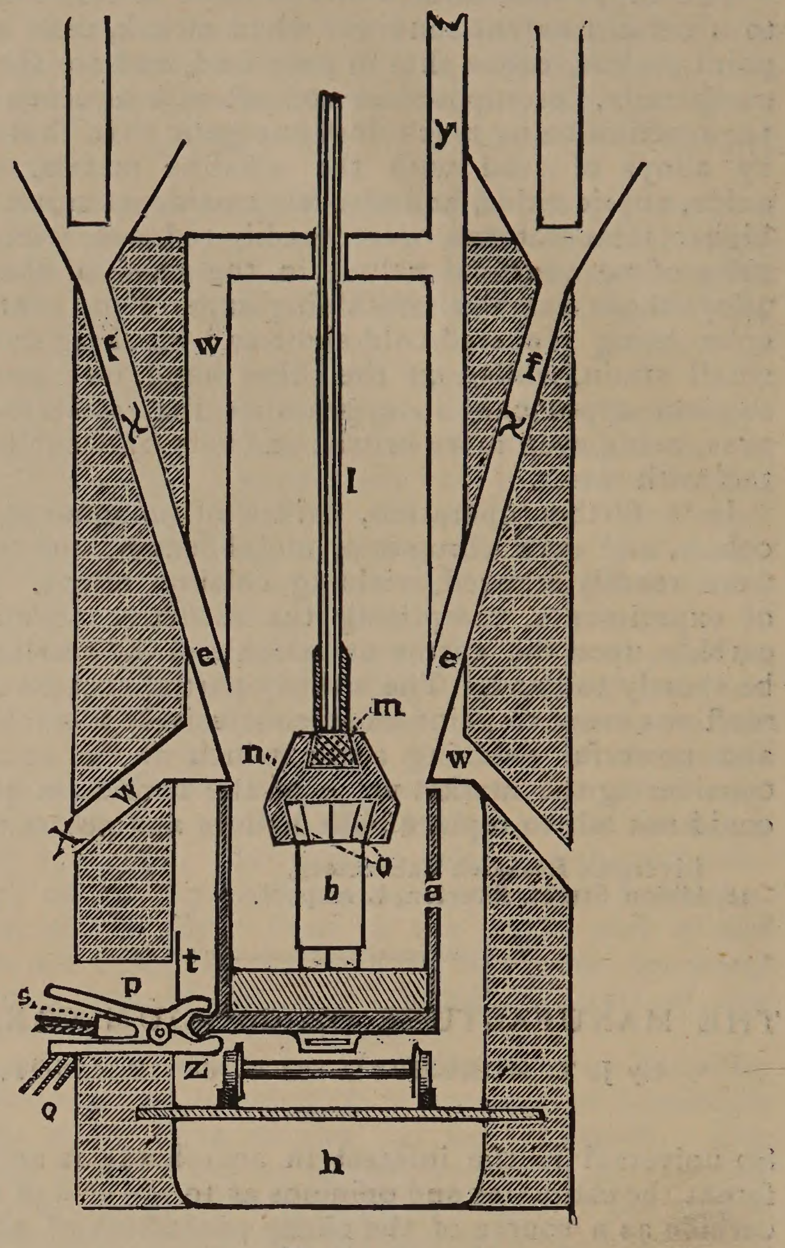


Fig. 2.

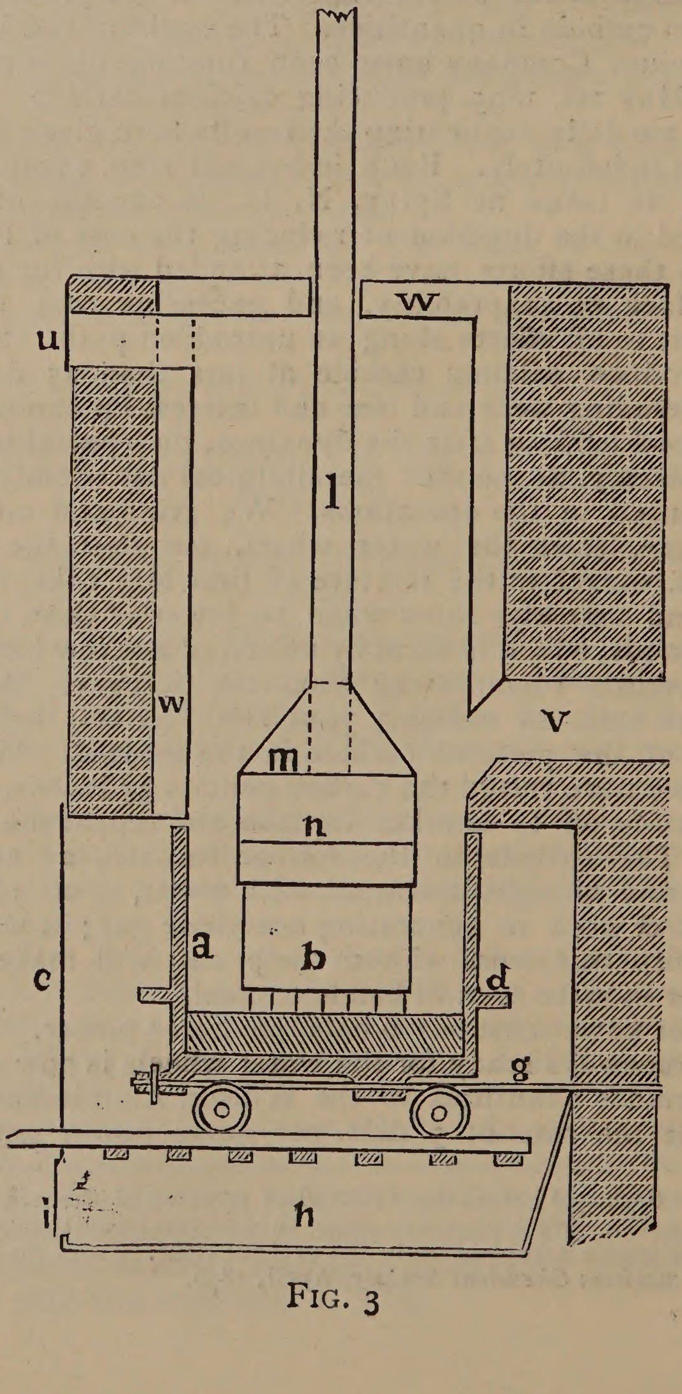


Fig. 3

are placed between the carbon holder proper and the pencils. These plates, *o*, are about 1 inch thick. They are fastened to the inside of the carbon holder by pins which are inserted in the holder, and fit in holes of the plates. These plates can be easily removed and replaced. It will sometimes happen that a small arc is started between the pencils and the inside of the carbon holder, and a part of the carbon holder will melt. In the case that the plates *o* are used one can simply replace these plates. The car *a* forms one of the electrodes, and is connected with the bottom cables, *q*, by two clamps, *p*. The lower clamp is stationary and the upper one can be opened. The clamps are tightened around the appendage *z* of the car by a wedge and screw, *s*. When the clamps are fastened the slide *t* is lowered so as to shut the opening. The electric connection with the car can also be and is better made through the bar *g*, which in that case is composed of an iron and a copper slab. It may also be made by two copper bars which run alongside of the car and are pressed against it with springs. The furnace is entirely closed. When it is started the door *c* is shut, but the door *u* is kept open till the carbon monoxide, which is formed in the reaction, has replaced the air in the furnace. This point is reached when the flame comes out of this door. Door *u* is then also closed and the gases escape through the chimney, *v*. The use of door *u* prevents explosions of the carbon monoxide in the closed furnace. Chimney *v* begins just over the car The carbon holder and the rod *l* are therefore not in the current of the hot gases. The upper part of the furnace is cooled moreover by an air jacket, *w*, through which a draught of air is maintained. The cold air enters through openings *x* and the warm air is led off by chimney *y*. The warm air may be utilised for heating the building. The chimney gases pass through flues or rooms, in which the lime dust is collected by proper means. Owing to valuable suggestions of our superintendent, Mr. J. C. King, this furnace is called the King Furnace. Besides these two types of furnaces, several others have been proposed.

In order to start our present furnace, we shut the lower iron door and lower the pencils to the bottom of the furnace. The current is turned on and the mixture of coke and lime fed in, the arc being kept covered with the mixture as high as one foot around the pencils. It is then easier to keep the arc steady. It is necessary to stoke from time to time, for the gases which are formed in the arc constantly make channels through the material, and especially if unslacked lime is used. These channels will not fall in, and less material will come into the arc. The feeding in of the material is continued for several hours. If the attendant at the hand wheel sees that the voltage becomes low, he raises the pencils. If the arc should be broken the ampèrage becomes zero and the voltage high, and in that case the pencils are quickly lowered. After shutting off the current it is well to allow the furnace to cool two or three hours before emptying it.

(To be continued).

QUANTITATIVE ANALYSIS OF SPECTRA.

A new method has been elaborated by G. and H. Krüss, and is now published by H. Krüss after the death of G. Krüss (*Zeit. Analyt. Chemie*).

If a substance in a layer of a substance, of a thickness = 1, enfeebles by absorption the light which it transmits from the intensity—

$$\text{I to } \frac{1}{n}\,\text{I}$$

(and has therefore the enfeebling factor $\frac{1}{n}$ for the stratum 1), the intensity I′ of the light passing through a stratum of the thickness *m* will be—

$$(1)\ ..\ \text{I}' = \frac{1}{n\ m}.$$

(This applies strictly for monochromatic light with only one factor of enfeeblement).

If we assume the original strength of the light = 1, we obtain the equation—

$$(2)\ ..\ \text{I}' = \frac{1}{n\ m}.$$

$$\text{Therefore log. } n = -\frac{\text{log. I}'}{m}.$$

Ir we call *e* the coefficient of extinction of the substance concerned,—that is, the reciprocal value of the thickness of the stratum which is necessary to reduce the transmitted light to $\frac{1}{10}$th of its original intensity,—then when—

$$m = \frac{1}{e}\ \text{I}' \text{ will } = \frac{1}{10}.$$

Hence follows log. *n* = *e*, or also—

$$(3)\ ..\ e = \frac{\text{log. I}'}{m}.$$

If we work with the stratum *m* = 1 we have—

$$(4)\ ..\ e = \text{log. I}'.$$

The coefficient of extinction is hence equal to the negative logarithm of the residual brightness. When this has been determined for the stratum = 1 it may be taken directly from the proper tables.

The authors justly point out that to many the process is rendered less intelligible by the circumstance that we do not measure the thickness of the stratum at which the brightness is reduced down to $\frac{1}{10}$, but in its stead that effected by a constant depth of stratum which is of different thickness for each body.

In order to draw a conclusion as to the concentration of a solution from its coefficient of extinction as thus determined, we must consider that the reduction of brightness depends only on the quantity of the absorbent substance present in a given depth of the solution, so that a greater concentration of the liquid at the same depth must have the same effect as the introduction of a corresponding deeper stratum of a solution of an unchanged concentration. Hence it follows that the ratio of the concentration, *c*, to the coefficient of extinction, *e*, for each absorbent substance, is a constant which must depend on the kind of the substance. It is known as the absorbed proportion—

$$(5)\ ..\ \text{A} = \frac{c}{e},$$

whence, if A is known, the concentration follows from the measurement of *e*.

$$(6)\ ..\ c = \text{A}.\,e.$$

The authors, in order to obviate the above difficulty, have modified the procedure, so that the depth of the stratum, *m*, which occasions a certain reduction of brightness, is really measured.

If the intensity, I, of the light, is reduced to I′ by a stratum, *m*, of a solution of the concentration, *c*, whilst a stratum of the thickness 1 of a solution of the same substance of the concentration 1 reduces the light to $\frac{1}{n}$, we have—

$$(7)\ ..\ \text{I}' = \frac{\text{I}}{n\ m\ c}.$$

If we put—

$$\text{I}' = \frac{\text{I}}{x},$$

then follows $x = x = n\, m\, c$, or log. $x = m\, c$, log. n.

$$(8) \quad .. \quad c = \frac{1}{m \log. n}.$$

n, the specific power of absorbing light, is for each substance a constant; accordingly also log. n_1 respecting its reciprocal value, we call k. Thus we have—

$$(9) \quad .. \quad c = \frac{k}{m}.$$

This magnitude k is nothing better than the absorptive ratio A as above reduced, for we had above $c = A.\, e$, and we have here further (if m is selected so that $x = 10$),—

$$e = \frac{1}{m},$$

whence there follows—

$$c = \frac{A}{m}.$$

The apparatus used by the authors cannot be intelligibly described without the accompanying figure.

In using the apparatus we pour into one of the vertical tubes the solvent liquid, and into the other the liquid to be examined, and we allow the light from a Hübner reflecting prism to fall upon a spectro-photometer, so adjusted that, with equal illumination, one-half of the field of vision has only one-tenth the brightness of the other half.—*Zeit. Analyt. Chemie.*

CASES OF ISOMERISM IN THE PYRAZOL SERIES.

By R. VON ROTHENBURG.

1. *The Question of the Constitution of the (c)-Phenylpyrazol Series.*

I have mentioned in the *Berichte* (xxvii., 789) that I have obtained Buchner's phenylpyrazol, melting at 228°, along with other more fusible products, by the action of hydrazin hydrate upon benzaldehyd.

Knorr, by the reciprocal action of the same substances, has obtained merely phenylpyrazol, melting at 78°. He believes, on the basis of theoretical speculations, that the phenylpyrazol melting at 228° must be (4)-phenylpyrazol, and hence declares my statement as "puzzling."

Recently, Buchner has contradicted the views of Knorr, and shown that neither his theoretical expositions nor their experimental proofs are in all respects trustworthy.

Before anew taking part in the discussion, it seems advisable to describe accurately the experiment which I formerly instituted.

Crude benzoylaldehyd—obtained in the ordinary manner—was mixed with ½ mol. hydrazin hydrate in an alcoholic solution, producing a violent reaction. The mixture was then heated for some time in the water-bath, poured into several times its volume of water, the oil was taken up in benzene, separated from the water, and the basic constituents were withdrawn from the oil by means of dilute hydrochloric acid. The solution thus obtained yielded the platinum salt which I have described (*loc. cit.*), and after neutralising with soda a crystalline mass which, on fractional crystallisation, yielded first slightly yellowish crystals melting at 228°, and subsequently fractions fusible below 100°, which I have already described as an isomer. The yield of product fusible at 228° was about 10 per cent of the amount to be theoretically expected.

That both phenylpyrazols (melting-points 228° and 78°) should be obtainable from benzaldehyd does not agree with Knorr's theory of the pyrazol nucleus, but it does not clash with the behaviour of phenylhydrazin with benzoylaldehyd; the less so, as both pyrazols were also obtained by means of diazoacetic ester, and in various proportions, without succeeding in exactly ascertaining the experimental conditions favourable to the formation of either isomer.

In spite of the brilliant experimental researches of Knorr on the pyrazols, which showed the formation of only one methylpyrazol from oxymethylenaceton, which allowed the same methylpyrazol to be obtained from two isomers of the phenol series, and in spite of the production of a (3, 4, 4, 5)-tetramethylpyrazol, no unobjectionable proof has been furnished that also (3)- and (5)-phenylpyrazol must be identical, since it is evident that the methyl and the phenyl-group must have a very different influence.

(5)-Phenylpyrazol, or pyrazol (5)-carbonic acid, must be obtainable by the oxidation of the (5)-phenylpyrazolin obtained by me from cinnamelydenazin. May I, since I cannot at present execute these experiments, address to Dr. Buchner the request that he would include these investigations within the scope of the oxidations which he has in view?

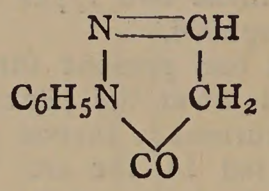
Buchner has pointed out that a resorcin fusion performed at too high a temperature is no proof for the presence of an *o*-dicarbonic acid; since resorcin alone, if heated for a long time at a sufficiently high temperature, or in presence of a condensation agent, yields strongly fluorescent melts. Knorr has totally overlooked this fact.

Buchner's resorcin fusion at a sufficiently low temperature, and my synthesis of hydrazin hydrate, require imperatively that phenylpyrazol (228°) must not be regarded as (3)- or (5)-phenylpyrazol.

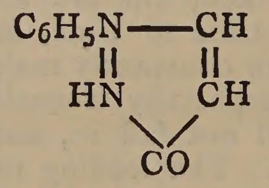
If Knorr does not view Buchner's or my statements as founded on air, he must admit that phenylpyrazol (228°) cannot be (4)-phenylpyrazol.

2. *On the Synthesis of Antipyrine.*

About a year ago I described (*Berichte*, xxvi., 2974) a method for obtaining a phenylpyrazolon (melting-point 155°), previously obtained by different methods, and I assigned it the constitution—



On the contrary, F. Stolz advocated the formula—



He grounded his opinion essentially upon the circumstance that the isomeric phenylpyrazolon melting at 118° must have the formula which I assumed for the phenylpyrazolon melting at 155°, since it is formed from oxalacetic ester hydrazon. I did not then touch upon this point, as the production of phenylpyrazolon melting at 118° from oxalacetic ester hydrazon takes place in a manner which admits of no inference as to its constitution. On the other hand, formalacetic ester forms with phenylhydrazin not the phenylpyrazolon fusible at 118°, but that melting at 155°.

Stolz certainly contests that this pyrazolon can here come into consideration, but he has not found it necessary in any manner to establish his opinion. Why, lastly, has he not obtained (1)-phenylpyrazolon from oxalacetic ester and phenylhydrazin in the same manner in which I obtained pyrazolon itself by means of hydrazin hydrate?

In the meantime there have appeared memoirs and patent specifications which induce me to oppose energetically the constitutional formula of Stolz as entirely untenable.

If, as Stolz assumes, phenylpyrazolon fusible at 118° were really the lower homologue of Knorr's (1)-phenyl-(3)-methylpyrazolon fusible at 127°, both would be obtainable in an analogous manner by the circuitous way of phenylethoxylpyrazol; but this is not the case.

Whilst the hydrazones of the β-ketonic esters when heated alone pass into normal pyrazolones, with abscission of alcohol, they are converted by acid condensation agents into alkyloxypyrazols, and by concentrated sulphuric acid into indol-derivatives.

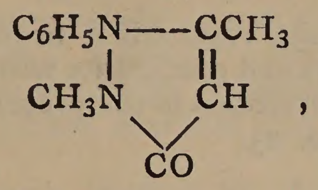
It seems to me free from doubt that the formation of indol, and that of the alkyloxypyrazols, occasionally occur collectively, and the non-symmetric hydrazines formed split off ammonia or water.

It is not surprising that in an acid solution the more basic pyrazol is formed rather than the very feebly basic pyrazolon. It can be explained only under these suppositions, that we do not obtain from acetacetic ester pyrazolon Knorr's pyrazolon fusible at 127°.

From the (1)-phenylpyrazolon-(3)-carbonic ester the Höchst Colour Works obtain (1)-phenyl-(2)-methylisopyrazolon of the melting-point 117°.

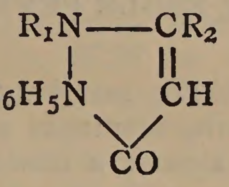
From Walker's (1)-phenylethoxylpyrazol there is certainly also formed a phenylmethylisopyrazolon fusible at 117°, but it must be (2)-phenyl-(1)-methylisopyrazolon, which melts at about the same temperature. The melting-points of the (1, 2)- and (2, 1)-isomers are so near together that they cannot be used for characterising and distinction.

Knorr's pyrazolon (127°), as already remarked, is different from the "phenylmethoxypyrazol" obtained on treating the phenylhydrazon of actetacetic ester with acid condensing agents and saponifying the alkyloxypyrazol. Consequently, their lower homologues may be different. The pyrazolon derivative,—

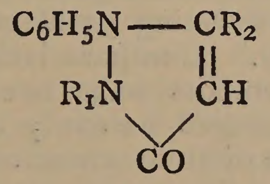


must be pseudoantipyrin.

The halogen-cretonic acid, produced according to the German patent No. 64444, is pseudoantipyrin, as Krauth has shown. This question is of no little scientific interest, since the antipyrins of the type—



are antipyretic medicines, whilst those of the type—



are poisons.

As appears from the above explanations, the elaboration of the pyrazolon region carried out by Stolz and the Höchst Colour Works is, from a scientific point of view, not unobjectionable.

The German Patent No. 66808 declares it possible to obtain pyrazolon derivatives by the oxidation of β-amidocrotonicanilidon, which is known to be impossible.

Finally, the Höchst Colour Works have not been able to refrain from announcing the notorious antipyrin alcohol for a patent, on January 5, 1892.

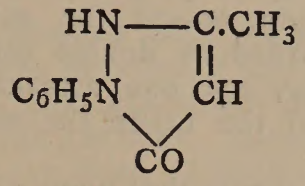
3. *On the Pyrazolon-sulpho Acids.*

C. Walker recently describes some sulpho-acids of the pyrazolons which he has obtained by means of concentrated sulphuric acid from the hydrazones of substituted acetacetic esters. To these sulpho-acids he ascribes a peculiar and at least improbable constitution.

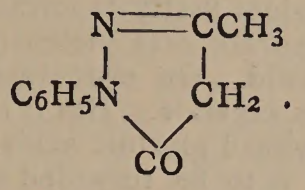
Walker's formulæ prove anew to what improbable assumptions the obstinate adherence of Neff and his school to the oxycrotonic formula of acetacetic ester and the isoconstitution of the normal pyrazolons must lead.

4. *On the Isomeric Benzoylphenylmethylpyrazolons.*

Neff believes, as is well known, that he has demonstrated for (1)-phenyl-(3)-methylpyrazolon (fusible at 127°) the formula—



because he has succeeded in producing two isomeric monobenzoyl-derivatives. The proof has, however, been in no respect supplied. He overlooks that all the other reactions of this pyrazolon fusible at 127° can be much more easily explained by the formula—



How will he explain the solubility of the pyrazolons and the insolubility of antipyrin in alkali by means of his formulæ?—*Journal für Praktische Chemie*, New Series, vol. li., p. 157.

ON SUBSTITUTED GLYCOLIC ESTERS AND GLYCOLHYDRAZID.

By TH. CURTIUS and A. SCHWAN.

This paper forms the fifth part of a prolonged account of the hydrazides and azides of organic acids, appearing under the name of Th. Curtius.

Some years ago one of the present writers found that if benzoylglycolic ester is exposed to the action of 2 mols. diammonium hydrate benzhydrazid and amidoglycocoll are produced with abscission of water and alcohol.

This remarkable reaction yielded the first representatives of two classes of organic substances hitherto unknown, the primary acidylhydrazides and the hydrazin acids.

As subsequent researches had shown that primary acidylhydrazides are quite generally formed by the action of hydrazin hydrate upon acid esters, we might have expected that benzoylglycolic ester with 1 mol. hydrazin hydrate would yield benzoylglycol hydrazid. The latter would then be resolved by the action of a second mol. of the base into benzhydrazid and glycolhydrazid.

One of the authors had previously expressed the view that the last-named substance would correspond to the constitutional formula $NH_2NH{\cdot}CH_2{\cdot}COOH$, and that therefore, in addition to benzhydrazid, there would appear hydrazinacetic acid or amidoglycocoll on the scission of benzoylglycolic ester.

We have established that our view here given is correct, and that the substance in question is the hydrazid of glycolic acid, $CH_2(OH)CONHNH_2$.

In the action of alcohols or acids upon diazoacetic ester one of us has found a method for producing substituted glycolic esters of any kind. By means of this process we have obtained a series of such bodies, hippurylglycolic ester, oxalylglycuric ester, succinylglycolic ester, benzylglycolic ester, and glycolic ester.

The organic acids react in some cases explosively upon diazoacetic ester even in the cold, especially oxalic acid. With other acids the reaction occurs only in heat, but then very energetically.

Pure water or alcohol reacts only with extreme difficulty upon perfectly pure diazoacetic ester, so that it has not been practicable thus to obtain a good yield of glycol esters.

As for the effects of hydrazin hydrate upon these esters the reaction might either take place as with ordinary esters, so that glycolhydrazides are produced in which the hydrogen of the hydroxyl group is substituted by an alkyl or acidyl group, or—as the substituted glycolic esters might be regarded as double esters—there might react simultaneously, the one attacking the esterified carboxyl group, and the other the etherified hydroxyl group.

Investigation has shown that upon alkylglycolic esters there reacts only *one* mol. of hydrazin hydrate, forming alkylglycol hydrazid and splitting off alcohol, whilst in the acidyl-glycolic esters there always react *two* mols. of hydrazin hydrate.

As for the constitution of the so-called hydrazin-acetic acid we have to consider firstly its formation from glycolic ester. Hydrazin hydrate acts violently upon this substance even in the cold. On evaporation there remains hydrazid in massive crystals. But if in place of glycolic acid we employ alkylised glycolic acids, then if the substance in question is to be regarded as hydrazin acetic acid, hydrazin acetic acid should also be formed with abscission of alcohol, instead of which we always obtain alkylised glycol-hydrazid.

Finally, the remarkable instability of the so-called amidoglycocoll in an aqueous solution as against dilute mineral acids, compels us to regard the compound as glycolhydrazid.

The authors then describe the preparation and properties of glycolic ester, of phenylglycolic ester, of benzylglycolic ester [$C_{11}H_{14}O_3$], of ethylglycolic ester, hipperylglycolic ester [$C_{11}H_{13}O_3N$], oxalylglycolic ethyl ester [$C_{10}H_{14}O_8$], succinylglycolic ester [$C_{12}H_{18}O_8$].

The authors next study the action of hydrazin hydrate on the substituted glycolic esters.

DETERMINATION OF PHOSPHORUS IN THE ASH OF COAL AND COKE.

By LOUIS CAMPREDON.

The proportion of phosphorus in the ash of coal or of coke yielded on carbonisation is particularly important, when the fuel is cast into the blast-furnace, for the manufacture of fine castings in which the percentage of phosphorus has to be as low as possible, In fact, all the phosphorus introduced into the melted mass with the ash of the reductive combustible enters into the metal.

Procedures Followed.

All authorites agree in advising the determination of the phosphorus in the ash given by the combustible when burning, and not in the combustible itself. The opinion of various authors concerning the mode of attacking the ash, so as to dissolve the phosphorus contained, differs slightly.

The attack with hydrochloric acid is recommended by Fresenius, by Post, and Munck. The last mentioned adds: "There is no reason to fear that in this primitive treatment iron phosphate may remain undissolved. In the experiments made on this point the contrary has always resulted; even the residue appeared very rich in iron."

On the other hand, Blair, Baron Juptner von Jonstorff, as well as Arnold, recommend the fusion of the ash as the preferable if not the only method.

Comparative Trials.

I have made numerous comparative trials on the ash of coals from English sources, proceeding as follows:—

1. *Attack with Hydrochloric Acid.*—I treated 0·600 grm. and 1·200 grm. of ash very finely powdered in a pear-shaped phial, covered with a watch glass with 30 to 40 c.c. of strong hydrochloric acid. A heat of 80—100° was applied by means of the water-bath or the sand-bath for fifteen to twenty hours. It was evaporated to dryness to render the silica insoluble; it was then taken up with a few c.c. of aqua-regia composed of equal volumes of nitric and hydrochloric acid. Heat was applied, and there were further added 5 c.c. of nitric acid to expel the hydrochloric acid. Lastly, it was diluted with cold water, and the whole poured into a flask graduated from 60 to 120 c.c. The volume is made up and the whole filtered through a dry filter-paper. We take 50 or 100 c.c. of the liquid (corresponding to 0.5 or 1 grm. of the substance), neutralise with ammonia, acidify slightly with nitric acid, heat to 60° in a small pear-shaped flask, and effect the precipitation by adding 20 to 30 c.c. of molybdic solution. Allow the mixture to settle for two to three hours at 30 to 40° C., filter the phosphomolybdic precipitate through a double tared filter; wash with water acidulated with nitric acid (40 c.c. acid per litre); dry the filter at 105° and weigh.

The weight of the phosphomolybdate multiplied by 0·0163 gives the weight of the phosphorus.

2. *Fusion with Alkaline Carbonates.*—Melt 0·600 grm. coal with 3 grms. of a mixture of equal weights sodium and potassium carbonates, and keep it in a state of fusion in a platinum crucible for ten to fifteen minutes. When cold the mass is taken up in water acidulated with hydrochloric acid. The liquid is poured into a porcelain capsule, adding then an excess of hydrochloric acid, and evaporating to dryness. The process is continued as in the first method.

To obtain accurate results it is necessary to fuse with alkaline carbonates and precipitate with molybdic solution according to the directions of the present paper.—*Comptes Rendus*, cxxiii., No. 23.

DERIVATIVES OF COLUMBIUM AND TANTALUM.*

By MARY ENGLE PENNINGTON.

Among the more metallic members of Group V. of the Periodic system are the elements columbium and tantalum, which, though almost a century old and counting among their devotees such investigators as Rose, Hermann, Marignac, Rammelsberg, and others of equal fame, still offer many interesting problems to the student of inorganic chemistry. Comparatively few of the compounds of these elements have been prepared. Those which have been studied narrowly enough to afford an accurate knowledge of their chemical behaviour form a much shorter list. The early literature is, in many instances, very contradictory, due to the supposed existence of such elements as pelopium and ilmenium, engendering as they did the fruitful controversy between Hermann and Marignac, which controversy resulted in the tacit acceptance by the chemical world of Marignac's statement, that columbium is elementary. The old doubt, however, appears to have been revived through the very careful work of Krüss in 1887, on the oxides of these metals, their separation from each other and also from the oxides which accompany them in their apparent minerals.

He found through the fractional crystallisation of the double fluoride of columbium and potassium, and by determining the atomic value of the various fractions, that something apparently contaminated the columbium. In some fractions the values obtained were far too low. This he accounted for by proving the presence of titanium.

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* From the author's thesis presented to the University of Pennsylvania for the degree of Ph.D., 1895. From the *Journ. Amer. Chem. Soc.*, xviii., January, 1896.

Other portions, however, were much too high, and this, it was csrefully proved, was not due to adhering tantalum. Just what the substance was which gave in one fraction an R^v having almost double the accepted atomic mass was left undecided.

A careful consideration of this question in the light of the various researches, makes it seem not improbable that the compounds of columbium, as we know them, are not perfectly free from contaminating substances. The many difficulties encountered in the separation of this oxide from others usually occurring with it, and the insufficiency of the prevailing methods of separation, seem to demand a more exact knowledge of the behaviour of the element in the purest condition obtainable, and also when mixed with the oxides of tantalum and titanium which usually adhere to it.

It was with the hope that some additional light might be thrown upon the general deportment of the derivatives of these elements that this research was undertaken.

The material used was obtained from a columbite from Wakefield, N.H. An abundant supply of the mineral was secured through the kindness of Prof. S. P. Sharples, of Boston, in whose possession it had been for some years, though it had never been analysed. Wakefield is a new locality for columbite. The deposit was discovered while mining for felspar. Near the columbite is quite a deposit of beryl.

Analysis of Wakefield Columbite.

The mineral occurs in large black lustreless masses. Scattered over the surface are little patches of a bright yellow substance. These proved to be uran-ochre, and gave evidence of the presence of the uranium which was later found in the mineral. Felspar occasionally penetrated the mass, though in small quantity. The specific gravity of picked material was found to be 5·662 at 4° C.

Decomposition was effected by the method usually employed for this class of minerals.

Fusion with Acid Potassium Sulphate.—The finely divided mineral was allowed to stand over calcium chloride for some hours. The desired amount of this dry, and almost impalpable, powder was weighed off and mixed with at least nine times its weight of fused potassium bisulphate. This must be an intimate mixture. Great care should be exercised when the heat is first applied, else loss by spattering will occur. Frequent stirring tends to prevent this, and also hastens the decomposition.

Some trouble was experienced by the fusion "climbing," and leaving far up on the sides of the crucible particles of mineral which could neither be driven down by heat or forced down by a platinum rod. To collect these particles the crucible containing the clear quiet fusion was slightly tilted and the adhering portions covered with a little bisulphate. Then by gently heating the whole mass was driven down until it met the main portion of the fusion. All decompositions by this method were made in a large platinum crucible or platinum dish. The latter was preferred. If the mineral is fine enough the fusion is complete in about five hours.

The fused mass was taken up in a large quantity of water, and boiled out with water several times. The insoluble portion consisted of the oxides of columbium, tantalum, titanium, tin, tungsten, and any silica which was present. Small quantities of these oxides invariably remained dissolved, although the solution was boiled for a long time; it is, therefore, advisable to let the filtrate stand twenty-four hours, then re-filter.

The moist oxides, according to Headden (*Amer. Jour. Sci.*, xli., 91, 1891), should "be digested with yellow ammonium sulphide" to remove all tin, tungsten, &c. Rose recommends that yellow ammonium sulphide should be simply poured over them, and that this solution should be evaporated to dryness and gently ignited, to render the columbium and tantalum oxides which have been dissolved by the alkali, insoluble. Wöhler ("Mineral Analyze," p. 140) claims that it is sufficient to treat the metallic oxides upon the filter with yellow ammonium sulphide. As some uncertainty existed as to the best course to pursue, the effect of ammonium sulphide when mixed with these oxides for a longer or shorter period of time was studied.

Heating in a porcelain dish on the water-bath for three hours gave 1·15 per cent of the mixed oxides; one and one-half days, 1·60 per cent; three days, 1·85 per cent; one week, 2·24 per cent. By pouring the sulphide over the oxides on the filter, as Rose and Wöhler advise, 0·24 per cent of the mixed oxides was obtained.

Apparently, the moist metallic oxides are more readily dissolved by ammonium sulphide than is generally supposed, and, therefore, when working with columbites containing the acid oxides, care must be taken, or a very appreciable error may result.

The ammonium sulphide solution was precipitated by dilute hydrochloric acid, and the precipitate was filtered, and washed with hydrogen sulphide water, alcohol, ether, carbon disulphide and ether. The mixed sulphides were carefully heated in the air, then reduced in a current of hydrogen gas. The residue treated with dilute hydrochloric acid gave tin in solution, and left undissolved a small quantity of a black compound which proved to be the tetroxide, Cb_2O_4, with possibly a little tantalum.

The moist oxides when treated with ammonium sulphide have not only the acids removed, but the iron contained in them is changed to sulphide. This is dissolved out by dilute sulphuric acid. Filter off the oxides and wash them thoroughly with boiling water. A pump is usually necesssary because of the precipitate being finely divided, and having a tendency to clog the pores of the filter. By this treatment the oxides should be entirely freed from iron and manganese. Nevertheless ignition gave a powder having a distinct pinkish yellow hue, showing the presence of these elements. The oxides were, therefore, re-fused with potassium bisulphate and treated as before. The second fusion gave a product lighter in colour, yet not perfectly white. Another fusion was resorted to, and no loss in weight was observed, as a small amount of iron still adhered to the oxides. In fact a *perfectly white* mixture of the oxides has not been obtained by this method.

The sulphuric acid solution of the iron which remained with the insoluble oxides was added to the aqueous extraction of the fusion. This solution now contained iron, manganese, uranium, and calcium, with a large excess of sulphuric acid and alkali salt. Yttrium, cerium, and calcium were looked for according to the plan presented in Rose's "Handbuch der Analytischen Chemie," ii., 335, which is, in brief, this:—The greater part of the free acid is neutralised with sodium carbonate; sodium acetate is added, so that acetic acid is in large excess. The earths are precipitated by ammonium oxalate, the precipitate being allowed to stand twenty-four hours. From 3 grms. of mineral only a very small amount was obtained. This was too small a quantity to investigate further, so that if any rare earths are present in the mineral they exist in traces.

To the filtrate which contained iron, manganese, and uranium, were added ammonium sulphide and ammonium carbonate. The iron and manganese were precipitated as sulphides, while uranium was held back by the ammonium carbonate. Beryllium, if present, would have been found here. This element was sought for, since the locality from which the mineral came made it a probable constituent, but none was detected. The sulphides having been filtered out, the filtrate was made acid with hydrochloric acid, the carbon dioxide boiled off, then the uranium precipitated by ammonium hydroxide. The uranium hydrate was filtered, washed, ignited, and weighed as U_3O_8. The sulphides of iron and manganese were dissolved off the filter in hydrochloric acid, oxidised, and separated by the basic acetate method, the manganese being finally weighed as manganese pyrophosphate.

The water contained in this columbite was determined by heating in a boat in a glass tube, and collecting the aqueous vapour in a weighed calcium chloride U-tube.

In the literature relating to columbites and allied minerals, while a ferrous content is given, the method by which it was determined is omitted. Perhaps this is due to the fact that the customary decomposition with sulphuric acid in a sealed tube naturally suggests itself, yet in applying this course to the columbite under examination unexpected difficulties were encountered. The experience is at least interesting.

To be continued).

NOTICES OF BOOKS.

On certain Main Problems of the Natural Sciences, and in particular on (I.) *The Mechanical Processes which lie at the Foundation of the Electrical Phenomena.* A Discourse by Dr. Anton K. Grünwald, Extraordinary Professor of Mathematics at the Imperial and Royal Technical High School of Prague. Delivered at the Annual Meeting of the Royal Bohemian Society of Sciences, January 31st, 1895. Prague: Published by the Royal Bohemian Society of Sciences. ("Ueber gewisse Haupt aufgalben der Naturwissenschaften, und zwor (I.) Ueber die Mechan Vorgänge welche den Electr. zu Grunde liegen").

Professor Grünwald is already most favourably known to British physicists for his mathematical investigations on spectroscopic phenomena. We find him now taking up a much wider question. In his introductory remarks he announces that, with the present discourse, he purposes commencing a series of unassuming presentations on some main questions of the Natural Sciences. Their solution by the co-operation of experimental and theoretical research will alone render it possible for us one day to elaborate an accurate representation—satisfactory to our craving for causality—of that certainly small portion of the universe which lies within our reach. He considers that, though his present theme is *in appearance* merely and specially physical, yet in reality it extends into the weightiest questions, not merely of physics, but also of chemistry, physical astronomy, and even of physiology. His immediate subject is the mechanical procedures which lie at the basis of electrical phenomena, or, as the author puts it more cautiously and modestly, which *seem* thus to lie at the foundation.

The misfortune is that Professor Grünwald's expositions are apt to be only dimly intelligible to other than physico-mathematical specialists. Had he been able to give some brief instances showing how his views lead us into questions of chemistry and physiology, he would have reached a wider, and certainly not less appreciative, circle of disciples.

As a summary of his results, he expresses himself to the effect that the exact mathematical elaboration of the mechanical theory of electrical phenomena still requires difficult and profound study. We must especially get rid of the unsatisfactory conception of *actiones in distans*—between matter and matter on the one hand, and between matter and ether on the other—as mysterious non-mediated effects through a space supposed void and entirely without influence.

In its place must come the new conception of these phenomena opened out by Faraday, Maxwell, Helmholtz, Lord Kelvin, Hertz, Boltzmann, and other illustrious minds, who regard such phenomena merely as the consequences of a chain of regular transferences of motion—or rather of semblances of motion—passing from body to body within a dynamic space which co-operates with them in an essential, or indeed decisive, manner.

According to the author's view, bodies are distinguished from each other, as *relatively* independent substances, by the substances of movement, and by their different position in universal dynamic space. The true independent and self-existing substance is the universe itself.

Quantitative Estimation of Sugars. With explanatory notes by Dr. Ernest Wein. Translated, with additions, by William Frew, Ph.D. (Munich), Wellpark Brewery, Glasgow. London: E. & F. N. Spon. New York: Spon and Chamberlain. Pp. 128. 1896.

The translator points out in his preface that to obtain comparable results of Fehling's procedure certain precautions are needful. He, in common with Dr. Wein, condemns the use of a fixed factor for converting either copper oxide or metallic copper into its equivalent of sugar. A common error committed is to boil the mixed solutions longer than the prescribed time. Another error is to add the cold Fehling's solution, heat and then boil for the specified time. In every case sugar solution must first be added when the Fehling's solution is in vigorous ebullition, and then continuing to boil for the specified time.

The arrangement for filtering off the precipitate of cuprous oxide in a Soxhlet tube is fully described.

Soxhlet tube filled is shown as a frontispiece. The bulk of the work consists of tables for the determination respectively of invert sugar in presence of beet-sugar, of invert sugar, of levulose and starch, and the volumetric determination of dextrose and maltose.

Dr. Wein's work in its original German form is highly approved of by practical men on the European continent, and it may be considered surprising that an English version has not appeared at an earlier date. Dr. Frew's translation only requires to be known to be highly valued.

Notes on Qualitative Analysis. Arranged for the Use of Students of the Rensselaer Polytechnic Institute. By P. Mason, Professor of Chemistry. Third Edition. Easton, Pennsylvania: Chemical Publishing Company Pp. 56. 1896.

Like not a few authors of elementary works on chemistry the writer admits that the world is overstocked with publications of a similar character, and makes the familiar excuse that he seeks to meet the requirements of his own classes. In the preface he informs us that it is his practice to hold a daily "quiz-class" upon points connected with laboratory work. A "quiz-class" is, we conjecture, what is known in Germany as a repetitorium. In the text we can find nothing objectionable, nor anything which has not been said already elsewhere.

Notes for Chemical Students. By Peter T. Austen, Ph.D., F.C.S., Professor of Chemistry in the Polytechnic Institute of Brooklyn. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. Pp. 110. 1896.

A book, we submit, rarely rises in public estimation if the author finds it necessary to tender an apology for its appearance. But Professor Austen has little occasion in this manner to crave favour, since his work is quite able to plead its own cause. We may, indeed, in some respects take exception to Dr. Austen's nomenclature. He writes "liter" for "litre." From the names of the halogens he lops off the final *e*, writing chlorin, bromin, &c. But why not chlor, brom, &c.? Carbonous oxid and carbonic oxid are, if we may use the expression, somewhat uncomfortable synonyms for carbon monoxide and dioxide.

In a quotation apparently from Professor Schiff, the author candidly admits that we have not the slightest idea of how to bridge the gap between matter and sensation, and proceeds as if the existence of matter were an undoubted fact. He holds that "few words have been more abused than 'affinity.'"

The section on "water factors" brings under our notice a source of error which the American student encounters over and above those which we enjoy. The U.S. gallon represents only 8·3311 lbs. distilled water, whilst the British Imperial gallon weighs 10 lbs. Hence confusion and misunderstanding may arise. The author regrets that the use of the two vol. unit in chemical calculations is frequently omitted in English and American text-books.

Vest-pocket Medical Dictionary. By ALBERT H. BUCK, M.D. London: Baillière, Tindall, and Cox. Pp. 529. 1896.

THE object of this small but useful work is to explain the technical terms and abbreviations encountered in medical literature, which multiply with such uncanny rapidity as to puzzle, not merely scientific men whose specialities lie outside the medical profession, but even practitioners who have graduated prior to the last ten or twelve years. It will occasionally save gentlemen of the daily press from ludicrous mistakes. We were once staggered to read in an eminent political and literary organ, of a noted character dying from a gun-shot wound in the *peritonitis!* This little book will preserve reporters and editors from committing themselves in such a manner.

General Catalogue of the National Millenary Exhibition at Budapest, 1896. ("Catalogue Général de l'Exposition Nationale du Millennaire, Budapest, 1896"). Group XVIII. Chemical Industry. Edited by Dr. LEO LIEBERMAN.

THE total number of works here enumerated as chemical is 1253, employing 5702 men. Of these, however, 900 are engaged at the various gas-works. In the production of soap and candles there are engaged 735 hands, and in the metal trades 697. Chemical manures engage 55 persons, margarine 8, and gunpowder 3, though the powder mills are given as 8 (?). The match industry is said to be decreasing. Some of the branches of chemistry are in a flourishing state, whilst others are far from satisfying the demands of the country.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiii., No. 23, December 7, 1896.

Pleurisy in Man studied by the aid of Röntgen Rays.—Ch. Bouchard.—A purely medical paper.

Composition of the Gases evolved from the Mineral Waters of Bagnoles de l'Orme.—Ch. Bouchard and M. Desprez.—The gases would have the following composition in volumes:—Carbonic acid, 5·0; nitrogen, 90·5; argon, 4·5; helium, traces; total, 100·0. The presence of argon has been recognised in other sulphur springs. The waters of Bagnoles are not sulphuretted, but they are silicated like those of Canterets.

Fr. Landolph submits to the judgment of the Academy a memoir on the optical analysis of urine, and the exact determination of the proteids, the glucosides, and the non-fermentable saccharoidal matters.

Determination of Phosphorus in the Ash of Coal and Coke.—Louis Campredon.—(See p. 8).

Property of Discharging Electrised Conductors communicated to Gases by X Rays, by Flames, and by Electric Sparks. — Emilie Villari. — A reply to the criticism of Ed. Brany (*Comptes Rendus*, Oct. 28th last).

On Lithium Nitride. — M. Guntz. — Hydrogen, on thermo-chemical considerations, must decompose lithium nitride, as it is readily observed on heating Li_3N in a current of hydrogen.

Formation Heat of Selenic Acid and of some Seleniates.—René Metzner.—A thermo-chemical paper. On comparing the different numbers with the corresponding values for sulphuric acid they are all found lower, except the heat of hydration. Whilst sulphurous acid fixes oxygen directly, the oxidation of dissolved selenious acid is never direct.

Analysis of Industrial Copper by an Electrolytic Procedure—M. A. Holland.—This paper will be inserted in full.

On Ozone and the Phenomena of Phosphorescence. — Marius Otto. — The luminosity produced when ozone and water are in contact is due to the presence in the latter of organic matters, animal and vegetable. Most organic matters are capable of producing phenomena of phosphorescence with ozone.

New Ammunition Bread. — Ballard. — This bread, unlike the old biscuit, contains salt and yeast.

No. 24, December 14, 1896.

The Röntgen Rays applied to the Diagnoses of Pulmonary Tuberculosis. — Ch. Bouchard. — In the diseases of the thorax radioscopy gives instruction comparable in all points to that obtained by percussion.

On Selenium Anhydride. — René Metzler. — A thermo-chemical paper. The endothermic character is observed very distinctly on treating monohydrated selenic acid with phosphoric anhydride, according to the procedure by which Berthelot succeeded in preparing nitric anhydride.

Analysis of Industrial Copper of the Electrolytic Process; Determinations of Antimony, Sulphur, and Alien Metals.—A. Holland.—Arsenic and antimony are determined in the mother-liquor from which the copper has been precipitated electrolytically. Nickel and cobalt are determined electrolytically in the solution of the double sulphate and ammoniacal sulphate; iron is determined by permanganate. If the original copper was rich in silver, the copper which has been deposited upon the cone is dissolved, as it contains all the silver. In the contrary case a fresh portion of the copper is dissolved in nitric acid, and the nitric solution—filtered if needful—is with a chloride. The lead is determined in a fresh portion of the original substance, and is dissolved in dilute nitric acid. The sulphur is determined as barium sulphate.

Antimono-tungstic Compounds.—L. A. Hallopeau.—Antimonic hydrate can combine with tungstic acid to form antimoni-tungstic compounds, comparable to the phospho-tungstic and arsenio-tungstic combinations.

Researches on Cobalt and Nickel Sulphides.—G. Chasneau.—It results, from the author's experiments, that the alkaline polysulphides, if saturated in the cold with sulphur, give in cobaltous salts a black persulphide, Co_2S_7, insoluble in alkaline monosulphides, but soluble, on the contrary, in these sulphides if saturated with sulphur. Under the same conditions the nickelous salts give a black sulphide, which appears to correspond with that of cobalt, but which, contrary to the latter, is scarcely soluble in sodium polysulphide, but decidedly soluble in the monosulphide.

New Process for the Determination of Glycerin.—F. Bourdas and Sig. de Raczkowski.—This paper will be inserted in full.

MISCELLANEOUS.

Society of Public Analysts.—The Annual Meeting of the Society will take place on Wednesday, January 13, 1897, at the Chemical Society's Rooms, Burlington House, Piccadilly, at 5 o'clock p.m. The Year's Accounts will be presented. The retiring President will deliver his Annual Address. The following Papers are announced:—"Some Analyses of Water from an Oyster Fishery," "Note on Weighing Out Fats," "Remarks on Formaldehyde," by Chas. E. Cassal; "A Specific Gravity Pipette," by W. F. Keating Stock; "A Modified Schmidt Process," by R. W. Woosnam.

MEETINGS FOR THE WEEK.

MONDAY, Jan. 4th.—Society of Chemical Industry, 8. "Smelting and Refining of Cyanide Bullion," by A. Caldecott, B.A. "Industrial Use of a Recording Pyrometer," by Prof. Roberts-Austen, C.B., F.R.S.
TUESDAY, 5th. THURSDAY, 7th. SATURDAY, 9th. } Royal Instituton, 3. (Christmas Lectures, 1896-7). "Visible and Invisible Light," by Prof. Silvanus P. Thompson, F.R.S., &c.

THE CHEMICAL NEWS.

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THE ESTIMATION OF MANGANESE IN SPIEGELS, &c.

By H. BREARLEY.

THE acetate method of separating iron and manganese is very old. Its surname, whatever it may have been, is little heard of now. This is rather complimentary, because the much used methods are the more prone to suffer this change. Amid the quick young methods it seems to have lost virtues it was once credited with. There is more than a rumour, too, that its consort, precipitating with bromine and ammonia, and weighing as Mn_3O_4, is not so reliable as it was formerly supposed to be.

Experience of the method in this laboratory has always been very satisfactory; but that opinion is by no means unanimous may be seen from the following references.

Blair ("Chemical Analysis of Iron," Second Edition, p. 108) distrusts the Mn_3O_4, and recommends weighing as $Mn_2P_2O_7$. A similar opinion is expressed in Crookes's "Select Methods" (Third Edition, p. 191). Fresenius ("Quantitative Analysis," Seventh Edition, p. 205) says that accurate results cannot be got with pyrophosphate unless the Mn is re-determined in the filtrate and washings; whilst the oxides, ignited out of contact with reducing gases, are finally converted with Mn_3O_4, whose weight remains unaltered. Arnold ("Steel Works Analysis," p. 81) says the ignition should be made in a hot muffle furnace, or the residue may not strictly conform to the formulæ Mn_3O_4, which, under the above conditions, it will possess. Reddrop and Ramage (*Jour. Chem. Soc.*, 1895, p. 268) show that the ordinary gravimetric method agrees with Pattinson's and the new one they describe.

Great stress has been laid on the evidence afforded by Pickering's researches (CHEM. NEWS, xliii., 226). McKenna (CHEM. NEWS, lxiii., 184) objects to Mn_3O_4 on the evidence afforded by these papers, but later shows that ammonium manganous phosphate is soluble whether washed with water, ammonium nitrate, or dilute ammonia. Pickering himself recognises that his results are probably vitiated by the permeability of the platinum basins and consequent reducing action of the gases. The experiments of Morse and Burton (CHEM. NEWS, lxvii., 175) made to test the point, furnish evidence in the same direction. It is plain that changes might take place in an open platinum basin, over a Bunsen flame, which could not happen in a muffle at full red heat. Under the latter conditions concordant results are always obtained.

The general instructions for separating Fe and Mn are: iron in ferric state, cold solution, neutral or thereabouts, and an excess of acetate. In case of spiegels and high manganese alloys, the acetate precipitate is always re-dissolved and re-precipitated to ensure a complete separation. It was thought that the modification applied to iron and nickel (CHEM. NEWS, lxxiv., 16) might apply also to iron and manganese, and thus obviate the need for a second precipitation.

The excess of acetate necessary is variously stated "more than sufficient excess to change all the iron and manganese by double decomposition to neutral acetates" (Crookes). 30 c.c. ammonium acetate* when half-a-grm. of spiegel is operated on" (Arnold). "Two grms. sodium acetate (crystallised) to precipitate 1 grm. of iron" (Blair).

To show the effect of free acetic acid 5 grms. of spiegel were dissolved and divided into five lots, neutralised, made up to nearly 1000 c.c. with cold water, 60 c.c. ammonium acetate added to each, and boiled. The hot solution was made up to a litre, cheesed,* 500 c.c. supernatant liquid filtered off, precipitated, ignited to constant weight, &c. The temperature at which the iron solutions became turbid was noted first at slight, and second, at decided turbidity. A "standard" sample was estimated at the same time by precipitating, washing, re-precipitating, &c., and gave first separation 21·616 per cent; second separation, 0·389 per cent; third separation, 0·063 per cent; total, 22·068 per cent.

The results of the five test estimations are collected in the following table:—

No.	Acetic acid.	Per cent manganese.	Temperature of turbidity.
I.	0 c.c.	20·66	56-60° C
II.	10 ,,	21·14	63-65 ,,
III.	20 ,,	21·88	65-67 ,,
IV.	40 ,,	22·02	72-74 ,,
V.	70 ,,	22·06	80-82 ,,

The Fe_2O_3, along with the Mn_3O_4, was certainly less than 0·0002 (except in V.), and this mostly due to a trace of iron in the bromine. The filtrates from the basic acetates were all clear; the precipitates and excess of solution were left over-night, and it was found that the precipitates were bulky inversely as the acid addition; I. was about three times as large as V., the others were intermediate. The supernatant liquids of the I., II., and III. contained no iron, IV. a trace, and V. a decided quantity. The precipitates also varied in colour. I propose to examine these physical properties more closely.

To wash the precipitated MnO_2 when it has been transferred to the filter "till free from ammonia salts" or "thoroughly" is very troublesome, and sometimes impossible on account of the tendency it has to run through the filter as the ammonia salts disappear. There seems no reason why it should be washed at all in ordinary cases, since all the ammonia salts are volatile. Determinations with and without washing give closely agreeing results, and two filtrates (about 800 c.c.) evaporated to dryness and ignited gave 0·0168 and 0·0134 grm. residue, which was mostly SiO_2. Not more than 10 c.c. of this solution can be in the precipitate, and not more than 5 c.c. need be if it is thoroughly aspirated, so that any error introduced is insignificant, for technical work at any rate. This, of course, does not apply when sodium acetate is used or the spiegel contains unusual impurities.

Some corrections which must be made when an aliquot part of a hot solution is taken, as above, will be mentioned later.

The great difference between the avidities of nitric and hydrochloric and acetic acid suggested the idea of adding acetic acid to the freshly dissolved spiegel, and then as much dilute ammonia as would neutralise the free HNO_3 and HCl, form the required amount of acetate and leave sufficient free acetic acid. The details need not be given, since the matter is curious rather than serviceable. After everything had been added the solution was dark coloured, but quite clear. The percentage found on the sample previously mentioned was 21·93. A fortnight later two others in the same way gave 21·92 and 22·05 per cent.

These modifications shorten the ordinary method with its re-precipitations, without in any way impairing its accuracy. But there is still the tedium of weighing and and re-weighing, and the contamination of the Mn_3O_4 and Cu, Ni, Co, &c., in case they are present in the sample.

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* Ammonium acetate used throughout refers to liquid acetic acid (33 per cent), neutralised with liquid ammonia.

* "Cheesed" means to wrap a duster round the beaker, and then fold another over the cover to prevent cooling.

I am not aware that Guyard's method of estimating manganese has ever been applied to the acetate filtrate. Of this method Sutton ("Volumetric Analysis," Fifth Edition, p. 190) says "Nickel, cobalt, zinc, alumina in moderate quantity are of no consequence. The method is easy of execution, and gives good results in cases where it can be properly applied, but such instances are few."

Hopefully the filtrate was nearly neutralised with ammonia, and the standard permanganate run in. The end reaction was fugitive, and the results at best were only fair. If a pink colour was produced, the precipitate at once filtered off, solution acidified in H_2SO_4, and excess of permanganate determined with $FeSO_4$, the results were always too high; and if filtered and allowed to stand the colour gradually disappeared, and MnO_2 was precipitated. This reaction continued long after all the manganese was precipitated, but was less decided in cold than hot solutions. It was found finally to be due to the ammonium acetate and other ammonium salts. This point was much elucidated later by reading that "ammonia boiled with a neutral solution of potassium permanganate was converted into potassium nitrate" (Tamm, Chem. News, xxv., 26).

The more acetate, the greater discrepancy; so that with as little as was necessary both of acetate and acetic acid the disturbing reaction might be inappreciable in the cold. But how little acetate and acid could be used to effect a perfect separation with one precipitation?

Experiment showed that 10 c.c. of ammonia acetate would precipitate 1 grm. of bar iron in 1 litre of solution. The supernatant solution was slightly turbid, but filtered crystal clear through asbestos. 20 c.c. of acetic acid with the same acetate did not prevent precipitation, but the solution needed twice filtering to make it crystal clear.

A series of estimations made are given in the following table. It shows the effect of varying the acetate and acid under constant conditions, thus answering the question at issue, and also supplementing the table given above.

Solutions of bar iron and $MnCl_2$ were mixed to approximate a 20 per cent spiegel. The solution was made up anew for each vertical column, as available leisure did not admit of consecutive work on the series, the variation between column and column is probably due to this cause. To support this view the samples marked with an asterisk in columns 10 and 60 were made on the same solution and side by side.

Acetate acid.	Ammonium Acetate,			
	10 c.c.	15 c.c.	30 c.c.	60 c.c.
0 c.c.	20·48*	20·29	20·00	19·50
5 ,,	—	20·35	—	—
10 ,,	—	20·37	20·38	19·74
20 ,,	—	20·35	20·46	19·91
40 ,,	—	—	20·48	20·19
60 ,,	—	—	—	20·18
				20·47*

If we assume that each perfect separation—the one with most acid in—represents an even 20 per cent, and calculate the other results proportionately, the influence of acid and acetate is more readily seen.

Acetic acid.	Ammonium Acetate.			
	10.	15.	30.	60.
0	20·0	19·94	19·52	19·33
5	—	20·00	—	—
10	—	20·02	19·90	19·56
20	—	20·00	19·98	19·73
40	—	—	20·00	20·01
60	—	—	—	20·00

Keeping the ammonia salts as low as possible, and precipitating with only 10 c.c, of acetate, and titrating with Wright and Menke's (*Jour. Chem. Soc.*, 1880) modification of Guyard's method, some very good results were obtained.

Soda acetate in minimum quantity with soda salts behaves well in either hot or cold solutions. Half-a-grm. of crystals, after neutralising 1 grm. bar iron with sodium carbonate, brought down a precipitate, but left a supernatant yellowish liquid no amount of filtering would decolourise. Three-quarter grm. of crystals gave a clear filtrate, and the tint imparted by two drops of N/10 $KMnO_4$ was not appreciably affected when the solution was heated to boiling. The difficulty might have been eliminated at once by using soda salts, but it was thought desirable to retain ammonia if possible, so that the gravimetric or volumetric methods might be applied to the filtrate at will.

Briefly the method is—Dissolve spiegel in HCl, oxidise the iron with HNO_3, neutralise with soda or ammonia, and precipitate Fe with acetate (sodium or ammonium) in minimum quantity. Nearly neutralise filtrate, and titrate with permanganate. This outline is given so that there may be something to definitely refer to. The method of titration preferred is Wright and Menke's in cold solutions. This is better than titrating in hot solutions because the $KMnO_4$ is less likely to be affected by accidental or unavoidable organic matter, &c. This is strongly emphasised by my experience. No distilled water was handy, our ordinary tap water was used, and titration performed in hot solutions. The results were very unsatisfactory. Of course, ordinary water ought not to have been used, but such a contingency in actual work is not unimaginable.

The following mixtures of iron and manganese chloride solutions, mixed to approximate spiegels and ferro-manganese, show that the method gives exceedingly accurate results.

Per cent manganese		N/10 $KMnO_4$ (approx.) required by—		Salts used.
Present.	Found.	Theory.	Sample.	
10	10·09	30·03 c.c.	30·3	Soda.
10	9·99	30·03 ,,	30·0	Ammonia
20	19·99	60·06 ,,	59·96	Soda
20	19·99	60·06 ,,	59·96	Ammonia
40	40·00	89·5 ,,	89·5	Soda
60	59·87	89·5 ,,	89·3	Soda

I am obliged to Mr. R. L. Leffler, the chemist in this laboratory, for making a trial of the method. I furnished him with an account of the method and some solutions marked with the approximate composition. He reported as follows:—

Given as (per cent)	12·00	23·00	40·00	65·00	82·00
Found (per cent)	10·76	21·99	40·16	64·40	79·78
They really contained (p.c.)	10·80	22·00	40·00	64·00	80·00

Soda salts were used throughout.

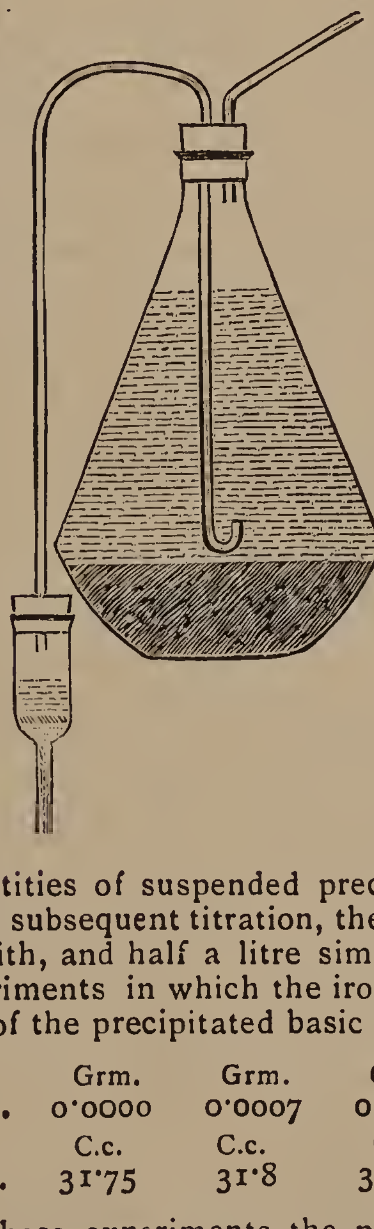
When so small a quantity of acetate is used, the iron solution must be neutralised pretty accurately, or it will not be clearly precipitated. A trouble of this kind might be obviated by adding soda carbonate to slight turbidity, and dissolve in, say, 5 acetic acid. The influence of this acetic, even when larger amounts of soda acetate are used, is seen from the following amounts of permanganate used.

Acetic acid.	Soda acetate (20 c.c.=¾ grm. crystals).			
	20.	30.	40.	60 c.c.
0 c.c.	59·5	58·9	58·1	56·5 c.c.
5 ,,	..	59·9	59·85	59·4 ,,

The quantity theoretically required was 59·75.

In such cases as the foregoing, where an aliquot part of a hot solution containing a precipitate is filtered off, there are certain corrections need making. Say the total bulk of solution and precipitate is 1000 c.c., and 500 c.c. of the clear solution is filtered off. From this 500 c.c. there must be subtracted (1) half the volume of the precipitate; (2) the volume contracted from the temperature when 1000 c.c. is measured to the temperature when 500 c.c. is measured; (3) a slight correction due to the concentration of the solution while filtering, &c. In case of spiegels the volume correction for bulk of precipitate is less than ½ c.c., so of no moment. The correction for contraction was carefully considered. The most convenient way seemed to be to note the temperature in the litre flask, the temperature in the half litre, and calculate the contraction due to cooling. To this end the contraction of an ordinary 20 per cent spiegel filtrate was observed, and found to behave so much like water that Kopp's tables for that body have since been used. In some scores of cases observed the temperatures have not varied more than 2° C. under uniform conditions of working. It is not easy to fix a value for the third error. It depends on the form of vessel used, the rapidity of filtration, and other incidents which vary in an indeterminable way. Arnold ("Steel Works Analysis," p. 82) allows 5 c.c. when the volume of solution is 600 c.c., and later only 1 c.c. when the volume is 300 c.c. These also include the volume of the precipitate.

It were best to avoid this error altogether if possible. The following means were taken to minimise, if not altogether eliminate it:—The precipitation was made in flasks, Taylor pattern, marked at 1000° C.; the boiling solution was transferred to a litre flask with graduated neck, the volume noted, and the litre inverted in the precipitating flask. The precipitate readily settled, and then the clear solution was filtered by the arrangement shown in the figure. The filtration is very rapid, because little or no precipitate falls on the filter.



If small quantities of suspended precipitate made no difference to the subsequent titration, the filter tube might be dispensed with, and half a litre simply syphoned off. Results of experiments in which the iron was introduced as an emulsion of the precipitated basic acetate were—

	Grm.	Grm.	Grm.	Grm.
Fe present ..	0·0000	0·0007	0·0033	0·0050
	C.c.	C.c.	C.c.	C.c.
$KMnO_4$ used..	31·75	31·8	31·75	31·6

Throughout these experiments the precipitated MnO_2 was frequently dissolved in ferrous am. sulphate, and the excess titrated with standard bichromate. This is an obvious way of confirming an estimation.

One other point, the standardisation of the permanganate solution, needs to be carefully noted. Simple standardisation with bar iron or flower wire, dissolved with precaution in H_2SO_4, has always given a value 1 or 2 per cent below what we had good reason to suppose was the real percentage. McD. Irby (Chemical News, xxx., 142) has shown that the small amounts of carbon present in the iron has an effect amounting to between 1 and 2 per cent, so that the iron solution needs to be oxidised to destroy the carbonaceous matter, then reduced and the titration performed. As this point seems to be generally overlooked, and as it introduces an error of several tenths per cent on a 20 per cent spiegel, it is being studied in connection with a series of experiments on Särnström's method of estimating manganese. Up to now we have found it convenient and accurate to standardise with a spiegel containing a known percentage of manganese, or with a manganese salt whose purity was beyond question. The value of the last lot of permanganate determined by three separate spiegels was—

1.	0·001662 Mn per 1 c.c.
2.	0·001667 ,,
3.	0·001664 ,,
By pure manganese salt	0·001664 ,,

Conclusion.

After the gravimetric part of this paper was done, I was under the impression that separating iron and manganese in presence of considerable quantities of acetic acid was a new idea; and the same may be said of precipitating with minimum amounts of acetate. I think i will make this paper more complete than otherwise if I give the references of papers that have come to my notice.

Debray (Chemical News, xxi., 53).—"The acetate of sesquioxide of iron separated, on boiling, into acetic acid and colloidal oxide. . . . . Colloidal oxide of iron is insoluble in ammonia salts, even in presence of a large quantity of acetic acid."

Jewett (Chemical News, xl., 273) shows that, with large quantities of soda acetate, acetic acid—amounting to 5 per cent of the volume of solution—causes the complete separation of Zn and Mn from iron, and a nearly complete separation in case of Ni and Co. On the authority of E. H. Smith, the same paper states that iron could not be precipitated, in presence of large amounts of acetic acid, by increasing the soda acetate. My observations are contrary to this. The error may be seen by precipitating, in presence of 70 c.c. acetic acid, with minimum acetate and several grms.

Kessler (Chemical News, xxvii., 14).—"The loss experienced in the estimation of the manganese by the acetate (soda) method is mainly due to the fact that too large a quantity of acetate of soda is employed, in consequence of which a portion of chloride of manganese is converted into acetate, which salts is readily converted into protoxide and acid."

I am sorry to have unknowingly gone over previously trodden ground, but the persistent way in which the instructions to use unnecessarily large amounts of acetate and neutralise all free acid are repeated, even in the most recent text-books, makes it perhaps not altogether inopportune that this matter should be again brought forward. It is plain that the results here set forth point to a modification of the method previously proposed for nickel and iron separation, in the interest of economy, if not accuracy.

Mr. Leffler suggests that the volumetric method be applied to steels. For steels of the ordinary class it offers no advantages over a number of already well-known methods, such as Ford and Williams'. In those cases, where several percents of chromium are present, it may prove useful, since such steels are frequently not completely soluble in nitric acid.

The various points enumerated are here collected into

The Method.

Dissolve 1 to 1·5 grms. of the spiegel (20 per cent) or proportionate amounts of other manganiferous irons, in hydrochloric acid, and oxidise the iron with nitric acid. If the silica present is likely to interfere with the neutralisation, pass through a small asbestos filter. Neutralise with soda carbonate, dilute to about 900 c.c., and add soda acetate at the rate of 20 c.c. per 1 grm. of iron. Ammonia and ammonia acetate may be used, bearing in mind its limitations. See that the boiling solution touches the litre mark on the flask. Transfer to the litre measure with graduated neck. Note temperature and volume, and replace in the precipitating flask. Cheese, syphon, or filter off half the noted volume, and take the temperature. Cool, destroy the free acid with soda carbonate, and then make slightly acid with acetic or dilute sulphuric. Run the amount of permanganate into a flask, and add 10 c.c, $ZnSO_4$, and run in the manganese solution with constant shaking. This may readily be done by placing a widestem funnel in the larger flask, holding it in position with the first finger of the right hand; the lower fingers grasp the neck with the flask resting against the thick of the hand; the solution is shaken, while the left hand pours the manganese solution through the nearly stationary funnel. The percentage of manganese in spiegel is generally approximately known. Failing this an approximation may be speedily obtained by syphoning off an additional 250 c.c. and precipitating hot (Guyard).

The well-shaken liquid containing the small excess of permanganate is allowed to settle a few minutes, an aliquot part filtered off, acidified, and determined with ferrous ammonia sulphate and permanganate.

After correcting the figures for volume contraction the calculations need no further explanation.

The following values, from Kopp's tables for water, given here, will save further reference.

If the volume of water = 1 at 0° C., it changes when heated to the following volumes:—

70° C., 1·02225; 85° C., 1·03189;
75° ,, 1·02544; 90° ,, 1·03540;
80° ,, 1·02858; 95° ,, 1·03909.

Reagents required:—

Potassa permanganate	3·156	grms. per litre.
Soda acetate	37·5	,,
Zinc sulphate	200	,,

Laboratory, Norfolk Works, Sheffield.

THE MANUFACTURE OF CALCIUM CARBIDE.*

By J. T. MOREHEAD and G. de CHALMOT.

(Continued from p. 5).

The carbide is always found in one piece between the pencils and the bottom. It has a conical form, being broader at the base, and can be 2½ feet high in our furnace. It, however, never has so great a diameter as to fill up the whole capacity of the furnace. The carbide is therefore entirely surrounded by a cover of the mixture of lime and coke. This mixture is so bad a conductor of heat that the brick walls of the furnace are not attacked. It is very easy to separate the carbide from the loose mixture, for the latter never melts together, while the carbide is hard and solid. The pieces of carbide are covered with a thin coating which is a little thicker at the top of the piece, and the same may be re-ground and again used. This coating contains mainly carbon, but also carbide and calcium oxide. It seldom yields more than half a cubic foot of gas per pound, but in some cases it yields 1·77 and even 2·10 cubic feet. This coating, however, is of little importance. If the mixture is well made this coating seldom exceeds from twenty to thirty pounds on a piece of carbide of from 300 to 400 pounds. The carbide itself is crystalline. The crystals are especially well developed near the top, and are more perfect with an excess of coke, low voltage, and when allowed to cool slowly. The centre of the piece of carbide stays liquid for some time after the electric current has been shut off. The liquid part, however, is of the same quality as the rest of the piece. We have, in fact, tapped out of the furnace carbide which was very pure and yielded 5·59 cubic feet of gas per pound. We do not wish to express an opinion as to the practicability of tapping the carbide as soon as it is formed. We will only mention that Mr. Price, in Newark, has, with a view of tapping the carbide, constructed and patented a new furnace, and that one of us (C.) has also devised a furnace for the same purpose.

Carbide of average quality (about 5 cubic feet of gas per pound) often has a reddish colour, especially if it has been made with a current of high voltage. Carbide of bad quality is often greyish or blackish, or will show streaks of graphite. Pure carbide yields more than 5·90 cubic feet of gas per pound. It has, however, been found to be more economical to produce carbide that yields only about 5 cubic feet of gas per pound. Samples of carbide of different qualities contained:—

Table I.

Cubic feet gas per pound.	Carbide. Per cent.	Free calcium oxide. Per cent.	Carbon Per cent.	Other impurities. Per cent.
5·7	96·6	0·6	—	2·8
5·5	93·2	4·2	—	2·6
5·1	86·4	9·5	—	4·1
5·025	84·7	10·7	1·6	3·0
3·6	61·0	27·5	3·2	8·3
3·45	58·5	1·1	25·6	14·8

The upper part of a piece of carbide is often purer than the under part.

The coke to be used should not contain much ash. Our coke contains about 7 per cent of ash. The carbide obtained with a coke of from 10 to 11 per cent of ash was perceptibly inferior to that obtained with our usual coke. It was found impracticable to make a good quality of carbide with a coke of 27 per cent ash. It is well that there should not be more than 10 per cent of ash in the coke. The coke should be ground very fine, and it should pass through a fifty-mesh sieve. The lime need not be as fine as the coke. The largest pieces should pass through a ten-mesh sieve. If the lime is coarser the quality of the carbide becomes inferior. That the state of the pulverisation of the lime is important can be seen by a comparison of the average amount of gas per pound (4·97 cubic feet), obtained with unslacked lime (Table II.), and that obtained with air slacked lime (5·27 cubic feet, Table III.). The unslacked lime was in several instances not quite as fine as the slacked lime. Unslacked lime is decidedly preferable to air slacked lime, as we will see afterwards.

The lime which we use contains 1½ per cent magnesia and 1 per cent of other impurities. The anhydrous lime should contain 95 per cent calcium oxide and no more than 5 per cent impurities. The presence of magnesia is especially detrimental to the production of carbide. We could not obtain a good quality of carbide with a lime in the following analysis:—Insoluble, 0·24 per cent; silica, 0·78 per cent; ferric oxide and alumina, 0·68 per cent; calcium oxide, 92·83 per cent; magnesium oxide 5·47 per cent. Further experiments showed that 2½ per cent of magnesia in the mixture has a marked influence on the production. The lime used for making carbide should not contain over 3 per cent of magnesia. That magnesia has such a bad influence upon the formation of carbide is probably due to its forming a veil between the carbon and the lime particles, preventing their combination. Magnesia does not unite either with lime or with carbon. The latter fact was first shown by Moissan (*Compt. Rend.*,

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* Read Sept. 3rd before the Springfield meeting of the A.A.A.S. by one of us (M). We have made since then several additions, so as to make the article complete up to the present time. From the *Journal of the American Chemical Society*, April, 1896.

118, 506), and our own experiments in this line fully confirm his results. The lime and the coke must be mixed very well or the carbide will be of inferior quality, and there will be much coating. Besides the carbide some mixture remains in the furnace. More carbon than lime burns out or volatilises in an open furnace. It is therefore necessary to add carbon to this mixture before using it again. The amount to be added is calculated from the result of an analysis of the mixture. If coke is added in the proper proportions the unsmelted portion of the material can be returned at least three times into the furnace and still yield good carbide. The impurities of the lime and the coke ashes remain as well in the carbide as in the residual mixture. It is therefore a good practice to add charcoal instead of coke to the mixture, so as not perceptibly to increase the amount of ash. The mixture that comes from the furnace is red hot, and it will stay hot for days. It will lose a large amount of carbon if allowed to lay in heaps in the air. It is better to mix in the necessary amount of carbon and use the mixture at once again. One can also keep the mixture in air-tight sheet-iron tanks. If the lime has been unslacked the mixture cools much quicker and does not lose as much carbon after it has been taken from the furnace. In the case of slacked lime water gas is probably formed in large amounts. The carbon pencils must be well cared for in order that they last for a long time. If sufficient coke is put in the mixture they are not attacked much at the end. They will shorten from 0·05 to 0·10 inch for every hour running. They become thinner for being exposed to the air when hot. They are mainly attacked after the electric current has been shut off, for if the furnace is working the gases from the arc come up around the carbons and shut the air off. In order to save the carbons best it is therefore well to keep the furnaces running with as little interruption as possible. In the closed furnace, which we have described, the carbons will be surrounded by non-oxidising gases, which will save them materially. In the open furnaces in Spray we surround the carbons with a sheet-iron cover that reaches from the carbon holder to within four inches of the bottom end of the carbons. This jacket is fastened with iron wires to the carbon holder. The space between the carbons and the jacket is packed with a mixture of coke and coal tar or pitch. This mixture is baked by surrounding the carbons and jacket with the red hot material that comes from the furnace, or by placing them in a fire. The jacket will generally last as long as the carbons. One set of the carbons in an open furnace, and with interrupted operations, will last on an average about 100 hours. These figures hold good where a current of from 1700 to 2000 ampères is used. The voltage has no perceptible influence on the result. Working with say 1700 ampères and 100 volts, and generating about 225 horse power, the production of carbide per hour can be reckoned to be easily eighty-five pounds, and one set of carbons can therefore make at least 8500 pounds of carbide, even in an open furnace. If the furnace is used continuously the carbons will last at least from 200 to 300 hours, and the cost of pencils for one ton of carbide will be about 1 dol.

The analytical part of our work has been very simple. After the piece of carbide has been broken open with a hammer, two or more samples, representing as nearly as possible the average quality of the carbide, and of about eight ounces each, are taken. These samples are broken in pieces of about half an inch in diameter, and from two to three ounces are taken for one gas test. The material is put into a dry bottle of about one quart capacity, which is provided with a rubber stopper, through which two glass tubes pass. The one tube bears a stop cock and drop funnel, the other tube conducts the gas through a series of U tubes and then through a small gas meter. The funnel is filled with water, and, by opening the stopcock, water is allowed to drop slowly on the carbide. The acetylene gas is generated and is cooled in the U tubes before it passes to the gas-meter. Much water vapour is condensed in the U tubes, for the gases generated in the bottle are hot. We make a correction for the temperature of the gas as it passes the gas-meter. We do not take into consideration the small amount of gas which passes through the gas meter by the expansion of the gas in the bottle when the latter becomes hot, and because a part of the bottle becomes filled with water. The error arising herefrom is of no consequence, for the volume of the bottle is only one quart, and the volume of the gas which passes from the gas meter is from ½ cubic foot to 1 cubic foot. The water, moreover, becomes saturated with acetylene. Our figures show the amount of moist gas at the temperature of 60° F.

In order to determine the lime in the mixture, two and five-tenths grms. are boiled with a slight excess of hydrochloric acid of known strength in a 250 c.c. bottle. The bottle is cooled and filled up. The liquid is filtered, and in 50 c.c. of the filtrate the excess of acid is determined by titration. The coke is determined by boiling 2 grms. of mixture with 25 c.c. of 12 per cent hydrochloric acid and filtering off the coke on a Gooch crucible. These methods do not make a claim to absolute accuracy, but they can be quickly executed and give a good estimate of the relation in which the coke and lime are present in the mixture, as the following figures show. The coke used for the original mixture contained 7·33 per cent of ash. The coke that remained from the mixture that had been boiled with 12 per cent hydrochloric acid contained $6\frac{8}{10}$ per cent of ash, and the coke which remained by the same treatment from a similar mixture that had been once in the furnace contained $7\frac{8}{10}$ per cent ash. The amount of lime found in mixtures by titration, and that found by gravimetric analysis, varied only by from ½ to ¾ per cent when the small amount of magnesia in the lime was known and taken into consideration. In controlling the different runs we have proceeded as follows:—

The carbide was weighed and the coating on it determined either by taking it off and weighing it or by estimating it on small and clean pieces. By deducting the weight of the coating from the weight of the piece of carbide we obtain the net yield of carbide. The gas therein is determined, the figure accepted being the average of the result of the analyses of at least two samples. In order to determine the power used, we multiply the voltage by the ampèrage and divide the product by 746 to obtain the number of horse power generated by the dynamos. In order to make a more proper comparison we found it necessary to deduct the loss of voltage sustained in the carbon pencils. Our pencils were made in different factories and had a different resistance. We therefore determined the difference in voltage as indicated by the usual reading of our meter and the voltage at the end of the carbon pencils. We touch the end of each pencil alternately with an iron rod that is connected with the volt meter by a copper wire. We call net power the power generated by the dynamos less the average loss in the six carbon pencils. Our meters are placed in the primary circuit and we have not taken into account the losses of ampèrage in the transformers and those sustained by leakage. We have further found that the readings of our meters are about 6 per cent higher than those of standard Weston meters. It may therefore be safely relied upon that all our estimates for the production of carbide per horse power are too low. The error is, however, in all cases in the same direction, so that it cannot have materially influenced our deductions, which are based upon a comparison of our results.

In the carbide there is also a considerable loss of voltage, and therefore of power. We found, for example, sixty-five volts in the bottom cables and only fifty volts at the top of a 2½ feet high piece of carbide just under the arc. This makes a loss of six volts for each foot of carbide. The average production during six to eight hours of continuous working is as large as that during two or three hours at the same power. It is, however, not advisable to make the carbide pieces higher than 2½ feet, since then the resistance of the carbide will begin to materially reduce the quantity of the production.

(To be continued).

DERIVATIVES OF COLUMBIUM AND TANTALUM.*

By MARY ENGLE-PENNINGTON.

(Contiuued rrom p. 10).

The mineral was ground very fine and heated in sealed tubes with sulphuric acid (1 part of concentrated acid to 2 parts water), the resulting decomposition being titrated with permanganate, with the following results:—

	Per cent FeO.
0·5 grm. heated one day at 210° C... ..	1·316
0·5 grm. heated two days at 230° C. ..	1·416
0·5 grm. heated five days at 230° C. ..	5·50

It seemed probable that this was not the total amount of ferrous iron in the columbite; hence attention was directed to an old method which is rarely used, yet seems to be worthy of greater attention than has been given it. Berzelius first suggested the method, though it is generally credited to Hermann. The finely ground mineral is mixed with fused and finely divided borax. A small platinum crucible is completely filled with this mixture, then covered with a platinum lid, and the whole placed in a larger platinum crucible. Dry magnesium oxide is packed around and over the inner crucible until it is completely covered, and so excluded from air contact. The heat of a good Bunsen lamp is applied for one-half hour, when the decomposition is complete. Longer heating, or too rapid cooling, causes the fusion to adhere very tightly to the crucible, and loss may result on endeavouring to remove it. When the whole is quite cold, the small crucible is taken out, freed from adhering magnesium oxide and weighed. The fusion, which is a clear green glass, is then freed from the crucible by sharply tapping; a piece may be broken off, weighed, ground in a mortar, dissolved in water and sulphuric acid, and titrated with potassium permanganate. Or, if the amount of ferrous iron is not large, it is better to crush the whole fusion in a diamond mortar, then place in a flask provided with a Bunsen valve, dissolve in water and sulphuric acid, and titrate. To prevent the oxidation of the iron during its solution, a quantity of sodium carbonate was placed in the flask with the ground fusion, and the water and sulphuric acid added carefully to this mixture. When a strong evolution of carbon dioxide had continued for several minutes, the cork carrying the Bunsen valve was quickly inserted, and the flask put aside until solution had taken place. It is necessary to shake the flask from time to time, otherwise the finely divided oxides which separate will enclose some particles of the fusion, and the result will be low. In one or two hours the insoluble residue should be a perfectly white, fine, homogeneous mass. The flask is then opened, more sulphuric acid added if necessary, and the iron titrated with permanganate. A number of fusions were made according to this method, the amount of ferrous oxide found being 6·426 per cent. The method seems to be, so far as columbite is concerned, perfectly trustworthy. It is rapid and the manipulation is not difficult. The oxides which separated out were perfectly white. In one experiment they were filtered off, washed with hot water, ignited, and weighed. The percentage of mixed oxides, 77·94 per cent, agrees quite well with that obtained by the bisulphate method.

The quantitative analysis of this columbite by fusing with bisulphate, as above described, gave the following results:—

	A.	B.	C.	D.	E.
Ta_2O_5 Cb_2O_5 TiO_2 ..	78·61	79·04	79·00	77·96	78·70
Fe_2O_3 ..	12·30	13·83	13·62	13·58	—
SnO_2 WO_3 ..	1·15	1·60	1·85	2·24	1·84
MnO.. ..	8·96	8·32	—	8·08	—
	101·02	102·79	—	100·86	—

One-half grm. of material was used in each case, The ferric oxide, as given above, includes the ferrous, which, estimated by the method of Berzelius, equals 6·42 per cent.

In a sixth analysis 3 grms. of material were taken and due attention was paid to those constituents which former analyses had shown to be present, but in such small quantities that their determination was not trustworthy. The results in this case were:—

	Per cent.
Ta_2O_5 Cb_2O_5 TiO_2	78·04
WO_3 SnO_2	0·24
U_3O_8	0·48
Fe_2O_3	5·22
FeO	6·42
CaO	0·02
MnO..	8·96
H_2O	1·22
Total	100·60

An interesting point in the composition of this columbite is the ferric oxide. Hermann records one analysis of some fragments of a columbite from Miask containing several per cent of it, and so far as I am aware this is the only columbite in which this constituent is mentioned. He also gives a Miask columbite containing 0·50 per cent of uranium oxide. Genth mentions a trace of uranium in a columbite analysed by him.

While no effort was made to separate the metallic oxides quantitatively, it was found from the preparation of pure material that the columbium was in decided excess. Titanic acid was proved to be present, and silica was found in very small quantities.

Many of the recorded analyses in which separations of columbic and tantalic oxides are given, fail to state whether any attempt had been made to eliminate or to prove the presence of titanium or silica. Given a mixture of tantalum, columbium, and titanium, the analyst will have no difficulty in separating tantalum from columbium by Marignac's double fluoride method. But the titanium double fluoride, when mixed with the columbium salt, shows an abnormal solubility which makes its separation very doubtful. This point will be more fully discussed later.

Fusion with Sodium Thiosulphate.—It occurred to me to try the decomposition of the mineral by fusion with sodium thiosulphate, believing that in this way tungsten and tin would be converted into sulpho-salts, and could then be more effectually removed from the other constituents. Without entering into detail, I may say the attempt was fruitless.

Decomposition by the Gibbs Method.—Some years ago Dr. Gibbs published a procedure (*Am. J. Sci. Arts*, xxxvii., 357, 1864) for the decomposition of the columbite minerals; and as my desire was to investigate the different methods of decomposition, I naturally turned to this suggestion. In mineral literature this course is given a second place to the bisulphate decomposition. My own

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* From the author's thesis presented to the University of Pennsylvania for the degree of Ph.D., 1895. From the *Journ. Amer. Chem. Soc.*, xviii., January, 1896.

experience compels me to prefer it to the latter method. The details of the Gibbs method are, in brief, as follows:—

The mineral must be fine, yet need not be in an impalpable powder, as is necessary in the bisulphate decomposition; it was intimately mixed, by grinding in a mortar, with three times its weight of potassium fluoride; the mixture was transferred to a platinum crucible and made into a paste with concentrated hydrofluoric acid. The mass heated up at once, and for some minutes the decomposition proceeded without the application of heat. It was found advantageous to let this mixture of acid salt and mineral stand for several hours, stirring occasionally, and adding more acid if the mass became hard. It was then heated on a water-bath until the excess of acid was driven off. After thoroughly drying on an iron plate, the free flame was applied. Hydrofluoric acid was driven out of the acid potassium fluoride, and at length the whole mass fused and formed a clear, quiet, easily handled fusion, which, upon cooling, became a beautiful pink-violet in colour.

The decomposition is not complete until every part of the mixture has assumed this colour, which does not change on further heating. In the early part of the fusion a deep blue colour appears. If the action be interrupted at this point an incomplete decomposition will result.

The violet mass was taken up with water and hydrofluoric acid in a platinum dish, then boiled and filtered. This extraction should be repeated several times. If the decomposition is not quantitative, the solution in water is much hastened by first grinding the fusion. Any silica which may have been present in the mineral will remain as potassium silicofluoride. This being a gelatinous compound, it is likely to enclose fine particles of the fusion and prevent their solution. If the amount of silica is not large, a separation may usually be effected by treating with concentrated hydrofluoric acid; but if much silica be present it is safer to evaporate to dryness with a little sulphuric acid, and take up the remaining potassium sulphate with water. If any insoluble substance is left it may be dissolved in hydrofluoric acid and added to the main portion of the solution.

If an analysis of the mineral is desired, hydrogen sulphide gas may now be passed through the acid filtrate, whereby any tin, tungsten, or molybdenum present will be precipitated as sulphide. Filter, and separate as usual.

The filtrate was evaporated to dryness, and enough sulphuric acid added to expel all the hydrofluoric acid. The excess of acid was driven off on an iron plate, not over a free flame, and the oxides of columbium, tantalum, and titanium precipitated by boiling with a large quantity of water. The boiling must be continued for several hours to insure a complete precipitation, but it is not so difficult to bring down the metallic oxides under these conditions as in the bisulphate decomposition. Filter, and wash the oxides with hot water, first by decantation, then on the filter. The ignition of the oxides gave a *perfectly white*, fine powder; and this, fused with sodium carbonate or potassium fluoride, yielded a colourless mass when cold. The oxides obtained from the bisulphate never did so, but formed with the carbonate a tinge of green, and with the fluoride a tinge of pink, showing the presence of manganese, and probably of iron.

The filtrate from the mixed oxides contained iron, manganese, and uranium. These were separated by ammonium sulphide and ammonium carbonate, following the plan given under the bisulphate method.

When the object is simply the extraction of pure mixed oxides, the above procedure may be somewhat varied. The fusion is made just as usual, then taken up with water insufficient for perfect solution, and a small quantity of hydrofluoric acid, boiled, and filtered. On cooling, the filtrate will be found to be an almost solid mass of the columbium double fluoride, $2KF.CbOF_3.H_2O$, which separates as a beautiful shining salt and consists of thin laminæ. At first the tantalum double fluoride remains undissolved, or is dissolved only in small quantity, as it is a very insoluble salt compared with the columbium compound, but if too much hydrofluoric acid is added the tantalum will be discovered with the columbium potassium fluoride, and larger amounts of iron and manganese will also contaminate it. From a very concentrated solution of the columbium double fluoride, such as would be obtained by this method, any tantalum double fluoride will, if present, separate almost immediately. These needles should be examined under a microscope for the thin transparent plates of the columbium salt. When these begin to appear filter at once and use a pump. The plates are a good indication that all tantalum is separated. The filtrate, on standing, will usually give the columbium salt, but it may have to be concentrated a little. The first crop of crystals may be coloured pink by manganese or iron. Re-crystallisation, however, removes this. The next crop is fairly pure. When working with large quantities a very satisfactory approximate separation of columbium from tantalum may be obtained by this method of extraction.

As boiling with pure water, or even with water containing a small amount of hydrofluoric acid, decomposes the tantalum potassium fluoride and leaves an insoluble compound, $2(2KF.TaF_5)Ta_2O_5$, while the columbium double salt is practically unaffected, this treatment leaves us in the end a white, finely-divided mass which is almost free from columbium. By heating this residue on a water-bath with a rather concentrated solution of hydrofluoric acid and a little potassium fluoride, the tantalum potassium fluoride is obtained, and may be purified by re-crystallisation.

The Gibbs method was used for the preparation of rather large quantities of tantalum and columbium potassium fluorides. I think it preferable to the bisulphate decomposition and subsequent solution of the oxides in hydrofluoric acid in that it does not consume so much time, and iron and manganese are more readily eliminated. The only objection is that large platinum vessels are needed; as a substitute for these, rubber beakers and funnels were sometimes used.

The method finally adopted is as follows:—

Separation of Columbium and Tantalum by their Potassium Double Fluorides.—The pure mixed oxides were placed in a platinum crucible with three times their weight of potassium fluoride, then moistened with hydrofluoric acid as described under the decomposition of the mineral by the Gibbs method. By treating the fusion with water and hydrofluoric acid an almost perfect solution was obtained, since only a trace of silica was present. Concentration gave the long pointed needles of tantalum potassium fluoride, $2KF.TaF_5$. These were filtered and the solution again concentrated. The crystal crop should be examined under the microscope, as it may be a mixture of tantalum and columbium. Usually it is only tantalum.

If a considerable excess of hydrofluoric acid and potassium fluoride is present in the mother-liquor, the next crop of crystals may be a complex mass about which the analyst can come to no definite conclusion. The fraction consists principally of long crystals much like the titanium double fluoride, and, to make the matter more puzzling, these crystals are not so soluble as those separating at the same time. They may be obtained pure by treating the mixture with a few drops of water and quickly filtering. Re-crystallisation from pure water gives the laminated salt $2KF.CbOF_3.H_2O$. If the acid and potassium fluoride are not in large excess, usually two, and sometimes three, crops of the laminated salt are formed, but in time the long needles are almost sure to make their appearance. These needles were tested for titanium, but no satisfactory evidence of its presence was obtained.

When the solution is very concentrated large thin plates separate from it. These do not give the reaction with gallotannic acid, but they react with zinc, hydrochloric acid, and potassium thiocyanate. This test for columbium compounds will be noticed later. Re-crystallisation does not give the laminated salt. The crystals are always found, and are by no means in small quantity. With zinc and hydrochloric acid they give a greenish colour which quickly becomes brown. They were repeatedly re-crystallised, then decomposed with sulphuric acid. The oxide obtained was white, and at 19° C. had a specific gravity of 4·57.

The oxide was placed in a platinum retort connected with a platinum condenser; hydrofluoric acid was poured over it, and a free flame was applied. The volatile products were collected in water in a platinum dish. Several evaporations were necessary for the volatilisation of this oxide. The solution in the dish was then treated with a small quantity of potassium fluoride and concentrated. The same large, thin plates crystallised out. These crystals were very beautiful, being frequently over an inch in length and 1½ inches in width. They were so transparent that often their presence in the dish was altogether unnoticed.

Analysis.

Substances taken. Grm.	K_2SO_4 found. Grm.	Cb_2O_5 found. Grm.
0·5000	0·5268	0·0059

This analysis would indicate that the salt is probably acid potassium fluoride with a small quantity of the double fluoride of columbium, yet it must not be forgotten that the reactions given above cannot be regarded as conclusive evidence of the presence of columbium.

Because of the brown colour with zinc and hydrochloric acid these crystals were also tested for titanium. Its presence could not be detected.

(To be continued).

ON THE

FORMATION OF ANTIMONY CINNABAR.

By J. H. LONG.

The composition of the pigment known as antimony cinnabar has been stated by several different formulæ, as may be seen by consulting the leading hand-books of chemistry. The substance was usually considered as a mixture of sulphide and oxide or as an oxysulphide with the formula Sb_2S_2O. The formula Sb_2S_3 is found also in some of the older works, and Baubigny (*Comptes Rendus*, October 22, 1894) has shown that this is undoubtedly the correct one. Experiments made by myself, and described in this Journal in February, 1895, led me to adopt the same formula.

The compound is usually prepared by boiling a solution of antimony chloride or tartrate with sodium thiosulphate or crude calcium thiosulphate. As obtained from the acid solution of the chloride, the product is not pure and not of constant composition, being frequently mixed with oxychloride. This mixture is a mechanical one, and analysis made from it has no value in establishing a formula. The precipitate obtained by boiling a mixture of pure solutions of tartar emetic and sodium thiosulphate, on the other hand, has a constant composition, and numerous analyses I have made of it in the past year lead to the formula already given (*loc. cit.*).

By analogy with other formulæ established in the paper referred to, I suggested there that the reaction between the tartrate and thiosulphate may be represented by this equation:—

$$2KSbOC_4H_4O_6+Na_2S_2O_3+H_2O = \\ = 2KNaC_4H_4O_6+Sb_2O_3+H_2S_2O_3,$$

the oxide and thiosulphate then acting on each other to form sulphide:—

$$Sb_2O_3+2H_2S_2O_3=Sb_2S_3+2H_2O+SO_2+5O.$$

The oxygen and sulphur dioxide are not liberated as such, but held as polythionates with the excess of thiosulphate used.

To throw further light on the reaction I have attempted the formation of the cinnabar by other methods. While the product is sulphide of antimony, it appears that it can be made with its characteristic colour only by the decomposition of a thiosulphate. All attempts to obtain the true precipitate by action of hydrogen sulphide or alkali sulphides and sulphur dioxide on antimony solutions failed. The only body formed was the amorphous sulphide, often mixed with sulphur. On the other hand, by the action of a neutral or acid mixture of an antimony compound and a thiosulphate on each other, the cinnabar red product is the only one formed. If the mixture is made alkaline by the addition of a drop or two of ammonia water, no sulphide whatever precipitates. A small amount of hydrated oxide of antimony separates, but the decomposition of the thiosulphate is prevented. On the addition, now, of enough weak acid to neutralise the ammonia a yellow precipitate soon appears, but this speedily changes to deep bright red. The formation of the true cinnabar seems to begin by the appearance of a yellowish intermediate product, which is compatible with the above equations.

In this connection it is interesting to note the behaviour of pure antimony trioxide with solutions of thiosulphate. The reaction of the latter with a soluble antimony compound is comparatively rapid, and experiments were made to show the action of the oxide under the same conditions. It was found that the latter, when added to a strong or weak neutral thiosulphate solution, is unable to effect a decomposition in the cold or by application of heat. When the mixture is boiled the oxide remains perfectly white. This is true even after heating in an autoclave under a pressure of eighteen atmospheres.

It was found, however, that with the addition of a little acid to the mixture of oxide and thiosulphate a reaction followed after a time, although it never became complete. In a series of experiments a constant weight, 0·576 grm. of the pure precipitated, washed, and dried oxide was taken and mixed with water, and a constant weight of sodium thiosulphate in solution, in each case 0·992 grm. of the salt. Definite volumes of half normal hydrochloric acid were then added, and water enough to make the total volume 50 c.c. in each case. The mixtures were made in small Erlenmeyer flasks, loosely stoppered, and were very frequently shaken. The amounts of hydrochloric taken are given in the table below. The reactions became apparent only after several minutes, and, after five hours, had advanced so far in the mixtures numbered one and two, that the products had become orange. The reactions in the other flasks were less marked, but later became strong. The mixtures were made on October 7th, and were shaken many times daily through two months; in fact, as long as any change of colour in them was noticed. On December 3rd the amount of sulphide of antimony present was found by the method of Rivot, oxidation by chlorine after preliminary treatment with strong potassium hydroxide solution. The sulphur is found as sulphate, and the amount of sulphide formed in each case is shown by the table.

No.	Amount of Sb_2O_3. Grm.	$Na_2S_2O_3$. Grm.	N/2HCl. C.c.	H_2O. C.c.	$BaSO_4$ found. Grm.	Sb_2O_3 converted. Grm.
1	0·576	0·992	2	48	0·155	0·064
2	0·576	0·992	4	46	0·293	0·121
3	0·576	0·992	8	42	0·384	0·158
4	0·576	0·992	12	38	0·427	0·176
5	0·576	0·992	16	34	0·454	0·187

In mixtures one and two no evolution of sulphur dioxide could be detected by the odour or by tests, but in the others it was apparent, weak in 3 and strong in 4 and 5. No free sulphur was precipitated in any case, or at any rate could not be found in the final product. Although but a small part of the oxide was actually converted, the colour of the products in mixtures 1 and 2 was a deep cinnabar, and perfectly characteristic. The amounts of sulphide formed or of oxide converted are not proportional to the volumes of acid used, and are much less than should be found on the assumption that the reaction begins by the production of antimony chloride from the oxide. If this were true, the sulphide formed by means of the soluble thiosulphate should increase with the acid taken. The reaction appears to take place between the oxide and thiosulphuric acid liberated by the hydrochloric acid, as was suggested by several experiments. In one case 0·500 grm. of antimony oxide was treated with 10 c.c. of half normal hydrochloric acid and 30 c.c. of water, as before, and allowed to stand twenty minutes, with frequent shaking. The mixture was then filtered, and to the filtrate 1 grm. of sodium thiosulphate in 10 c.c. of water was added. In a short time a precipitate of sulphur formed, perfectly light coloured, showing the absence of even a trace of the antimony. The rapidity with which the thiosulphate was decomposed showed that the hydrochloric acid taken must be in the filtrate and not in the residue, as oxychloride for instance. Titration of the filtrate showed this in a similar case. In a second experiment the acid and thiosulphate, in amounts equal to those of the last experiment, were mixed, and after the lapse of one minute the now opalescent mixture was added to some antimony oxide. Although the reaction between the first substances had gone into its second stage, showing that the hydrochloric acid was now certainly in combination, a precipitation of antimony sulphide began almost immediately, and in a short time the cinnabar colour was distinct.

Thiosulphuric acid is usually spoken of as quite unstable, but Landolt has shown (*Ber. d. Chem. Ges.*, xvi., 2958) that in dilute solutions it may exist many seconds, even minutes. The interval before precipitation is lengthened by dilution. If decomposition begins in presence of compounds of the heavy metals, a sulphide, sulphur dioxide, and polythionates may form. A large excess of thiosulphuric acid is necessary to complete the reaction in this manner, as suggested by the experiments of Vortmann (*Ber. d. Chem. Ges.*, xxii., 2307).

In Experiment No. 1 of the table above the amount of hydrochloric acid taken is just one-eighth of that necessary to complete this reaction with the thiosulphate:

$$2HCl+Na_2S_2O_3=2NaCl+H_2S_2O_3.$$

By full conversion enough acid would be liberated to complete the equation assumed at the beginning,

$$Sb_2O_3+2H_2S_2O_3=Sb_2S_3+2H_2O+SO_2+5O,$$

with the amounts of oxide and thiosulphate taken. It follows, therefore, that not over one-eighth of the antimony oxide taken should be found converted into sulphide, and the result of the experiment shows slightly less than this. According to this theory we should have 0·072 grm. of oxide changed. The test shows 0·064 grm. In the second and following experiments the amount of oxide converted is relatively still less. The acid taken in the last experiment is sufficient to decompose all of the thiosulphate and thus permit the conversion of all of the oxide. But the result shows that slightly less than one-third the oxide has been changed. In the first experiment no escape of sulphur dioxide was noticed, while in the last it was quite marked, and this fact has doubtless some connection with the low amount of sulphide formed. The reaction which takes place in a weak solution of thiosulphuric acid is evidently different from that in the strong solution, inasmuch as the greater portion of the sulphur seems to be given off as sulphide in the one case and as sulphur dioxide in the other.

In the somewhat similar reaction with arsenious oxide Vortmann (*loc. cit.*) suggests this equation—

$$As_2O_3+9H_2S_2O_3=As_2S_3+3H_2S_4O_6+3SO_2+6H_2O,$$

in which but one-sixth of the sulphur present is used to form sulphide. By increasing the amount of hydrochloric acid added to the thiosulphate the decomposition of the latter is hastened.

It is possible that after a time, with increased liberation of sulphur dioxide, the formation of sulphide may be retarded, as was suggested by this experiment, I mixed half a grm. of the antimony oxide with one grm. of sodium thiosulphate in 10 c.c. of water, and added 10 c.c. of half normal hydrochloric acid and 30 c.c. of moderately strong solution of sulphur dioxide free from air. By using water instead of the last solution, precipitation would appear in a few minutes, but in this case it was delayed several hours, and then but a slight amount of yellowish product appeared. The thiosulphate is therefore protected from decomposition by the presence of the sulphur dioxide.

The cinnabar is easily formed from the oxychloride of antimony without addition of acid. Some recently precipitated and well washed oxychloride was mixed with water and thiosulphate solution of the strength used before. The characteristic colour soon appeared, and in a short time the whole product seemed to be cinnabar. The reaction is doubtless aided by the hydrochloric acid liberated by the decomposition of the oxychloride in presence of water. The acid in turn attacks the thiosulphate, and so the process becomes continuous and rapid. These reactions are all much hastened by application of heat and the quantitative relations are also altered, but at a temperature of 20° C. thiosulphuric acid seems to be the active precipitating agent in the cases investigated.—*Journal of the American Chemical Society*, xviii., No. 4.

DETECTION OF CARAMEL IN WINES. POSSIBLE CONFUSION WITH THE COAL-TAR COLOURS.

By A. J. DA CRUZ MAGALHAES.

Caramel is frequently employed—at least in Portugal—to give a factitious appearance of age to white liqueur wines. There exist methods for the recognition, and even for the quantitative determination, of caramel in wines, but we do not find in literature any indication as to the possible confusion between the coal-tar colours and those of caramel. Now this confusion may take place, and lead to grave errors.

In the course of some researches on the colouring matter of Portuguese wines I was led to try, on a liqueur wine from Oporto which, as I afterwards recognised, had been strongly caramelised, the general reactions given for the detection of coal-tar colours. The following are the results:—

1. I boiled 100 c.c. of wine for ten minutes with 10 c.c. of a solution of potassium sulphate and a flock of mordanted wool. The wool was dyed and retained its orange-yellow colour after plentiful washings in water and with ammonia.

2. 20 c.c. of wine were mixed with 10 c.c. lead subacetate and were filtered after agitation. The filtrate passed through with a distinct orange-red colour, and gave up its colour, on shaking, to amylic alcohol.

3. 100 c.c. of wine, supersaturated with ammonia, and shaken up with amylic alcohol, gave up their orange-yellow colour to this solvent.

4. 10 c.c. of wine were agitated (both in cold and in heat) with 0·2 grm. yellow mercury oxide for one minute, and filtered after settling. The filtrate was coloured an orange-yellow in each case.

We might therefore infer that the wine in question was coloured an orange-yellow with one or more coal-tar derivatives.

I repeated the same experiments with a wine of the same type, of my own vintage, to which I had added pure caramel made with ordinary sugar. The results were absolutely the same.

On operating with the same wine without the addition of caramel nothing similar was obtained.

I repeated these experiments with pure caramel; the results obtained were exactly those to which I had added caramel. Without any doubt the colours of caramel may therefore be confounded with those derived from coal.

To throw light on a second point of this interesting subject, I prepared caramel from dextrose and saccharose, both very pure.

The two solutions of caramel thus prepared were treated with lead boric acetate and agitated with amylic alcohol. This remained colourless with dextrose caramel; with saccharose caramel the alcohol took a deep orange-yellow.

If both were supersaturated with ammonia and then shaken up with amylic alcohol, the first gave a greenish-yellow colour to the alcohol, and the second a very deep orange-yellow.

With the former ether takes no colour, but it takes an orange-yellow with the latter.

Mordanted wool took a yellow colour with the former, but an orange-yellow with the latter.

Cazeneuve's test does not alter the original colour of the two solutions.

The author is continuing the researches.—*Comptes Rendus*, cxxiii., No. 21.

THE OCCURRENCE OF TITANIUM.

By CHARLES E. WAIT.

It is not my present purpose to repeat what has been already frequently published relative to the presence of titanium in minerals, typical rocks, meteorites, clays, soils, blast furnace products, &c. I wish merely to call attention to the fact that some of the bodies with which we have much to do contain titanium, and that, probably owing to the difficulties formerly experienced in its estimation, it has been more frequently overlooked than is generally supposed.

In the recent examination of food materials, under the direction of the United States Department of Agriculture, I have had occasion to make analyses of the ashes of some plant materials, and, this having led to further investigations, I was interested and surprised to find titanium present in every plant ash thus far examined.

This is, in fact, surprising, as it is stated by some writers (Roscoe and Schorlemmer) "that it does not appear to form part of the animal or vegetable kingdom."

The amount of titanic oxide found in the ash of some vegetable material is as follows:—

Oak wood	0·31 per cent
Apple and pear wood (mixed) ..	0·21 "
Apple	0·11 "
Cow peas	0·01 "
Cottonseed meal	0·02 "

From the above determinations we are reasonably safe in assuming that titanium is assimilated by plants. If this is true, it seems very strange that reference to this fact has not been made by recent writers upon agricultural chemical analysis, and upon the chemistry of vegetable life.

In fact, in consulting treatises on ash analysis with tables (Wolff), I do not find any mention whatever of the presence of titanium. If this is a fact, can it be true that it has escaped the attention of chemists for so long a time?

The examination of the ash of bituminous and anthracite coal shows the presence of titanic oxide. The results of some determinations are as follows:—

Jellico (Tenn.) bituminous coal	0·69 per cent
Coal Creek (Tenn.) bituminous coal ..	0·95 "
Pocahontas (Va.) bituminous coal	0·94 "
Middlesborough (Ky.) bituminous coal ..	0·83 "
Pennsylvania anthracite coal	2·59 "

With reference to the presence of titanic oxide in the ash of coal, it may be fairly assumed that, partly owing to the infiltration of clay and earthy materials, it would be found there, but is it fair to assume that its presence is wholly accounted for in that way? If mention has been made of the presence of titanium in the ash of coal, it has thus far escaped my attention.

The method employed in the above determination is that of A. Weller (*Ber. d. Chem. Ges.*, 1882), which is based upon the fact that hydrogen peroxide, when added to a solution of titanium, produces a compound of an intensely yellow colour. There are precautions necessary in the execution of this method which have already been pointed out (*Journ. Amer. Chem. Soc.* xiii., 210.)

It will be my pleasure to report additional notes at an early day concerning the presence of titanium in the vegetable kingdom. Valuable service has been rendered in the above work by Messrs. J. O. LaBach and C. O. Hill.—*Journal of the American Chemical Society*, xviii., p. 402.

GOVERNMENT LABORATORY OF TASMANIA.

By the courtesy of Mr. W. F. Ward, Assoc. Royal School of Mines, we have been favoured with the report of the Government Laboratory for the year 1895.

There has been a falling off in the number of samples analysed for municipalities and private individuals, though the work in the latter case is largely gratuitous, and in the former exclusively so. On the other hand the work done for the Government more than compensates this deficiency. The increase of duty on "oils" imported for eight months more than defrays twice over the total yearly cost of the laboratory. The departments of mines, railways, police, health, and agriculture obtain more or less analytical work free of cost. On the other hand, Customs' duties have to be paid even on the chemicals imported for the use of the laboratory. So that this department is much more than self-supporting.

The total number of samples analysed in the Government laboratories during the year 1895 was 2197, 1550 of which were teas, 12 of which were found adulterated or defective. Only one sample of coffee was examined and condemned as consisting one half of chicory. Seven samples of spirit of wine tested for the Customs were not sufficiently methylated, *i.e.*, not made undrinkable. On this we may remark that we have known methylic alcohol (not methylated spirits) be drunk to a serious extent by men engaged in dye and colour works. It does not appear that Tasmania has adopted the absurdity of requiring an addition of mineral "naphtha" to methylated spirits. The Tasmanian fiscal authorities, as well as those in the Home Kingdoms, should awake to the fact that a minimum of Dippel's animal oil renders alcohol undrinkable without interfering with its technical uses.

Nineteen samples of water have been analysed. The composition of two may, it is hoped, prove exceptional. One of them contained 0·98 part of albumenoid ammonia per million of water, as well as 1·3 grains per gallon of chlorine. Another contained 97 grs. per gallon of chlorine. Much of this was in the state of magnesium chloride. The water was taken from the premises of a milk-vendor. Quackery flourishes in the Colonies as well as in the Home Kingdoms. A "self-cure" for nervous debility, advertised and sold at one guinea per ounce, was found to be merely Peruvian bark in powder, the present retail price per ounce being about one shilling!

A fatal case of poisoning with strychnine is cited. Thirty-six grs. of the poison were separated from the contents of the sugar basin. There is also mention of wholesale malicious poisoning in Queensland. There is no mention of poisoning with any substance unknown to European pharmacologists. In this direction much work remains to be done, and much of it might be done by local analysts.

It will not be deemed an unpardonable digression if we mention that malicious poisoning—as we learn from private sources—is exceedingly rife in South Africa. The deadly drug, or drugs, are introduced into the victim in the state of snuff, of which the Kaffirs are passionately fond. But they will now rarely accept a pinch from a stranger without careful scrutiny. To return to Mr. Ward's report, a number of samples of ores and tailings have been examined for the Secretary of Mines. In addition to gold and silver, nickel, cobalt, copper, tin, antimony, bismuth, zinc, and lead have been determined. We find no mention of platinum. A sample from M. Dundas contained silver at the rate of 1·057 ozs. per ton, and gold specimens gave 60 to 63 ozs. Arsenical pyrites are found, and prove a source of great annoyance.

PROCEEDINGS OF SOCIETIES.

ACADEMIE DES SCIENCES.

AT the meeting of the Academie des Sciences, on Monday, Dec. 21st, M. A. CORNU delivered the following Presidential Address:—

When Lavoisier, Schwann, and Cagniard Latour studied the fermentation of beer, and Pasteur, taking up the question, patiently followed the development of those microscopic beings in generations called spontaneous in the diseases of wine or of silk-worms, who could have foreseen that a day would come when this admirable research would have so important a bearing on the welfare of humanity, demonstrating that these infinitely minute beings rank among the most important factors of human life. Pasteur, in his long and fruitful career, has taught us that it is possible to specify these organisms—to combat and even to direct them, according as they are our allies or our enemies. They have the power of conferring immunity or of conducting us infallibly to death.

The public see only final success; they mostly ignore the starting point of such researches; they ignore the efforts and the perseverance required to lead to what is vulgarly called a practical discovery; they are even prone to disdain abstract science, and to estimate the merit of the savant by the immediate market value of his discoveries.

Utilitarianism is, in fact, one of the maladies of the present age, perhaps one of the gravest, because it tends to crush the upward flight of the human spirit, and to fetter it to the exclusive worship of material interests.

Prof. Röntgen's discovery of the X rays has been, both for the public and for savants, *the* scientific event of the year. The speaker gave a luminous summary of the researches which have led to this discovery, laying due emphasis on the "brilliant experiments" of Mr. Crookes. The Röntgen rays are spoken of as a fresh benefit to be placed to the credit of pure science. After touching on the merit of the illustrious savants recently lost to the Academy and to science, the speaker mentioned that this year the Arago medal has been conferred in duplicate on M. Antoine d'Abbadie and on Prof. Sir W. Thompson, now known as Lord Kelvin. He on a recent occasion had pronounced France as the *alma mater* of his scientific youth. It is added that modern nations, though bent under the yoke of material interests, and crushed under the treacherous law of iron and blood, are still able on great occasions to raise their eyes to the serene regions above hatred and envy and to join in celebrating the great men whose labours increase the common patrimony of intelligence at the same time as the well-being of mankind.

NOTICES OF BOOKS.

The Practical Methods of Organic Chemistry. By LUDWIG GATTERMAN, Ph.D., Extraordinary Professor in the University of Heidelberg, with numerous illustrations, translated by WILLIAM SHOBER, Ph.D., Instructor in Organic Chemistry in the Lehigh University. Authorised translation. New York: The Macmillan Company. London: Macmillan and Co., Ltd. 1896. Pp. 329.

WE have here an excellent work written in German, translated by an American, and printed in America. The language and the orthography employed are not in all cases idiomatic English as written and spoken on this side of the Atlantic. Thus we find magenta invariably designated by the term "fuchsine."

In the first or general part we have instructions for necessary operations, well thought out and clearly described. We may call particular attention to the directions for fractional distillation, to the management of autoclaves, and distillation at reduced pressures.

Next follow the methods for ultimate organic analysis, the determination of nitrogen being performed exclusively by the method of Dumas.

We now come to the special part; the performance of synthetical operations in the aliphatic, aromatic, pyridine, and quinolene series. Lastly comes an inorganic part, viz., instructions for obtaining in a state of purity substances required as reagents in organic research. It will be at once observed that the author does not give a series of recipes. He described representative reactions, *e.g.*, the nitration of a hydro-carbon, the reduction of a nitro-compound to an amine, the reduction of a nitro-compound to an azoxy-azo or hydrazo compound. The student who has carefully worked out these directions in the laboratory will find himself prepared for entering upon the wide fields of organic research without losing his way. One who has made no such preparation is in danger of "messing about" at random, and if he comes upon something valuable may not recognise what he has done.

We therefore strongly recommend the careful study of this work, regretting only that the distinguished publishers have not seen their way to having the English translation executed by an Englishman and brought out in England.

Catalogue of Chemical Apparatus, Balances, Drying-Ovens, Furnaces, Laboratory Stands, &c., also special and general Glass Apparatus, Hydrometers, Thermometers, Porcelain and Clay Ware, Jena Laboratory Glass Ware, and Glass Tubing. A. GALLENKAMP and Co., 2, 4, and 6, Cross Street, Finsbury, E.C. 1896.

AN important feature in this catalogue is the special description of Jena laboratory glass. This ware, we are told, surpasses the best Bohemian glass, Kavalier's make, in its insolubility in water, whether at ordinary temperature or at 80°. On treatment with caustic soda it is slightly inferior to Bohemian glass, but it has the superiority as regards resistance to sodium carbonate. The Jena glass has a great power of resisting sudden changes of temperature. Medium sized flasks, containing boiling toluidin (200°), bear immersion in cold water. Jena laboratory glass can be heated over a Bunsen flame without wire gauze.

Evaporating basins are catalogued of Berlin, Thüringen, and Meissen porcelain, as well as of aluminium and enamelled steel, of pure nickel, platinum, silver, and platinum gold for melting potash. There is mention of autoclaves for bearing a pressure of 50 atmospheres, and apparatus for boiling in a vacuum or at a reduced pressure. Fletcher's devices for the production and distribution of heat are quoted in great variety. Apparatus for practical distillation as devised by Hempel, Linneman, Glinsky, and others, are also quoted and shown.

Of filter-pumps there is also good variety, of the constructions of Fischer, Bunsen, Volhard, Finkener, Geissler, Alvergniart, and others, as also filtering apparatus in conjunction with pumps.

Various kinds of filter paper are quoted, some of which retain such precipitates as zinc sulphide.

The balances and weights described are those of Sartorius, Becker, Verbeck and Peckholdt, and Beranger.

Bacteriological apparatus is figured and described at great length.

Spectroscopes figure here at length unusual in catalogues of laboratory requisites. Catalogues of microscopes, including the renowned instruments of Zeiss, will, it is said, be supplied on application.

Of chemicals we find only a list of standard solution. Experimentalists may often find here some newly devised apparatus which will prove exceedingly useful. We cannot help expressing our regret that Messrs. Gallenkamp find themselves unable to get their printing done in Britain.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxv., No. 2.

Uses of Acetylene.—R. K. Duncan proposes to set out from acetylene to form, either by way of polymerisation of benzene, C_6H_6, whence there may be obtained the innumerable series of aromatic compounds, or ethylene by the action of nascent H. Acetylene, on account of its endothermic character and its explosive properties, cannot compete with coal gas or electricity for the lighting of cities. This compound was first met with by Davy in 1836, and described in full by Borchen in 1891. It yields per kilo. 280—300 litres of acetylene gas. Acetylene is less poisonous than ordinary coal gas. Its liability to explosion is a serious obstacle to its use on the large scale.

Action of Coal Gas upon Caoutchouc.—Gossheintz.—Black tubing is the least suitable, then the red quality, but the grey kind is the best.

Treatment of Rich Iron Ores and Use of Acid Slags.—Franz Büttgesbach.—The author has made use of ores containing 68 to 70 per cent of iron, with the addition of sufficient slags free from iron to such an extent that the slag may reach at least 25 per cent of the cast metal.

Series 3, Vol. xxxv., No. 3.

Copper Industry in Japan.—Japan now occupies the fourth rank among the copper-yielding countries. In 1892 it produced 20,000 tons of copper. The ore is distributed over the entire country. The yield will soon exceed that of Chili.

THE CHEMICAL NEWS.
Vol. LXXV., No. 1938.

A RAPID DETERMINATION OF THE EQUIVALENT OF SULPHURIC ACID AND ITS PLACE IN THE TEACHING OF CHEMISTRY.

By WILLIAM ACKROYD, F.I.C.

The quantitative experiments on neutralisation usually given to elementary students are few in number, and of one type; the following variation is suggested as part of a scheme of quantitative work.

a c.c. of aqueous sulphuric acid are found to be neutralised by *b* c.c. of solution of sodium hydroxide.

To *a* c.c. of the acid a weighed quantity of magnesium is added (from 0·1 to 0·2 grm.), and when all action has ceased *b* c.c. of the alkali are added. The indicator used (methyl orange) shows that all the free acid has been neutralised, and it may readily be proved that all the metal is precipitated as hydroxide. Now run in, from the burette, sulphuric acid of known strength until the magnesium hydroxide is exactly neutralised.

From the data obtained calculate the equivalent of sulphuric acid.

Example.—Strength of sulphuric acid used, 0·04945 grm. per c.c. 20 c.c. of the acid requires 21·5 c.c. of alkali for neutralisation. 0·146 grm. of magnesium is dissolved in 20 c.c. of the acid, and after addition of the necessary 21·5 c.c. of alkali 12·4 c.c. of the acid are required to neutralise the magnesium hydroxide. Whence, taking 12 to be the magnesium equivalent, we get—

$$\frac{12{\cdot}4 \times 0{\cdot}04945 \times 12}{0{\cdot}146} = 50{\cdot}4.$$

Other students obtained the numbers 49·9, 49·7, 48·7 &c., and the figures give some idea of the degree of accuracy to be expected under ordinary circumstances. The time taken for the estimation is much under an hour.

By neutralising the magnesium hydroxide with hydrochloric acid of known strength, the equivalent of this acid may be similarly ascertained. Results within a unit of the accepted number are readily obtained.

A recent alteration of the syllabus of the Science and Art Department has introduced the salutary course of taking quantitative work from the commencement instead of leaving it until the student's third year. These first efforts are necessarily only, in many cases, rough approximations, but they serve to familiarise the worker with the laws of combination in definite and reciprocal proportions, equivalents, &c. The methods to be employed, and their order, are left to the discretion of the teacher, who has the help of such excellent little works as those of Ramsay, Reynolds, and Tilden.

I take it that in an ideal course for the elementary student each quantitative experiment ought to be preceded by the qualitative work necessary for its comprehension, and it ought to require as little time as possible for its performance, so that it can be tried often; the experiments ought to follow one another in logical order, each one more or less built on those going before, with the continuity found in a series of geometrical problems, and collateral work in theory and practice should proceed abreast with them.

The determination of equivalents will form the backbone of the work, and magnesium, because of its purity and rapidity of action, lends itself admirably for the purpose, as in the following experiments:—

1. Determination of the magnesium equivalent by finding what weight of it is required to liberate 11·16 litres of hydrogen at normal temperature and pressure, *i.e.*, 1 grm. from sulphuric acid.
2. Determination of the oxygen equivalent by finding how much of it combines with 12 grms. of magnesium in the course of ignition of the latter in a porcelain crucible.
3. Determination of the sulphuric and hydrochloric acid equivalents by finding what weight of each is required to neutralise the hydroxide formed from 12 parts by weight of magnesium.
4. Determination of the equivalent of caustic soda by finding what weight of it neutralises an equivalent of sulphuric acid.

In this order, where each experiment is based on a preceding one, the equivalents 1 (assumed), 12, 8, 49, 36·5, and 40, would be obtained for H, Mg, O, H_2SO_4, HCl, and NaOH respectively, and each experiment is typical of others which will suggest themselves to the teacher. I think it is of importance to stick to the unit weight of hydrogen for comparisons, as subsequently there is nothing to unlearn. Where many units of other elements are employed in empirical comparisons, as, *e.g.*, the ratio 1 : 0·66 in experiment 2, instead of 12 : 8, much confusion arises in many minds, and the ratio 12 : 8 is equally available as an example of combination in fixity of proportions.

It appears therefore inadvisable to follow the historic order in this respect with elementary students, however interesting it may be when they have a better grasp of the subject.

OPTICAL ANALYSIS OF URINE AND EXACT DETERMINATION OF THE PROTEIDS, THE GLUCOSIDES, AND THE NON-FERMENTIBLE SACCHAROID MATTERS.

By F. LANDOLPH.

1. *Sugar in Urine.*—Normal healthy urine always contains from 0·01 to 0·20 grm. sugar per litre; the exact determination can only be effected by fermentation. Setting out from 0·40 grm. of sugar per litre, the physician should turn his attention to the slow and progressive development of diabetes, which may be considered established when 2 grms. per litre of fermentible sugar is found. There are only pathological urines containing albumen, pus, &c., which often contain no trace of sugar.

2. *Optical Determination of Sugar.*—The saccharimeter is generally incompetent to demonstrate the presence of 1 grm. to 2 grms. sugar per litre, because normal urine always deflects from 1° to 3° to the left. It is only on setting out from 2° to 3° deviation to the right that we are almost certain of the presence of sugar in the urine, and it is only beyond 10 grms. per litre that the diabetometer gives us fairly exact results; the more exact the higher the quantity. Hence, to obtain results beyond dispute, it is indispensable to have recourse to fermentation, whilst for quantities above 20 grms. per litre the two methods give approximately the same results.

3. *Direct Coefficient and Indirect Coefficients of Reduction.*—The direct coefficient of reduction can only be obtained with urine boiled and filtered, because raw urine in treatment with the cupopotassic liquid always holds a certain quantity of cuprous oxide in solution. To 10 c.c. of urine boiled and filtered we use 10 c.c. water and 40 c.c. of Fehling's solution. We heat the mixture to ebullition, and keep it up, when once the reaction has commenced (which generally requires from three to five minutes), for twenty minutes; we filter, wash the cuprous oxide with boiling water, dry, and ignite. The weight of copper oxide obtained, calculated per thousand, gives

the *direct* coefficient of reduction; the third of this weight gives fairly well the quantity of non-fermentible saccharoid matter in a litre of urine, deducting the quantity of oxide corresponding to the fermentible sugar and the quantity of oxide corresponding to the uric acid, of which one part is approximately equal to four parts of copper oxide.

A quantity of non-fermentible saccharoid matter exceeding 3 grms. per litre is the certain sign forerunning diabetes. Further, for these salts of urine with strongly diabetic disposition the duration of the introduction of the reaction often does not exceed half a minute.

To obtain the indirect coefficients of reduction, we first split up (at first in raw urine, and then in a portion boiled and filtered), the mucine and analogous proteids, as well as the glucosides of mineral acids. We then fix in the urine thus treated, filtered, and adjusted to their primitive volume, the coefficients of reduction as for the determination of the direct coefficient of reduction. The difference between the figures of the two indirect coefficients gives the quantity of mucine in copper oxide, and the difference between the direct coefficient of the boiled and filtered urine and the indirect coefficient of the same urine boiled and filtered gives the quantity of the glucosides in copper oxide, the third part of which represents the weight of these compounds.

4. *Polaristrobometric Examination of Urine.*—When a urine contains pus and analogous pathogenic elements, the deflection to the left in the very sensitive polaristrobometer of Pfister and Streit becomes stronger, reaching 5°, and even 8°, which is evidently due to the polarising force of the nuclei of the granulated leucocytes of pus. In this case it even happens that the field of vision becomes totally obscure in an extent of some degrees. This fact is especially very important when the cellules and pus granules have already disappeared under the microscope, since this procedure alone permits us to know if there has been an anterior presence of pathogenic elements or not.

Analogous studies are pursued to recognise and determine the nitrogenous organic compounds preceding albuminuria.—*Comptes Rendus*, cxxiii., No. 26.

THE SEPARATION OF VANADIUM FROM ARSENIC.

By CHARLES FIELD and EDGAR F. SMITH.

As vanadium and arsenic occur associated in minerals and likewise in artificial products, their separation becomes a matter of consequence.

The course usually pursued in carrying out this separation is that long since recommended for the removal of vanadic acid from its solutions; namely, its precipitation as ammonium metavanadate. Other methods have recently appeared in the literature bearing on analysis. Reference is here made especially to the publication of Fischer ("Bestimmung von Vanadinsäure," Dissertation, Rostock, 1894).

Experiments made in this laboratory on the behaviour of vanadates (*Journ. Am. Chem. Soc.*, xvi., 578) and arsenates (*Ibid.*, xvii., 682) heated in an atmosphere of hydrochloric acid gas, in which both acids were volatilised, suggested the thought that if the sulphides of vanadium and arsenic were exposed to the same vapours perhaps they would show a variation in deportment. And so it has proved. Perfectly dry arsenic trisulphide, previously washed with alcohol, carbon disulphide, and ether, then dried at 100° C., when exposed in a porcelain boat, placed in a combustion tube, was almost completely expelled from the retaining vessel at the ordinary temperature. The last traces were driven out at a temperature little above 150° C. Brown vanadium sulphide, in a perfectly dry condition, treated in the same manner, was not altered. It only remained then to prepare mixtures of known amounts of the two sulphides and subject them to the action of the acid vapour. To this end the following experiments were made:—

I.—0·1303 grm. of vanadium sulphide,
0·1302 grm. of arsenic sulphide.

The arsenic sulphide was volatilised without difficulty and left 0·1297 grm. of vanadium sulphide.

II.—0·1290 grm. of vanadium sulphide,
0·2242 grm. of arsenic sulphide,

gave after exposure of one hour to hydrochloric acid vapour a residue of vanadium sulphide, weighing 0·1297 grm.

III.—0·0828 grm. of vanadium sulphide,
0·0582 grm. of arsenic sulphide,

left 0·0827 grm. of vanadium sulphide.

IV.—0·1306 grm. of vanadium sulphide,
0·2028 grm. of arsenic sulphide,

gave a residue of 0·1308 grm. of vanadium sulphide.

V.—0·1403 grm. of vanadium sulphide,
0·2409 grm. of arsenic sulphide,

left 0·1404 grm. of vanadium sulphide.

The temperature in these experiments was not allowed to exceed 250° C., as beyond that point there is danger of affecting the vanadium and causing its partial volatilisation.

The method worked so well and with such evidently favourable results that the following course was adopted in the analysis of a specimen of the mineral vanadinite. 0·2500 grm. of air-dried and finely divided material was placed in a porcelain boat; the latter was then introduced into a combustion tube and gently heated in a current of dry hydrochloric acid gas. By this treatment vanadic and arsenic oxides were expelled, leaving lead phosphate and chloride. The receiver containing the vanadium and arsenic was made alkaline and digested with ammonium sulphide. From the solution of the sulpho-salts the vanadium and arsenic sulphides were set free by a dilute acid. After washing and careful drying these sulphides were separated as indicated in the preceding lines, then changed to oxides and determined in the usual manner. The sum of the total constituents determined as lead oxide, phosphoric oxide, vanadic and arsenic oxides, with some lead chloride, amounted to 0·2501 grm.

The method, in addition to being satisfactory in the analytical way, certainly forms a very excellent means of purifying and freeing vanadium from arsenic.—*Journal of the American Chemical Society*, xviii., No. 12.

THE SEPARATION OF MANGANESE FROM TUNGSTIC ACID.

By WALTER T. TAGGART and EDGAR F. SMITH.

The necessity of obtaining pure tungstic acid from time to time, using wolframite as the starting out material, has frequently suggested the inquiry as to what course would probably prove the best in the quantitative separation of this acid from oxides, such as those of iron and manganese.

In the experiments recorded in this communication only the results obtained from a study of mixtures of a manganous salt and a soluble alkali tungstate will be given. The directions taken in the experimentation were, 1st, to effect the separation by the use of yellow ammonium sulphide in the presence of ammonium chloride; 2nd, to eliminate the acid oxide by the use of an alkaline carbonate.

Following the first course, mixtures of definite amounts of ammonium tungstate and manganous chloride were made. To these was added water and a considerable excess of yellow ammonium sulphide, together with ammonium chloride. The mixtures were digested on a water-bath at 70° C. for several hours, and the vessels containing them were then closed and allowed to stand during the night. The manganese sulphide was filtered out, and, after solution, was changed into sulphate and weighed as such, or it was finally obtained as protosesquioxide in the customary way.

Results.

Manganous oxide present.	Manganous oxide found.
Grm.	Grm.
0·1950	0·2121
0·1949	0·2255
0·1290	0·1708
0·1287	0·1720
0·1291	0·1760

In every trial tungstic acid adhered to the metallic oxide.

In trying the second suggestion the soluble tungstate and the soluble manganous salt were digested for some hours in a platinum dish, upon a water-bath, with an excess of a 10 per cent potassium carbonate solution, after which the whole was evaporated to dryness, the residue boiled up with water, the manganous carbonate filtered out, washed, and finally converted into protosesquioxide.

Results

Manganous oxide present.	Manganous oxide found.
Grm.	Grm.
0·1949	0·1516
0·1949	0·1534

Several trials were made using a 50 per cent solution of potassium carbonate.

Results.

Manganous oxide present.	Manganous oxide found.
Grm.	Grm.
0·1951	0·1745
0·1950	0·1528

The experimental evidence given in the preceding paragraphs leaves no doubt as to the insufficiency of the two methods which were tried in effecting the desired separation. It is probable that fusion with an alkaline carbonate will alone answer for this purpose. How complete that course would be can only be ascertained by careful experimentation.

In the course of analysis molybdenum is quite often obtained as sulphide. Its conversion into a weighable form is attended with more or less difficulty. Trials made in connection with its estimation show that if the sulphide, as generally obtained, be dried, then intimately mixed with anhydrous oxalic acid, its careful ignition to trioxide can be made quite rapidly.

Results.

Molybdenum trioxide taken.	Molybdenum trioxide found.
Grm.	Grm.
0·3000	0·3009
0·3000	0·2990
0·1007	0·1011

—*Journal of the American Chemical Society*, xviii., No. 12.

On Dibromo 1—3 Propene. — R. Lospieau. — Epidibromhydrine, β: $CHBr=CH-CH_2Br$, is a colourless liquid which irritates the eyes and the skin. Its density at 0° is 2·097. If cooled to $-75°$ it congeals, but afterwards melts at $-52°$. It boils at 155—156°. Its molecular weight is $=200°$.—*Comptes Rendus*, cxxiii., No. 25.

THE SEPARATION OF BISMUTH FROM LEAD.

By ARTHUR L. BENKERT and EDGAR F. SMITH.

Many methods have been suggested to effect this separation. In a recent issue of the *Zeitschrift für Angewandte Chemie* (1895, p. 530), Olav Steen reviews thirteen of these methods, and concludes that an early proposal of Rose (*Ann. Chem. Phys. Pogg.*, cx., 425), in which the lead is thrown out as chloride and weighed as sulphate, another by Löwe (*Journ. Prakt. Chem.*, lxxiv., 348), in which the bismuth is removed as basic nitrate, and a late suggestion made by Jannasch (*Ber. Chem. Ges.*, xxv., 124), viz., the expulsion of the bismuth as bromide from a mixture of lead and bismuth sulphides by an air current carrying bromine, are the most satisfactory. At least these methods gave Steen the best results. The separation of bismuth from lead frequently confronts the analyst, and any novelty in this direction cannot be absolutely devoid of interest; hence the present communication, which brings data that may perhaps prove of service in the hands of others who are interested in the solution of this analytical problem.

It will be recalled that Herzog (*Ztschr. Anal. Chem.*, xxvii., 650) proposed to separate bismuth from lead by precipitating the former as basic acetate. The method required considerable time for execution, and in other hands than those of its author apparently has not yielded entirely satisfactory results.

An idea closely related to that of Herzog would be the substitution of a formate solution for that of the acetate. This was done, with results that are very interesting.

Solutions of lead nitrate and bismuth nitrate in nitric acid were made up of such strength that 20 c.c. of the first contained 0·2076 grm. of lead oxide, and 20 c.c. of the second 0·1800 grm. of bismuth trioxide. The lead and bismuth were accurately determined after dilution to a litre. 20 c.c. of these two nitrate solutions were then introduced into a beaker glass, carefully diluted and almost neutralised with sodium carbonate, or until the incipient precipitate dissolved slowly, when considerable sodium formate solution of sp. gr. 1·084 and a few drops of aqueous formic acid were added. The total dilution of the liquid was 250 c.c. It was gradually heated to boiling and held at that point for five minutes. The precipitate was then allowed to subside, but was filtered while yet hot. The basic formate separates rapidly, and is easily washed if not boiled too long. It was washed with hot water, then dissolved in dilute nitric acid, and precipitated with ammonium carbonate. The ignited bismuth trioxide weighed too much; it contained lead. However, the impure oxide was dissolved in nitric acid, diluted to 250 c.c., and after the addition of sodium carbonate to almost complete neutralisation, sodium formate and free formic acid were added as before, and *the precipitation of basic formate repeated.* This precipitate after solution and the bismuth thrown out by ammonium carbonate, gave 0·1804 grm. of bismuth oxide instead of 0·1800 grm. as required by theory. Seven additional separations, in which the quantities of bismuth and lead were the same as indicated above, gave—

0·1806 grm. of Bi_2O_3.
0·1806 ,, ,,
0·1803 ,, ,,
0·1804 ,, ,,
0·1804 ,, ,,
0·1805 ,, ,,
0·1796 ,, ,,

The conditions in these determinations were similar to those previously outlined.

With a solution containing 0·3600 grm. of bismuth oxide and 0·2076 grm. of lead oxide, operating in an analogous manner, two results were obtained:—

0·3595 grm. of Bi_2O_3.
0·3605 ,, ,,

nstead of the required 0·3600 grm.

The residual bismuth trioxide was examined for lead, but none was found.—*Journal of the American Chemical Society*, xviii., No. 12.

DETERMINATION OF THE ATOMIC MASSES OF SILVER, MERCURY, AND CADMIUM, BY THE ELECTROLYTIC METHOD.*

By WILLETT LEPLEY HARDIN.

Introduction.

A glance at the literature on the determinations of the atomic masses of silver, cadmium, and mercury, will show that, with the exception of cadmium, the electrolytic method has not been tried. Aside from the fact that certain errors involved in the washing and drying of the precipitates are eliminated by this method, its simplicity at once gives it preference over the usual methods of gravimetric determinations. Inasmuch as these three metals are completely precipitated from certain of their solutions by the electric current, and as it is desirable to determine the atomic mass of any element by different methods, it was thought advisable to apply this method in a re-determination of the atomic masses of these elements.

General Considerations.

Before taking up the different metals separately, the following general considerations may be mentioned:—

1. A careful preliminary study was made in the selection of compounds. Some compounds, which from a theoretical standpoint seemed to offer certain advantages, were found by experiment not to meet the requirements of exact determinations. Salts which can be sublimed were used whenever possible; and in all cases only those salts were used which form well-defined crystals.

2. All reagents used were either prepared or purified by myself, and carefully tested for impurities.

3. The metals were deposited in platinum dishes of about 200 c.c. capacity and about 65 grms. in weight. When the precipitation was complete, before interrupting the current, the solution was syphoned from the platinum dish, pure water being added at the same time: this was continued until the solvent used was completely removed from the dish. The current was then interrupted, and the deposit washed several times with boiling water, with the hope of removing any occluded hydrogen. After drying, the dishes were placed in a vacuum desiccator over anhydrous calcium chloride, and allowed to remain in the balance room until their temperature was the same as that of the room. Atmospheric dust was excluded from the platinum dishes during the process of deposition by means of two glass plates which formed a complete cover; the moisture which collected on this cover was washed back into the dish from time to time. The dishes were handled with nickelled tongs tipped with rubber.

4. The balance used was made expressly for this work by Henry Troemner, of Philadelphia. The beam and pans were made of aluminum, the beam being about 20 c.m. long. The framework was plated with gold to prevent corrosion. The sensibility for different loads and the ratio of the length of the two arms were carefully determined. The balance is sensitive to the fortieth of a m.grm., and the sensibility is almost independent of the load up to 75 grms. The difference in the length of the two arms is so slight that no correction need be applied. The balance was kept in a large quiet room of nearly constant temperature.

The larger weights used were made of brass, and the fractions of a grm. made of platinum. The weights were all previously compared against each other, and standardised with reference to the largest weight. The small corrections found in comparing them were tabulated and applied to all results. The weighings were made by the method of oscillations. The temperature and barometric pressure were noted at the time of each weighing, and all weighings were reduced to a vacuum standard. As the density of the atmosphere at the time of weighing the empty platinum dish was different from that at the time of weighing the dish and deposit together, the following formula was applied to obtain the weight of the deposit *in vacuo*:—

$$\left[\text{Weight of (dish + deposit)} - \frac{\text{weight of dish}\left(1+\frac{\lambda}{\Delta}-\frac{\lambda}{f}\right)}{1+\frac{\lambda'}{\Delta}-\frac{\lambda'}{f}}\right] \times \left[1+\frac{\lambda'}{\Delta'}-\frac{\lambda'}{f}\right] = \text{weight of deposit } in\ vacuo.$$

Where λ = density of air at the time of weighing the empty dish.
λ' = density of air at the time of weighing the dish + deposit.
Δ = density of platinum dish.
Δ' = density of metallic deposit.
f = density of weights.

As the weights were all standardised with reference to the 100-grm. brass weight, it is evident they must all be calculated as having the same density, equal to that of brass.

5. The atomic masses of the different elements involved in the calculation of results were taken from Clarke's latest report (*J. Am. Chem. Soc.*, xviii., 197).

Part I.

Determination of the Atomic Mass of Silver.

The mean of all the earlier determinations, as calculated by Clarke, gives 107·923 for the atomic mass of silver,—a result almost identical with the mean (107·93; O = 16) of the determinations of Stas.

Preparation of Pure Metallic Silver.

The silver used in this work was purified by the Stas method. Two hundred grms. of silver, about 99 per cent, pure, were dissolved in dilute hot nitric acid. The solution was evaporated to dryness, the nitrate heated to fusion and maintained in a fused condition until the oxides of nitrogen were no longer evolved. The residue, after cooling, was dissolved in as little cold water as possible, and after standing forty-eight hours the solution was filtered through a double filter to remove any suspended matter. The clear solution was then diluted with thirty times its volume of distilled water, and to it was added an excess of pure hydrochloric acid. The silver chloride which separated was allowed to subside, and was then thoroughly washed by decantation, at first with water containing a little hydrochloric acid, and finally with pure water. The precipitate was then collected on a cheesecloth filter, pressed strongly, and allowed to dry. When perfectly dry, the silver chloride was powdered finely and digested for three days with aqua regia; it was then thoroughly washed by decantation with distilled water. After obtaining the pure chloride of silver, it was necessary to purify the caustic potash and milk-sugar used in reducing the chloride to the metallic state. The caustic potash was heated to the boiling-point, and to it was added a concentrated solution of potassium sulphide to precipitate any heavy metals which might be present. The

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* Contribution from the John Harrison Laboratory of Chemistry No. 13. From the author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Ph.D.—From the *Journal of the American Chemical Society*, xviii., p. 990.

solution was filtered, and the filtrate digested for some time with freshly precipitated silver oxide, and again filtered to remove the excess of potassium sulphide. The milk-sugar was purified in a similar manner. The silver chloride was then placed in large porcelain dishes and covered with a solution of caustic potash and milk-sugar. The dishes were placed on a water-bath, and heated to a temperature of 70° to 80° until the reduction to finely divided metallic silver was complete. The alkaline solution was then poured off, and the grey metallic silver was washed with distilled water until the alkaline reaction disappeared. The metal was then digested with pure dilute sulphuric acid, and finally washed with dilute ammonia water. The silver thus obtained was mixed, when dry, with 5 per cent of its weight of fused borax containing 10 per cent of pure sodium nitrate. The mixture was fused in a clay crucible and the silver poured into a mould. The metal obtained in this way was almost snow-white in appearance, and dissolved completely in nitric acid to a colourless solution.

Preparation of Pure Nitric Acid.

To obtain pure nitric acid, one-half litre of the commercial C. P. acid was mixed with an equal volume of concentrated C. P. sulphuric acid and distilled from a retort provided with a knee-tube and condenser. The first portion of the distillate was rejected. The process was stopped when half of the nitric acid present had been distilled over. The distillate was mixed with an equal volume of pure sulphuric acid and re-distilled. The second distillate was collected in a flask, the mouth of which was closed with glass wool. When the process was complete the flask was closed with a doubly perforated cork, and placed in a water-bath at a temperature of 40°. A current of pure dry air was then conducted through the acid to remove any oxides of nitrogen. The acid was kept in a dark place.

Experiments on Silver Oxide.

If pure, dry silver oxide could be prepared, the atomic mass of silver could be compared directly with that of oxygen. A large number of experiments were made on this compound with the hope of determining the ratio of the atomic mases of these two elements.

Preparation of Silver Oxide.

A portion of the pure metallic silver was dissolved in pure dilute nitric acid, and the solution evaporated to crystallisation. The crystals of silver nitrate were dissolved in pure water, and to the solution was added a solution of pure sodium hydroxide, prepared by throwing pieces of metallic sodium on distilled water in a platinum dish. The 25 grms. of silver oxide prepared in this way were washed by decantation with 20 litres of water. The material was then dried at the ordinary temperature, after which it was finely powdered and dried for twenty-four hours in an air-bath at 100°. The oxide was kept in a weighing tube in a dark place.

Several analyses were made by dissolving a weighed portion of the material in pure potassium cyanide, electrolysing the solution, and weighing the resulting metallic silver. The observations invariably gave less than 95 for the atomic mass of silver. The oxide was re-dried at a temperature of 125°, and analysed as before, but the quantity of silver obtained was far below that calculated for the compound Ag_2O. Observations were also made on material dried at 140° and 150°. The results showed that it was impossible to prepare the silver oxide in a pure, dry condition.

After making these observations my attention was called to an article by Carey Lea (*Am. J. Sci.*, xliv., 240), in which were given the results of a series of analyses of silver oxide dried at different temperatures varying from 100° to 170°. These observations prove conclusively that oxygen is given off at a much lower temperature than that required to remove the last traces of moisture. From these observations and the results obtained by myself, it was evident that any further attempt to determine the atomic mass of silver from the oxide would be useless.

Although no careful study was made as to the nature of this compound, it might be added that, from my own observations, it seems very probable that the oxide contains some hydrogen in the form of hydroxyl.

(To be continued).

THE MANUFACTURE OF CALCIUM CARBIDE.*

By J. T. MOREHEAD and G. de CHALMOT.

(Continued from p. 18).

Taking into account the weight of the product, the time in which it has been produced, and the number of horse-power used, we calculate for each run the amount of pounds produced per horse-power in twenty-four hours. By multiplying these figures by the number of cubic feet of gas produced per pound we obtained the number of cubic feet of gas produced per horse-power in twenty-four hours. In the accompanying table we give the results of experiments, wherein everything has been determined, wherein both unslacked and slacked lime have been used, and voltage, ampèrage, and duration of runs were varied. Since these results were obtained we have had many visitors from all parts of the country, and for each party we have made a test run. The results of these runs have all confirmed our previous results, with one exception, which was due to the presence of 5½ per cent magnesia in the lime.

It is obvious that the results obtained from unslacked lime are far better than those with air-slacked lime. This is undoubtedly due to a loss of power used in decomposing the hydrated lime. The unslacked lime used by us contained, after being ground, from 5 to 9 per cent of water. In practice it is necessary to use the mixture that comes from the furnace again. This mixture always contains some carbonate of lime; but if it be mixed when still hot with the necessary amount of carbon, and put again into the furnace, the lime has no opportunity to slack. The unslacked lime has the further advantage that it weighs less and is much less bulky, and that the mixtures made from it cool much faster than those made from slacked lime. The only disadvantages of unslacked lime are, that it must be ground, and that mixtures made from it require more stoking if put into the furnace. The mixtures of unslacked lime can stand up against the sides of the furnace under a very steep incline, and they can leave a hole all around the pencils. The mixture to be used should, on an average, contain 100 parts of lime and 64 to 65 parts of carbon, in order to obtain a carbide of about 5 cubic feet of gas per pound. If the voltage is increased to 100 it is better to take a little more carbon (100 lime and 66 to 67 carbon). If the voltage is 65 or less, 63 to 64 parts of carbon are sufficient. If the amount of carbon is increased the carbide becomes purer, but there is often more coating.

The largest amount of gas per horse-power is obtained if the carbide yields about 5 cubic feet of gas per pound. The yield of carbide in pounds varies inversely with the quality. In the following table we give the results of a series of experiments made with slacked lime and with a current of 65 volts and from 1700 to 2000 ampères. Several of these experiments have not been taken up in Table II., becaue the amount of slag on all the pieces of carbide has not been determined.

Carbide has been made successfully in Spray by the use of both the direct and the alternating current. We cannot express an opinion as to what current can be used

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* Read Sept. 3rd before the Springfield meeting of the A.A.S. by one of us (M). We have made since then several additions, so as to make the article complete up to the present time. From the *Journal of the American Chemical Society*, April, 1896.

Table II.—*Unslacked Lime.*

Date.	Time of experiment.	Volts.	Ampères.	Loss of voltage in the pencils.	Horse-power.	Production in 24 hours, including slag.	Net production.	Cubic feet of gas per hour.	Cubic feet of gas per horse-power in 24 hrs.
	Hours.			Per cent.		Pounds.	Pounds.		
June 27	2·50	100	1700	7·0	214	9·87	9·42	4·83	45·50
July 2	3·00	100	1666	8·0	205	10·34	9·76	5·25	51·24
,, 1	2·25	100	1700	10·0	205	10·66	10·10	4·66	47·06
June 24	3·20	100	1600	7·0	214	11·50	10·73	4·93	52·90
,, 28	2·50	100	1700	10·0	205	11·70	11·10	4·75	52·72
July 18	3·00	65	2000	5·0	165	9·63	9·15	4·95	45·29
,, 19	3·00	65	1900	5·0	158	10·40	9·62	4·83	46·46
,, 5	3·75	65	2000	5·0	165	8·38	8·15	5·40	44·01
,, 9	4·50	65	2000	5·0	165	9·50	9·05	4·99	45·16
Aug. 10	6·00	65	1800	8·0	144	9·34	9·00	5·39	48·51
,, 13	6·00	65	1800	8·0	144	10·83	10·44	4·82	50·32
July 31	7·00	75	1800	8·5	166	11·44	10·53	4·83	50·86
						Average ..	9·75	4·97	48·33

Table III.—*Air-slacked Lime.*

						Per horse-power.		Per pound.	
Jnne 25	5·00	100	1700	7·0	214	8·34	7·96	5·30	42·19
,, 29	4·00	100	1700	10·0	205	8·78	8·34	4·98	41·53
,, 19	5·50	100	1700	7·0	214	9·25	—	4·89	—
,, 22	4·00	100	1600	7·0	199	9·80	9·65	4·74	45·75
Aug. 14	4·50	75	1700	7·0	159	7·88	7·13	5·50	39·22
July 12	3·75	85	1800	3·5	198	—	6·33	5·55	35·13
,, 26	8·00	75	1800	5·0	172	8·40	7·23	5·33	38·54
,, 12	5·50	85	1775	8·0	185	—	7·32	5·32	38·94
,, 6	5·00	80	1020	3·0	200	8·78	8·16	5·11	41·70
,, 23	3·00	65	1800	5·0	150	6·83	6·40	5·78	56·99
,, 22	2·00	65	1800	5·0	150	7·13	6·40	5·62	35·97
,, 22	2·00	65	1800	5·0	150	7·20	6·40	5·64	36·09
,, 25	9·00	65	1800	5·0	150	7·72	7·27	5·54	40·28
,, 20	4·00	65	1800	5·0	150	8·60	8·00	5·01	40·08
,, 23	5·00	65	1800	5·0	150	9·02	8·00	5·07	40·56
,, 24	8·00	65	1800	5·0	150	9·30	8·03	4·97	39·91
						Average ..	7·51	5·27	39·52

Table IV.

Date.	Production per horse-power including slag. Pounds.	Cubic feet of gas per pound.
July 23	6·85	5·78
June 14	7·10	5·80
July 22	7·13	5·62
,, 22	7·20	5·64
,, 25	7·72	5·54
Aug. 14	7·88	5·50
May 21	8·10	5·20
,, 22	8·30	5·10
July 26	8·40	5·33
June 4	8·46	5·52
July 20	8·60	5·01
June 5	8·76	4·94
May 28	8·80	5·20
,, 23	8·82	5·10
July 23	9·02	5·07
June 8	9·06	5·10
,, 24	9·30	4·97
July 11	9·30	4·33
Aug. 12	9·44	4·51
May 31	9·87	4·30
Aug. 8	10·52	4·23

to the best advantage, for we are not able to compare results. All of the results communicated in this paper have been obtained by the use of the alternating current. That electrolysis plays a part in the carbide manufacturing process of Mr. Wilson is therefore out of the question, and we do not need to use a furnace of the Moissan construction to prove this. It is not desirable to increase the ampèrage over 2000 if only six carbons of 4 inches square are used. The higher the ampèrage the greater the loss of voltage in the pencils, and therewith that of power. The carbons will also last longer if the ampèrage is low, because they do not become so hot. Lastly, we did not obtain as great a yield per horse-power if the ampèrage was high and the voltage correspondingly low. We obtained the best yield of gas per horse-power by using a current of 100 volts, which can be seen by comparing the average of the results given in Table II.

Table V.

	Volts.	Horse-power.	No. of experiment.	Average cubic feet of gas per horse-power in 24 hours.
Unslacked lime ..	100	205—214	5	49·88
	65—75	144—165	7	47·23
Slacked lime ..	100	200—214	3	43·15
	75—85	159—100	5	38·71
	65	150	7	38·55

It must be taken into account that we measured the primary current, and that the losses of ampèrage in the transformers probably have been higher when we did not use the highest voltage, *i. e.*, 100. We do not know in how far it would be advisable to increase the voltage over 100, since our dynamos cannot give us a current of more than 100 volts. We believe, however, that the heat yielded by an arc of 100 volts, and from 1700 to 2000 ampères, is about the largest amount to be profitably used for the production of carbide in one furnace with six pencils, as it is used in Spray. We base our assumption on the following facts:—The quality of the carbide becomes better if the voltage decreases. We experienced some trouble in obtaining large carbide crystals with an arc of 100 volts and 1700 ampères, and in order to obtain a carbide that yields more than 5 cubic feet of gas per pound the mixture should contain an excess of carbon. If a current of 100 volts and 1700 ampères is used, the furnace requires more attendance and stoking than if a lower power, and especially a lower voltage, is used. The higher the voltage the faster the pencils must be raised, for if the voltage is low (50 or 65) the carbide spreads out much more than if the voltage is high (100 volts). In the latter case the carbide builds up as a long thin piece, and it is oftener necessary to empty the furnace. As to the time that one furnace should be used continuously, we wish to say that we did not perceive a difference in the quantity and quality of the product whether we ran three hours or from three to nine hours. We must, however, remark that in the case where we used 100 volts and 1700 ampères with mixtures of unslacked lime we could not continue running for much more than three hours, because the construction of the furnace did not admit of raising the pencils quite 3 feet. With slacked lime we made also with this high power very satisfactory runs of five and five and a half hours. During the first hour the production is somewhat lower. It seems that more heat is lost probably for heating up the furnace.

The mixture used in all of the following experiments contained lime 50·08 per cent, and coke (of 92·17 per cent of carbon), 39·22 per cent. The current was of 65 volts and 1800 ampères, the loss of voltage in the pencils 5 per cent, and the net horse-power 150.

Table VI.

Time of experiment. Hours.	Production per hour in pounds.	Cubic feet of gas per pound.	Cubic feet of gas per hour.
1	37	5·63	208·31
2	40	5·62	224·80
2	40	5·64	225·60
3	40	5·78	237·20

(To be continued).

DERIVATIVES OF COLUMBIUM AND TANTALUM.*

By MARY ENGLE PENNINGTON.

(Continued from p. 20).

Qualitative Reactions.

Throughout this investigation the following questions constantly arose: How shall the purity of the columbium and tantalum compounds be determined. When is columbium free from tantalum? When is it free from titanium?

In the earlier work upon columbium we find Hermann describing a new element which he obtained from the mother liquors of the columbium potassium fluoride. This element, he states, gave a dark brown solution when reduced with zinc and hydrochloric acid, while the pure columbium compound gave a blue colour. Both these solutions, on standing in the air, reverted to the white hydrate. Marignac replied that the brown colour was not due to ilmenium, but to titanium, a view which is now generally accepted.

He also declares that a brown colour is produced when the potassium columbium oxyfluoride is treated with zinc and hydrochloric acid, the acid being in considerable excess. Then, by titrating with permanganate, he found that an intermediate oxide had been formed, to which he gave the formula Cb_3O_5.

Crystals of the columbium salt, prepared as described above, continued to give this brown solution even after they had been subjected to five or six re-crystallisations. Following the plan of Krüss and Nilson (*Ber. d. Chem. Ges.*, xx., 1676), the atomic value of the oxide contained in such crystals was determined by decomposing with sulphuric acid, weighing the pentoxide and the potassium sulphate, then, by the ratio $2K_2SO_4 : Cb_2O_5$, determining the value for Cb^v. This was found to be 85·7. Iron and manganese has been eliminated; titanium therefore was the probable cause of this low atomic value. The salt used was perfectly white, yielding a pure white oxide. This oxide was tested for titanium by the most delicate reactions known for the metal, but its presence could not be proved by any of them.

1. *Colour and Reduction Reactions.*—It has been found that the qualitative tests given in the various text-books for these three elements do not always hold good when the solution used is a double fluoride. As it is in this form that the separations are usually made, it has been thought advisable to note the action of some of the common reagents on these salts.

Gallotannic acid, which is considered the most characteristic test for columbium salts, behaves differently with different double fluorides. An acid solution of the laminated salt gives almost instantly a deep brick-red precipitate. The salt, crystallising in long needles, gives a lighter red precipitate which does not separate so rapidly. The large, thin, transparent plates previously mentioned give only a slight precipitate, and this is yellow in colour. These reactions are most delicate if the salt be dissolved in water, a drop of hydrochloric acid added, then a little gallotanic acid dissolved in alcohol. After standing several hours all the precipitates assume the same colour —a dark brick-red.

Tantalum double fluoride gives a sulphur-yellow colour with gallotannic acid. This, however, on standing, becomes brick-red, as the columbium does.

Titanium compounds are said to give a brownish colour with gallotannic acid, which changes quickly to an orange-red. The potassium titanium fluoride gave a straw-yellow colour with this reagent; in time a flaky precipitate forms, but the colour does not materially alter.

The following colour reaction serves for the detection of very small quantities of columbium, and is applicable to any soluble columbium compound. An excess of potassium thiocyanate is added to a small quantity of the dissolved substance; then some pieces of zinc followed by strong hydrochloric acid. At once the solution becomes a bright golden brown, which, if much columbium be present, may be almost red. A brisk and continued evolution of the gas does not alter this tint, which is also stable for more than twenty-four hours in the acid solution. Neither titanium nor tantalum give any reaction with potassium thiocyanate under the above conditions.

Hyposulphurous acid, H_2SO_2, gives noteworthy colour reactions with these salts. The tests were conducted in the following manner:—A few cubic centimetres of a concentrated solution of sulphur dioxide were placed in a test-tube provided with a cork, and granulated zinc was added. The liquid changed to a greenish colour, and hydrogen was liberated. As soon as the evolution of the gas had ceased the solution containing the hyposulphurous acid was poured into the salt solution to be tested.

A solution of titanium double fluoride gave an orange-yellow colour at once. The oxide, when treated in like manner, became yellow.

Columbium double fluoride gave no colour, but a white hydrate was soon precipitated. Columbic oxide gave a slight yellow tinge.

Tantalum double fluoride gave no colour, but after standing a white precipitate separated. Tantalic oxide remained colourless when treated with hyposulphurous acid.

The white precipitates from the tantalum and columbium salts were probably hydrates due to the oxidation of the acid and its consequent action upon these salts.

Zinc and hydrochloric acid gave no reaction with the double fluoride of tantalum. With titanium a clear delicate green was obtained. The columbium salts always gave a colour with these reagents. The solution is at first dark blue, then a greenish brown, and finally a dark

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* From the author's thesis presented to the University of Pennsylvania for the degree of Ph.D., 1895. From the *Journ. Amer. Chem. Soc.*, xviii., January, 1896.

	$2KF.CbOF_3.H_2O$.	$2KF.TaF_5$.	$2KF.TiF_4$.
Lead acetate.	White precipitate.	White precipitate.	White precipitate.
Mercuric chloride.	Slight precipitate in 24 hours.		
Mercurous nitrate.	Yellow precipitate.	Yellowish-green precipitate.	Yellowish-green precipitate.
Potassium chromate.	White precipitate, soluble in H_2O. Partly soluble K_2CrO_4 solution.		Precipitate soluble in water.
Potassium bichromate.		Precipitate after standing.	
Potassium cyanide.	White precipitate on boiling.	White precipitate.	White precipitate.
Potassium ferrocyanide.	Green-blue precipitate on boiling.	Yellow precipitate on boiling.	Precipitate on boiling.
Potassium thiocyanate.	White precipitate.	White precipitate soluble in the cold. Comes down by boiling.	
Potassium iodide.	White, granular precipitate. Iodine is liberated.	White granular precipitate.	No precipitate, but iodide is liberated.
Disodium hydrogen phosphate.		White precipitate after standing.	White precipitate.
Silver nitrate.		White precipitate after standing.	
Sodium bisulphite.	White precipitate.	White precipitate.	White precipitate.
Sodium pyrophosphate.		Slight cloudiness.	Precipitate.
Hypophosphorous acid.			Precipitate.
Sodium metaphosphate.		Slight cloudiness.	
Potassium bromide.	White precipitate.		

brown. Frequently a brown precipitate separates, which, on standing, becomes white.

The hydrochloric acid solution of columbic oxide, and also the potassium columbium fluoride, were tested with hydrogen peroxide, this being accepted as one of the most delicate reagents for titanium. No yellow colour in either case was obtained.

2. *Reactions with Wet Reagents.*—A number of the ordinary reagents have been tried with these salts, the results being given in the table above. The reactions for the greater number are very different when the metal tested is as double fluoride. The ferrocyanides, in particular, have quite abandoned their ordinary colours with these compounds.

Disodium hydrogen phosphate, when added to titanium double fluoride, precipitates the titanium completely. The filtrate, tested with ammonium hydroxide, gave no precipitate. Columbium double fluoride, on the contrary, is not affected by this reagent. After boiling a long time in a platinum dish a few white flocks were observed in the solution, but in such small quantity that they were disregarded. Whether this behaviour may or may not be made the basis of a separation of these two elements is not yet determined, because of the difficulty in getting rid of the phosphoric acid. Fusion with sodium carbonate, extraction with water, and subsequent precipitation by sulphuric acid gives a mixture of sodium salt and columbic oxide. Some columbium remains in solution. Fusion with potassium acid sulphate is more satisfactory, yet is not complete.

Deportment of Tantalum, Columbium, and Titanium Double Fluorides toward the Electric Current.

1. A solution of potassium columbium double fluoride, $2KF.CbOF_3.H_2O$, in water, was treated with a small amount of sodium acetate. The precipitate formed was dissolved in acetic acid, and through this solution a current of one ampère, obtained from a thermopile, was conducted for five hours. A white precipitate, seemingly a hydrate, was formed. On breaking the current, this rapidly went into solution.

2. (*a*) A solution of the salt in water was subjected to the same current for eight hours. Almost immediately the bottom of the platinum dish was covered with a blue deposit. This gradually spread over the whole surface exposed to the action of the current, and became in a short time iridescent. As the deposit increased, the deep blue tint changed to more of a grey, and remained so until the current was broken. It was washed quickly with water, then with alcohol, and it was dried on the hand.

0·1315 grm. of the salt was taken; the deposit weighed 0·0282 grm. This metallic-looking substance did not alter in the air, but, on subjecting it to a red heat, a white, shining, apparently crystalline compound resulted. It was readily soluble in hydrofluoric acid.

(*b*) A second experiment, with 0·2195 grm. of the substance, gave, under the same conditions, a deposit weighing 0·0388 grm. This, when ignited in the air, burned to a white oxide weighing 0·0312 grm. The blue compound is, in all probability, a lower hydrated oxide of columbium.

3. The electrolysis of an aqueous solution of a sodium columbate gave a white flocculent hydrate, not adherent to the dish. The precipitation was not complete. A current of one ampère was employed for a period of seven hours.

4. With a much stronger current (two ampères), a solution of the double salt $2KF.CbOF_3.H_2O$, gave first a white hydrate, then, beneath the outer edge of the anode appeared a dark brown ring which gradually grew in towards the centre of the dish, never reaching it, however, but stopping when about half an inch in width.

This brown substance was slightly adherent to the dish, but just as soon as the current was broken, and the liquid poured off, it reverted to the white hydrate. This change was so rapid that it was impossible to separate the brown from the white substance.

Thinking that this brown compound might be a contaminating element, about 1 grm. of the double salt was dissolved in water and electrolysed until the brown ring had appeared. Then the liquid was poured into another dish as quickly as possible, and the current run through again. The brown ring appeared as before, and was treated in the same manner. After changing the dish four times only a trace of brown could be seen. When the remaining solution was evaporated it was found that almost the entire quantity of the columbium had been precipitated. The brown substance here formed resembles in its behaviour that produced in a like solution by zinc and hydrochloric acid.

The resistance of this solution is very high.

5. Potassium tantalum fluoride, in aqueous solution, was subjected to the action of a current of two ampères for six hours. A small quantity of hydrate was found in

the liquid, and on the dish a very slight iridescent deposit mixed with some white hydrate.

6. Potassium titanium fluoride was treated in the same manner as the previous salt. A small quantity of hydrate was found here, some of which adhered to the dish. The iridescent deposit, however, was wanting.

Action of Hydrofluoric Acid upon the Oxides of Tantalum, Columbium, Titanium, and Silicon.

The well-known volatility of the oxides of tantalum and columbium, when heated with hydrofluoric acid, led to the hope that in this behaviour might lie a separation from titanium, and also from silica.

Rose states that a very appreciable loss occurs when the first two oxides are treated as suggested, but he makes no attempt to separate them from the latter two. To this end 1 grm. of the mixed oxides of tantalum and columbium was evaporated to dryness with hydrofluoric acid, the residue being heated over the free flame for a few minutes. By this treatment dense white vapours were driven off. Upon weighing the residual oxides they were found to equal 0·5464 grm. A second evaporation gave further loss, but as both columbium and tantalum continued to remain, the method is without value.

The separation of silica from these oxides can be accomplished by the heat of an iron plate after evaporating to dryness on a water-bath. The final heating must be carefully done, and the acid should not be in too great excess.

I have never found it impossible to dissolve either the mixed or the pure oxide in hydrofluoric acid, even though strongly ignited. It is true, concentrated acid is necessary, and a little time is often required, but a perfect solution does take place.

Tantalic oxide, containing columbic oxide, is far more soluble in hydrofluoric acid than the pure oxide. The same behaviour has been observed with pure columbic oxide, though it is not so pronounced as with tantalic oxide. Titanium dioxide, ignited, is very difficultly soluble in this reagent, though columbic oxide, containing titanic oxide, went quickly into solution.

Double Fluorides of Tantalum, Columbium, and Titanium, with Rubidium and Cæsium.

The potassium double fluorides of tantalum and columbium have been found of great service in separating these two metals. Marignac first showed that a separation could be effected through these salts, and he also demonstrated that the sodium and ammonium salts were inapplicable.

Of the potassium double fluorides of tantalum and columbium we possess considerable information. A number have been isolated and studied. The sodium salts crystallise so poorly that their history is not so well known. It seemed probable that rubidium and cæsium would form double fluorides of definite crystalline character with these three metals. At least, a study of their behaviour might be found instructive. Before taking up their preparation, however, the simple fluorides of rubidium and cæsium may be discussed.

Rubidium Fluoride (RbF).—An examination of the literature on rubidium showed that its fluoride had not been prepared. In order to procure this rubidium iodide was dissolved in water, and moist silver oxide added to precipitate the iodine. The solution of rubidium hydrate resulting was filtered off and evaporated in porcelain dishes. A very appreciable quantity of silver oxide was held in solution by the rubidium hydroxide, so that it was necessary to evaporate it almost to dryness, then to take it up in the smallest possible quantity of water, and filter. This treatment may have to be repeated two or three times before the solution is perfectly colourless. When quite free from silver, the concentrated solution was made slightly acid with hydrofluoric acid, and evaporated. If hydrofluoric acid be present it is almost impossible to obtain crystals, a thick syrup being formed which defies all attempts in this direction. The solution is therefore evaporated with water several times until the excess of acid is expelled. The rubidium fluoride then crystallises in long, transparent plates. These were drained, and dried between filter paper. The salt was anhydrous. Conversion into sulphate by evaporating with sulphuric acid gave, from 0·5 grm. of the salt, 0·5236 grm. rubidium sulphate. This corresponds, therefore, to the formula RbF.

Cæsium Fluoride.—Cæsium chloride was dissolved in water, and the chlorine precipitated by moist silver oxide. The solubility of the oxide of silver in cæsium hydrate is even greater than in rubidium hydrate, therefore some difficulty was experienced in obtaining a hydrate free from silver. It was finally accomplished by evaporating to dryness repeatedly, taking up the cæsium hydrate in a very small quantity of water, and filtering it. The pure hydrate was then neutralised with hydrofluoric acid and evaporated. A thick syrup was obtained which refused to crystallise. Upon heating in an air bath to 130° C., a crystalline mass formed, but it was always in such a sticky condition, and absorbed moisture so rapidly, that it could not be analysed satisfactorily. This mass was dissolved in water and added to the solutions of the metals in hydrofluoric acid.

Double Fluoride of Columbium and Rubidium.—One-half grm. of columbic oxide was dissolved in hydrofluoric acid and the calculated quantity of rubidium fluoride added. The solution was evaporated on a water-bath to expel the excess of acid. The residue was taken up in hot water and allowed to crystallise spontaneously. White microscopic plates separated. These were filtered off, dried between filter paper, and analysed. Two-tenths grm. of the dry salt gave—

	Found.	Calculated for $2RbF.CbF_5$.	Difference.
Cb_2O_5 ..	0·0670	0·0673	−0·0003
RbF ..	0·1048	0·1049	−0·0001

The formula of the salt is therefore $2RbF.CbF_5$, corresponding to the tantalum salt usually obtained with potassium fluoride.

The filtrate from this first crop of crystals was slightly concentrated, when small, shining, or even iridescent crystals, apparently plates, separated. Upon standing a short time, these changed over into crystals like those first mentioned. This salt is very soluble in water containing hydrofluoric acid, and also in pure water. It is insoluble in alcohol.

Double Fluoride of Rubidium and Tantalum.—Rubidium fluoride in slight excess was added to tantalic oxide dissolved in hydrofluoric acid. Small white needles crystallised out. An excess of acid must be present, otherwise heat decomposes the double salt, giving a fine, white, insoluble compound, as is the case with the potassium salt.

Analyis of $\frac{2}{10}$ grm. gave

	Found.	Calculated for $2RbF.TaF_5$.	Difference.
Ta_2O_5 ..	0·0915	0·0913	+0·0002
RbF ..	0·0861	0·0859	+0·0002

Double Fluoride of Titanium and Rubidium.—The preparation of this salt was conducted as described with preceding salts. The crystals here were also microscopic needles. Some difficulty was at first experienced in completely drying the salt, but this was overcome by several re-crystallisations from pure water, when an anhydrous product was obtained. One-tenth grm. of the salt gave, on analysis—

	Found. Grm.	Calculated for $2RbF.TiF_4$. Grm.	Difference.
TiO_2 ..	0·0238	0·0240	−0·0002
RbF ..	0·0622	0·0626	−0·0004

*Double Fluorides of Tantalum and Cæsium.**—This double salt was formed by the addition of a solution of the cæsium hydrate in hydrofluoric acid to a solution of tantalic oxide in hydrofluoric acid. Very beautiful white needles separated, which were not easily soluble in water, and were not decomposed by re-crystallisation from pure water. The aqueous solution may be evaporated on a water-bath with perfect safety, this salt being apparently much more stable than either the potassium or rubidium salt.

The crystals were dried in the air, then heated to 125° C. in an air-bath. No loss in weight was observed. 0·25 grm. gave, on analysis—

	Found.	Calculated for $15CsF.TaF_5$.	Difference
Ta_2O_5 ..	0·0212	0·0217	−0·0005
CsF	0·2232	0·2228	−0·0004

The formula deduced from the analytical data varies widely from that generally followed by tantalum double fluorides. Neither is it in accordance with Remsen's law for the double halides (*Am. Chem. J.*, ii., 291), though it will be observed that its fluorine content bears a simple ratio to the fluorine in combination with the tantalum.

Double Fluoride of Columbium and Cæsium.—This double salt was formed in the manner described for the preparation of the cæsium tantalum fluoride. It is very soluble in water containing hydrofluoric acid, and in pure water, from which it crystallises in needles. These, when pure, are anhydrous. Boiling with pure water does not decompose the salt. Analysis of $\frac{2}{10}$ grm. gave the following result:—

	Found.	Calculated for $7CsF.CbF_5$.	Difference.
Cb_2O_5 ..	0·0216	0·0213	+0·0003
CsF	0·1694	0·1698	−0·0004

This salt, which appears to be $7CsF.CbF_5$, is even more erratic in its constitution than the tantalum cæsium compound. There is apparently no relation here between the fluorine in combination with the columbium and the number of molecules of cæsium fluoride present.

Double Fluoride of Titanium and Cæsium.—This salt separates in very small, shining crystals when cæsium fluoride is added to a rather concentrated solution of titanic oxide in hydrofluoric acid. It is more readily soluble in water than the tantalum cæsium compound, and is not decomposed by pure water. The air-dried crystals showed no loss in weight after heating for some time at 125° C. An analysis of 0·25 grm. gave the following amounts of titanic oxide and cæsium fluoride:—

	Found.	Calculated for $4CsF.TiF_4$.	Difference.
TiO_2 ..	0·0269	0·0271	+0·0002
CsF	0·2071	0·2076	−0·0005

The figures point to the formula $4CsF.TiF_4$. This is a departure from the usual titanium double fluorides, and agrees with the law laid down by Remsen for these salts.

When we consider the atomic masses of tantalum, columbium, and titanium, the first 182, the second 94, and the third 48, and also consider the quantities of cæsium fluoride which unite with a molecule of each of the metallic fluorides, we find that with tantalum the quantity (fifteen) is nearly twice that with columbium (seven), and the latter almost double that (four) uniting with titanium, just as 182 is about twice 94, and 94 nearly twice 48.

These new cæsium compounds tend to confirm the conclusion drawn by Wells and others (*Amer. Journ. Sci.*, xlvii.) from their work on the cæsium double halides. The compounds investigated by these chemists show that the cæsium double halides are not wholly conformable to Remsen's law.

The method of analysis pursued for the determination of these double salts is, briefly, as follows:—

The dry substance was decomposed in a platinum crucible by a few drops of concentrated sulphuric acid. The hydrofluoric acid was driven off, and the excess of sulphuric acid was then expelled on a sand-bath. The temperature must be just sufficient to drive off the acid. The metallic oxide was obtained from the sulphate by long boiling with a large quantity of water. It was then filtered, washed about twenty times with boiling water, ignited, and weighed. The filtrate containing the alkaline sulphate was evaporated, the excess of acid neutralised with ammonium carbonate, and the solution then evaporated to dryness on a water-bath. A saturated solution of ammonium carbonate was added, and the mixture evaporated again to dryness. The ammonium salts were expelled by careful heating. Constant weight can generally be obtained after two or three evaporations with ammonium carbonate. The rubidium sulphate decrepitates on heating, which necessitated great care while expelling ammonium salts, and also rendered the method proposed by Krüss (heating in a stream of ammonia gas) untrustworthy. The alkalies were then weighed as normal sulphate, and the cæsium or rubidium content calculated. This method, while slow, has been found very satisfactory for these rare alkalies.

(To be continued).

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* This and all the other cæsium double fluorides are being subjected, at this writing, to further study in this laboratory.—E. F. Smith.

OBITUARY.

THE LATE DR. EMIL DU BOIS REYMOND.

This most distinguished physiologist concluded his fruitful and honourable career on December the 26th. The deceased, perhaps our highest authority in the wide and interesting region of animal electricity, was born at Berlin on November 7th, 1818. As his name indicates, he was of French descent. He studied firstly theology, at the University of Berlin, but soon turned his attention to the more congenial subject of medicine, becoming one of the most prominent pupils of Johannes Müller, and soon acquired—as, indeed, he richly merited—a world-wide celebrity. In 1851 he was elected a member of the Royal Prussian Academy of Sciences, and in 1867 he was appointed Perpetual Secretary, an office which he filled up to his death. His eminence was needed as a counterpoise to the quackery which was and is still seeking to degrade the study of animal electricity.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiii., No. 26, December 28, 1896.

An interesting ceremony took place at the Institute Pasteur on the transfer of the remains of the late illustrious *savant* to the crypt specially designed for his reception. The principal personages present were:—M. Rambaud, the Minister of Public Instruction, on behalf of the Government; M. Baudin, President of the Municipal Council, on behalf of the city of Paris; Sir Joseph Lister, President of the Royal Society of London, Foreign Associate of the Academy of Sciences, on behalf of the Royal Society, and of the Royal College of Surgeons of London; Sir W. Priestley, on behalf of the Universities of Edinburgh and St. Andrews; Sir Dyce Duckworth, on behalf of the Royal College of Physicians of London; M. A. Cornu, President of the Academy of Sciences; M. Bergeron, Perpetual Secretary of the Academy of Medicine; M. L. Passy, Perpetual Secretary of the Society of Agriculture; and M. Duclaux, Director of the Institute Pasteur.

New Application of Radioscopy to the Diagnosis of Maladies of the Thorax.—Ch. Bouchard.—Details of some cases of no chemical interest.

The Energy expended by a Muscle in Static Contraction for the Maintenance of a Charge after Respiratory Exchanges.—A. Chauvereau, with the collaboration of M. Tissot.—The conclusion from the authors' first series of experiments is, that the quantities of oxygen absorbed and of carbonic acid exhaled—*i. e.*, of the energy expended for the maintenance of a charge—increase with the muscular contraction, although the charge remains constant. The conclusion from the second series of experiments is that the oxygen absorbed and the carbonic acid exhaled—*i. e.*, the energy brought into play for the maintenance of a charge—increase sensibly in the same manner as such a charge.

New Radioscopic Facts concerning Intrathoracic Lesions—J. Bergonié.—This paper has no chemical bearings.

Action of Lithium upon Carbon and certain Carbides.—M. Güntz.—This paper will be inserted at some length.

On the Chlorine Carbide, C_3Cl_3.—Paul Lemoult.—A thermo-chemical paper.

Action of the Carbonic Acid of Waters upon Iron.—P. Petit.—The action of iron upon calcium bicarbonate and upon carbonic acid in solution enables us to explain the attack of iron pipes and tanks in certain waters. It gives also the mechanism of the purification of waters by iron, and the purification of syrups by iron-filings in the sugar manufacture.

Action exerted upon Solutions of Alkaline Haloid Salts by the Acids present.—A. Ditte.—On adding the acid to the solution of a neutral salt, we determine at first a decrease of the solubility, but it does not increase without limit with the quantity of acid added.

Action of Phosphorus upon Platinum.—A. Granger.—Until recently only platinum biphosphide was known. In 1884 two American chemists, Clarke and Joslin, obtained a definite compound, Pt_3P_5, which dissolves partially in *aqua regia*, leaving an insoluble protophosphide, PtP. The dissolved matter contains the biphosphide, PtP_2. The author, on repeating this experiment, obtained a subphosphide, Pt_2P. At white redness the mass retained only 4 per cent as phosphorus.

Action on Gaseous Hydrochloric Acid upon the Alkaline Sulphites.—Albert Colson.—Experiment shows that, contrary to the opinion of some *savants* of authority, sodium sulphate, SO_4Na_2, is attacked in the cold by dry HCl. There exist small series of tensions of hydrochloric acid gas.

The Reduction of Tungsten by Coke in the Electric Furnace.—Ed. Defacqz.—This memoir will be inserted in full.

New Instances of Normal Rotatory Dispersion—Ph. A. Guye and P. A. Melikion.—The substances being arranged according to the increasing values of $[\alpha]_D$ we remark that the specific rotatory dispersions remain of the same order of magnitude, but they are not proportional to the specific rotatory power.

Transformation of the Sulphonated Camphophenols into Dinitro-orthocresol.—P. Cazeneuve.

On Hexa-diimediol.—R. Lespieau.

The Congelation-point of Milk.—J. Winter.—A controversial memoir in reply to MM. Bordas and Génin.

A Contribution to the Study of the Borneols and their Ethers.—J. Minguin.—These last papers are not adapted for abstraction.

Optical Analysis of Urine and Exact Determinations of the Proteids, Glucosides, and Non-fermentible Saccharoid Matters.—F. Landolph.—(See p. 25).

Revue Universelle des Mines et de la Metallurgie.

Series 3, Vol. xxxvi., No. 1.

Determination of Sulphur in the Products of Siderurgy.—The methods for the determination of sulphur in siderurgical products are classified under the following heads:—Procedures for the direct oxidation of sulphur by the moist or the dry method, followed by precipitation as barium sulphate either with or without a previous elimination of iron; procedure for direct chlorination by the dry method, and precipitation as barium sulphate; procedures by hydrogenisation of the sulphur in the dry way; procedures of evolution, H_2S being liberated by the action of dilute acids and either oxidised to form SO_3 or absorbed by saline solutions; mixed procedures. This lengthy memoir, which extends to 90 pages, requires the accompanying figures.

MISCELLANEOUS.

To Soda and Ultramarine Manufacturers.—Rud C. Gittermann writes as follows from Odessa, South Russia, under date January 8th, 1897:—"It may interest your readers that we are in great want here of manufactories of soda and ultramarine, and that competent English makers of these articles are sure to make their fortunes by establishing here. A part of the necessary capital could needs be found here. If this interests any of your readers I shall be happy to give details on enquiry."

Our Weights and Measures.—A Practical Treatise on the Standard Weights and Measures in use in the British Empire, with some account of the Metric System, by H. J. Chaney, will be published early in January. It will contain much information derived from authorised sources, and the writer's position as Superintendent of the Standards Department, Board of Trade, assures us that the information given—information now for the first time published—will be of practical use to local officers, and especially to traders generally. It is hoped also that the book will even be of use to the chemist and physicist, and that the antiquarian will find something of interest in its pages. The information given with reference to "metric" weights and measures should be of particular use to scientific authorities and to manufacturers.

MEETINGS FOR THE WEEK.

MONDAY, 18th.—Society of Arts, 8. (Cantor Lectures). "Material and Design in Pottery," by Wm. Burton, F.C.S.

— Society of Chemical Industry, 8. "The Character of the London Water Supply," by W. J. Dibdin, F.I,C., F.C.S.

TUESDAY, 19th.—Royal Institution, 3. "Animal Electricity," by Prof. A. D. Waller, F.R.S.

WEDNESDAY, 20th.—Society of Arts, 8. "The Roller Boat of Mons. Bazin," by Emile Gautier.

THURSDAY, 21st.—Royal Institution, 3. "Some Secrets of Crystals," by Prof. H. A. Miers, F.R.S.

— Chemical, 8. "Studies of the Properties of Highly Purified Substances—I. The Influence of Moisture on the Production of Ozone from Oxygen, and on the Stability of Ozone; II. The Behaviour of Chlorine, Bromine, and Iodine with Mercury; III. The Behaviour of Chlorine under the Influence of the Silent Discharge of Electricity and in Sunlight," by W. A. Shenstone. "Action of Diastase on Starch," Part III., by A. R. Ling and T. L. Baker. "The Solution, Density, and Cupric Reducing Power of Dextrose, Levulose, and Invert-Sugar," by Horace J. Browne, F.R.S., G. Harris Morris, Ph.D., J. H. Millar. "Derivatives of Maclurin," Part II., by A. G. Perkin.

Friday, 22nd.—Royal Institution, 9. "Properties of Liquid Oxygen," by Prof. Dewar, F.R.S.

—— Physical, 5. "An Exhibition of some Simple Apparatus," by W. B. Croft, M.A. "On the Passage of Electricity through Gases," by E. C. Baly.

Saturday, 23rd.—Royal Institution, 9. "Neglected Italian and French Composers," by Carl Armbruster.

Errata.—P. 14, col. 1, line 23 from top, *for* "Potass. Nitrate" *read* "Potass. Nitrite." P. 15, col. 2, line 33 from bottom, *for* "large amounts" *read* "larger amounts."

THE CHEMICAL NEWS.

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TUNGSTEN HEXABROMIDE.

By HERBERT A. SCHAFFER and EDGAR F. SMITH.

The most recent work upon tungsten bromides is that of Roscoe (*Ann. Chem.*, Liebig, clxii., 362), who endeavoured to prepare a hexabromide, but obtained instead a penta derivative from which the dibromide was subsequently made. By reference to the literature bearing upon this subject it will be noticed that bromine, diluted with carbon dioxide, was made to act upon tungsten metal exposed to a red heat. Experimental evidence is at hand that tungsten at high temperatures deoxidises carbon dioxide, thus allowing ample opportunity for the production of oxybromides, which, in spite of the greatest care, are sure to appear in larger or smaller amount. The thought also suggested itself that possibly the "red heat" at which the action was allowed to occur might have been detrimental and have indeed prevented the formation of the hexabromide.

Hence, we determined to operate in an atmosphere of nitrogen and to apply a very gentle heat to the vessel containing the tungsten. In this connection it may be mentioned that the nitrogen was conducted through a series of vessels charged with chromous acetate, sulphuric acid, caustic potash, and phosphorus pentoxide, respectively. It then entered an empty vessel, into which dry bromine was dropped from a tap-funnel, and after passing through a tall tower, filled with calcium chloride, entered a combustion tube resting in a Bunsen furnace. The anterior portion of the combustion tube was contracted at intervals, forming a series of bulbs, and at its extremity was connected with an empty Woulff bottle, followed by a calcium chloride tower, and finally a receiver filled with soda lime and broken glass. A steady current of nitrogen was conducted through this system for a period of three days. On the fourth day bromine was introduced. The tungsten contained in the combustion tube was heated very gently. In a short time brown vapours appeared. These condensed to a liquid beyond the boat and eventually passed into blue-black crystalline masses that separated from the walls of the tube, when perfectly cold, with a crackling sound. Very little heat was required to melt them, and they could with care be re-sublimed in distinct blue-black needles. The latter was collected in one of the bulbs (No. 2) previously mentioned. Other products were observed and isolated. All were analysed. Bulb No. 1—that nearest the tungsten metal—contained a black velvety compound, which upon analysis showed the presence of tungsten dibromide. Bulb No. 2 contained 0·2103 grm. of the blue-black crystals, which yielded 0·0577 grm. of tungsten, or 27·43 per cent, and 0·1543 grm. of bromine, or 73·53 per cent. The theoretical requirements of tungsten hexabromide are 27·72 per cent tungsten and 72·28 per cent bromine. The bromine percentage found is high. This may be due to traces of bromine that had not been driven out from the crystalline deposit, or to adherent silver tungstate, as some tungstic acid remained in the solution from which the silver bromide was precipitated.

A fresh portion of the blue-black crystals was prepared as before and analysed. The bromine determination was unfortunately lost. The determination of the tungsten resulted as follows:—0·4351 grm. of material gave 0·1222 grm. of tungsten, or 28·08 per cent.

A third preparation was made. On subjecting 0·1775 grm. of it to analysis these results were obtained:—

0·0496 grm. tungsten or 27·94 per cent.
0·1266 grm. bromine or 71·32 per cent.

Tabulating the series, we have:—

		Found		Mean.	Required for hexabromide.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Tungsten ..	27·43	28·08	27·94	27·81	27·72
Bromine ..	73·53	71·32	—	72·33	72·28

These figures give evidence that the body analysed is tungsten hexabromide.

In analysing the third portion of the blue-black needles the bromine was determined by placing the material in a small Erlenmeyer bulb, covering it with nitric acid and then distilling. The liberated bromine was passed into a silver nitrate solution.

The tungsten hexabromide prepared by us consists, as already observed, of blue-black needles. Moderately elevated temperatures decompose the compound. It gives off fumes when brought in contact with the air. Water decomposes it with the formation of a royal-blue coloured oxide. Ammonia water dissolves it, the solution remaining colourless. A vapour density determination resulted negatively, as decomposition was apparent early in the experiment.—*From the Journal of the American Chemical Society*, December, 1896.

THE MANUFACTURE OF CALCIUM CARBIDE.*

By J. T. MOREHEAD and G. de CHALMOT.

(Concluded from p. 31).

We have now still to consider a very important question, namely, how much coke and lime are necessary to produce one pound of carbide. The formation of carbide taking place according to the following formula,—

$$\underset{56}{CaO} + \underset{36}{3C} = \underset{28}{CO} + \underset{64}{CaC_2},$$

0·563 pound of carbon and 0·875 pound of calcium oxide are theoretically necessary to yield one pound of carbide. The carbide of 5 cubic feet of gas per pound contains, however, free calcium oxide. We therefore might expect that more calcium oxide and less carbon are used. In practice, however, some calcium oxide and carbon are volatilised or burned. For a succession of experiments we have weighed the mixture that was put into the furnace and that which was taken out, and analysed both. We have experienced considerable trouble in weighing the red hot material accurately, and in obtaining fair samples. We have therefore not been able to observe as to how far the consumption of calcium oxide and of carbon is influenced by the circumstances that alter the quantity and quality of the product. We found, however, that less mixture is used if properly stoked, and if the arc is kept covered. We found also that the losses of carbon are always more considerable than those of calcium oxide.

Table VIII.

No. of experiment.	Mixture into the furnace. CaO.	C.	Mixture out of the furnace. CaO.	C.
	Per cent.	Per cent.	Per cent.	Per cent.
1	54·70	36·32	57·01	36·89
2	54·51	34·18	57·29	33·36
3	56·23	36·46	57·00	35·62
4	55·66	36·51	55·47	35·02
5	59·70	34·43	58·16	32·94
6	56·65	36·09	55·60	32·61
7	55·44	36·32	54·93	31·09
8	50·64	34·43	51·81	34·29
9	52·08	29·39	52·09	28·90
10	49·34	33·85	41·45	28·27

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* Read Sept. 3rd before the Springfield meeting of the A.A.A.S. by one of us (M). We have made since then several additions, so as to make the article complete up to the present time. From the *Journal of the American Chemical Society*, April, 1896.

TABLE VII.

Number of experiment.	Amount of CaO put into the furnace.	Amount of C put into the furnace.	CaO obtained from the furnace.	C obtained from the furnace.	Amount of CaO used.	Amount of C used.	Production of clean carbide.	Amount of CaO per lb. of carbide.	Amount of C used per lb. of carbide.
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lb.
1	675	448	417	270	258	178	195	1·32	0·91
2	739	463	415	242	324	221	285	1·13	0·78
3	859	557	601	375	258	182	190	1·36	0·96
4	612	402	415	262	197	140	190	1·04	0·74
5	851	491	498	282	353	209	280	1·26	0·75
6	906	577	478	280	428	297	375	1·14	0·79
7	1067	699	420	238	647	461	555	1·17	0·83
8	552	375	253	167	299	208	223	1·34	0·95
9	374	211	207	115	167	96	132	1·27	0·73
10	675	461	244	134	431	327	345	1·25	0·95
						Average	.. .. ..	1·228	0·837

The average figures of Table VII. are rather high, for where much coke and lime have been used this is certainly partly due to losses of material by weighing into and out of the furnace, and also by insufficient stoking. In the King furnace, the under part of which shuts hermetically tight and excludes draught, and which is stoked mechanically, the amount of coke and lime necessary for making one pound of carbide will certainly be much reduced. In the figures given in Table VII. we have left the outside coating out of the calculation. In a plant where the acetylene gas is generated at once from the carbide it would pay to use this coating also for making gas. From Table VII. we see that a very large percentage of the mixture is not acted on by the arc. We have, however, reduced this amount to one-third of the mixture, and could reduce it still more without either injuring the furnace, the quantity and quality of the carbide, and without increasing the amount of carbon and lime necessary for making one pound of carbide. In the furnace used in Spray the inside is square instead of octagonal, and the dimensions are rather too large. We thereore feed more material into the furnace than is necessary.

Besides coke we have used several other carbonaceous materials for making carbide. We have used soft coal, anthracite, charcoal, pitch, tar, rosin, and asphalte, and obtained in all cases carbide. Most of these materials are not of sufficient importance to be taken into consideration, and we will only add some words about the first three.

Charcoal, owing to its small percentage of ash, yields a very pure carbide. The only drawback, besides its price, is that it is so light that the gases carry it off to a considerable amount. It is therefore necessary to add from 5 to 10 per cent more carbon to the mixture if charcoal is used than if coke is used.

We used a soft coal which contained volatile matter 19·84 per cent and ash 1·48. The mixture with soft coal gave a terrific blaze. The carbide was covered with a large amount of very porous slag, in which there was much graphite. The average of results of two runs are 6·41 pounds per horse-power in twenty-four hours and 4·33 cubic feet of gas per pound, which equals 27·75 cubic feet of gas per horse-power in twenty-four hours.

We used anthracite coal, which contained volatile matter 7·95 per cent and ash 4·02 per cent. We made two runs with slacked and two with unslacked lime. There was no appreciable difference in the use of slacked and unslacked lime. The average result of the four runs was 7·64 pounds per horse-power in twenty-four hours and 4·03 cubic feet of gas per pound, which equals 30·79 cubic feet per horse-power in twenty-four hours. These results are much lower than those obtained with coke. We cannot therefore recommend the use of either anthracite or soft coal for making carbide. The superiority of coke and charcoal over anthracite is probably due to the porosity of the former materials, which must facilitate the volatilisation of the carbon in the electric arc, which probably must precede the formation of carbide.

DERIVATIVES OF COLUMBIUM AND TANTALUM.*

By MARY ENGLE PENNINGTON.

(Concluded from p. 34).

Products obtained on Heating the Oxides of Tantalum and Columbium with Phosphorus Pentachloride.

ONE-HALF grm. of columbic oxide was heated with phosphorus pentachloride, the quantity being calculated from the following equation:—

$$Cb_2O_5+5PCl_5=2CbCl_5+5POCl_3.$$

The experiment was conducted in a sealed tube from which all air had been expelled, the temperature being maintained at 180—200° C., for seven hours. The resulting mass was moist, and a dirty green. The tube was opened, connected quickly with a small test-tube, and then heated in an air-bath. A small quantity of liquid distilled into the front part of the tube. This was a yellowish green, and gave with water a white precipitate, apparently a hydrated columbic oxide.

At a higher temperature, about 200° C., yellow vapours collected in the cool portion of the tube. These settled on the glass as yellow, oily drops, and on cooling solidified, long yellow needles being detected here and there. Nearly all of the substance in the tube, however, remained as the greenish mass, which had become dry. No change was observed on heating above 360° C. The tube was then wrapped in copper gauze and heated with a Bunsen lamp. The green substance swelled up, became white, iridescent, and almost filled the tube. No green colour remained. Analysis of this compound showed it to be columbium oxychloride, $CbOCl_3$. The long yellow needles which had been observed in the front part of the tube changed gradually on heating, and became white and iridescent like the remainder of the substance.

This behaviour indicated the formation of a pentachloride which was then changed to oxychloride by the small quantity of air which entered the tube when it was connected with the receiver.

A second tube, heated for eight hours at 230—235° C., gave a dark yellow, semi-fluid mass. Great care was taken in this experiment to exclude all traces of moisture, and the distillation was conducted under reduced pressure. Phosphorus oxychloride in considerable quantity distilled over, leaving in the tube a yellow crystalline

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* From the author's thesis presented to the University of Pennsylvania for the degree of Ph.D., 1895. From the *Journ. Amer. Chem. Soc.*, xviii., January, 1896.

substance, which, on treating with water, decomposed with hissing and an evolution of hydrochloric acid gas. This compound was analysed according to the method of Marignac (*Ann Chim. Phys.*, viii., 5). The ignited oxide weighed 0·5642 grm. As only ½ grm. of columbic oxide was used in the experiment, the contaminating substance was sought, and was found to be phosphorus. Two fusions with bisulphate were necessary for the extraction of this element. Phosphoric acid was also found in the filtrate from the pentoxide.

The question now arose regarding the position of this phosphorus. Is there a compound formed containing columbium, phosphorus, and chlorine, or is the phosphorus content due to an incomplete expulsion of the excess of phosphorus pentachloride?

Another experiment was therefore tried under the following conditions:—One-half grm. columbium pentoxide was heated with the calculated quantity of phosphorus pentachloride at a temperature not exceeding 210° C. for eight hours. The tube contained a yellow mass as before. It was placed in an air-bath and connected with a chlorine generator, the receiver having been previously filled with chlorine. At 190° C. a very volatile substance collected in the front part of the receiver. This was a lemon-yellow, and, when analysed, gave 15·85 per cent columbium and 6·095 per cent phosphorus.

At 190—200° C., long yellow needles collected; some of these were nearly half an inch in length. Analysis gave 27·37 per cent columbium and 32·19 per cent phosphorus.

The substance, which did not volatilise at 200° C., was brownish-yellow, and apparently crystalline. Analysis gave 28·11 per cent columbium, and 1·34 per cent phosphorus.

In none of these analyses could the chlorine content be determined, because of the violence with which water acts upon the compounds, resulting invariably in the loss of some hydrochloric acid.

It seemed probable that the brownish-yellow residue in the tube was columbium pentachloride, enclosing a small quantity of phosphorus pentachloride. To determine all three elements, the following method was used:—

The more volatile compounds having been removed by distillation in a stream of chlorine gas, the residual substance was quickly weighed and thrown into a dilute solution of silver nitrate. The precipitate of silver chloride, silver phosphate, and hydrated columbic oxide was then filtered, and washed on the filter with dilute nitric acid. The phosphoric acid obtained was determined by a magnesium mixture. Dilute ammonium hydroxide was then poured over the mixture of silver chloride and columbic oxide. It was found that all the silver salt could not be removed by this means. The mixture was therefore transferred to a porcelain crucible and reduced in a stream of hydrogen gas, the metallic silver being dissolved out with dilute nitric acid, then precipitated as chloride. The columbium remained in the form of a violet compound, which, on ignition in the air, went over to pentoxide.

A small quantity of phosphorus was obtained, which was calculated into pentachloride and deducted from the material taken.

Rose states that a columbate of silver, $Cb_2O_5.Ag_2O$, is formed on the addition of silver nitrate to a solution of sodium columbate. As, upon the addition of water to columbium pentachloride, an almost perfect solution is produced for a few moments, the columbium in solution may combine with the silver. In such a case the silver chloride finally weighed would represent both the silver in combination with chlorine and that with columbium.

The analytical results are as follows:—

Substance taken = 0·8917 grm.
Phosphorus found = 0·02596 grm.

This, as phosphorus pentachloride, requires 0·14829 grm. of chlorine.

Substance taken minus PCl_5 = 0·7175 grm.
Columbium found = 0·2485 grm.
Columbium required = 0·2484 grm.
Chlorine found = 0·66509 grm.

Taking from this 0·14829 grm. of chlorine, which is in combination with phosphorus, we have chlorine = 0·5168 grm.; columbium pentachloride requires 0·4691 grm. Calculating the quantity of silver which, according to Rose's formula, would combine with the amount of columbium oxide found, and deducting the chlorine corresponding to it, 0·4699 grm. of chlorine is found to be in combination with the columbium.

The volatile compounds mentioned above were recalculated into phosphorus pentachloride and columbium pentachloride. It was found that, by removing the phosphorus as pentachloride, satisfactory analyses for columbium pentachloride were obtained from the residues.

Tantalic oxide was also heated with phosphorus pentachloride, the same conditions being maintained as in the columbium experiments. A yellow mass was formed, lighter in colour than the columbium compound, and only slightly moist. The tube was placed in an air-bath, and distilled at a temperature not exceeding 245° C. This distillation was conducted under reduced pressure. A small quantity of phosphorus oxychloride distilled over, and in the front part of the tube a little phosphorus pentachloride collected. The tantalum compound remaining was light yellow, dry, and powdery—apparently amorphous. It combined with water with hissing, liberating tantalic oxide, which contained no phosphorus. A small quantity of this element was found in the filtrate from the oxide. It was calculated into phosphorus pentachloride, and deducted from the total quantity.

Weight of substance taken = 0·6700 grm.
Weight of tantalum found = 0·3389 grm.
Required tantalum = 0·3391 grm.

Tantalum pentachloride is, therefore, formed when tantalic oxide is heated with phosphorus as pentachloride.

Reduction of the Compounds of Columbium and Tantalum to Metal.

Two experiments aiming at the preparation of columbium and tantalum in the metallic state have been tried during this research, and I regret exceedingly that lack of time has prevented a more careful study of the reactions obtained. It is my intention to go more deeply into the subject than I have been able to do.

Experiment 1.—An iron cylinder, 3 inches in diameter, having an inch bore, was charged in the following manner:—First, a layer of dry salt, then a layer of metallic sodium, above which were placed about 7 grms. of potassium tantalum fluoride, this being followed by another layer of sodium. The cylinder was then tightly packed with dry salt, and a heavy lid screwed on. It was then placed in a wind furnace, the temperature of which was comparatively low. In less than one half-hour it was found that the cylinder had melted down, and no trace of the charge could be found.

Experiment 2.—Marignac obtained an alloy of columbium and aluminum by heating the potassium double fluoride with aluminum scales in a carbon crucible. In the experiment to be described columbic oxide was used, salt and cryolite being employed as a flux. The following layers were placed in a graphite crucible:—

1. Salt.
2. Cryolite.
3. Aluminum clippings.
4. Columbic oxide.
5. Aluminum clippings.
6. Cryolite.
7. Salt.

The proportion of these substances used were:—

2 parts Cb_2O_5.
10 parts cryolite.
15 parts aluminum.
x parts sodium chloride.

The graphite lid was firmly luted on with fire-clay, the crucible was buried in a wind furnace which was kept at a white heat for eight hours. At the end of this time it was found that the graphite crucible had been severely attacked. It was reduced to a shapeless mass, but on breaking a powdery substance was found, in which were contained many little metallic buttons varying in size from a large pea to those of microscopic proportions. These were carefully picked out, and various reagents tried upon them.

Single acids do not attack them. Aqua regia makes a slight impression on long heating. Fusion with bisulphate affords only a partial decomposition. The substance is exceedingly light; it is dark grey, and does not alter in the air. A partial oxidation occurs after prolonged heating in the air. The substance is not brittle.

Summary.

1. The decomposition of columbite is more readily and satisfactorily accomplished by the Gibbs than by the bisulphate method. This method is also more valuable for the preparation of large quantities of pure oxides.

2. The qualitative reactions of columbium, tantalum, and titanium, when existing as double fluorides, are not the same as when the metals exist as tantalates, columbates, and titanates.

3. The action of the electric current upon tantalum and columbium double fluorides gives a lower hydrated oxide. The precipitation is not complete.

4. It was hoped that in preparing the double fluorides of columbium, tantalum, and titanium with rubidium and cæsium, a difference in solubility of the salts would be found which would afford a better separation of these metallic oxides under discussion. This hope has not been realised.

5. Heating the oxides of columbium and tantalum in sealed and vacuous tubes with phosphorus pentachloride yields the pentachlorides of these metals and phosphorus oxychloride.

I take pleasure in acknowledging the kindness shown, and the interest taken in the preceding work, by Dr. Edgar F. Smith, of the University of Pennsylvania, in whose laboratory it was carried out.

DETERMINATION OF THE ATOMIC MASSES OF SILVER, MERCURY, AND CADMIUM, BY THE ELECTROLYTIC METHOD.*

By WILLETT LEPLEY HARDIN.

(Continued from p. 29).

First Series.

Experiments on Silver Nitrate.

The nitrate of silver seems to fulfil the conditions necessary for accurate analyses, inasmuch as it is stable and crystallises in well-defined crystals, which can be fused without decomposition.

Preparation of Silver Nitrate.

The material used in these experiments was prepared by dissolving pure silver in pure aqueous nitric acid in a porcelain dish. An excess of silver was used, and after complete saturation the solution was poured off from the metal into a second dish, and evaporated to crystallisation. The perfectly transparent rhombic plates of silver nitrate which separated were dissolved in pure water and re-crystallised. The crystals were then carefully dried, placed in a platinum crucible which rested in a larger platinum dish, and gradually heated to fusion. After cooling, the perfectly white opaque mass was broken up and placed in a ground-glass stoppered weighing-tube, and kept in a desiccator in a dark place.

Mode of Procedure.

The platinum dish in which the deposit was made was carefully cleaned with nitric acid and dried to constant weight. It was then placed in a desiccator over anhydrous calcium chloride, and this, together with the desiccator containing the tube of silver nitrate, was placed in the balance room, where they were allowed to remain until their temperatures were the same as that of the room. After weighing the platinum dish, the tube of silver nitrate was weighed and part of the salt removed to the dish, after which the tube was re-weighed. The difference in the two weighings, of course, represented the weight of silver nitrate used in the experiment. Enough water to dissolve the nitrate was added to the dish, and then a solution of potassium cyanide, made by dissolving 75 grms. of pure potassium cyanide in 1 litre of water, was added until the silver cyanide first formed was completely dissolved. The dish was then filled to within a quarter of an inch of the top with pure water, and the solution electrolysed with a gradually increasing strength of current. The following Table will show the strength of current and the time through which it acted:—

Time of action.	Strength of current.
2 hours.. ..	$N.D_{100}$=0·015 ampères.
4 ,, ...	$N.D_{100}$=0·030 ,,
6 ,, ...	$N.D_{100}$=0·075 ,,
4 ,, ...	$N.D_{100}$=0·150 ,,
4 ,, ...	$N.D_{100}$=0·400 ,,

By gradually increasing the strength of current in this way the silver came down in a dense white deposit. When the deposition was complete, before interrupting the current, the liquid was syphoned from the dish, pure water being added at the same time. This was continued until the cyanide was completely removed. The dish with the deposit was washed several times with boiling water, and carefully dried. It was then placed in a desiccator, and allowed to remain in the balance room until its temperature was the same as that of the room, when it was re-weighed.

Weight of platinum dish = 71·27302 grms.
Weight of silver nitrate = 0·31198 grm.
Temperature, 22°.
Barometric pressure, 770 m.m.
Weight of platinum dish + silver deposit = 71·47104 grms.
Temperature, 22°.
Barometric pressure, 760 m.m.
Density of silver nitrate = 4·328.
,, brass weights = 8·5.
,, platinum dish = 21·4.
,, metallic silver = 10·5.
,, atmosphere at the time of weighing the empty dish and silver nitrate = 0·001212.
,, atmosphere at the time of weighing the platinum dish + silver deposit = 0·001196.

Computing on this basis we have the following:—

$$0{\cdot}31198\left(1+\frac{0{\cdot}001212}{4{\cdot}328}-\frac{0{\cdot}001212}{8{\cdot}5}\right)=0{\cdot}31202=\text{weight of}$$

AgNO$_3$ *in vacuo.*

$$71{\cdot}27302\left[\frac{1+\dfrac{0{\cdot}001212}{21{\cdot}4}-\dfrac{0{\cdot}001212}{8{\cdot}5}}{1+\dfrac{0{\cdot}001196}{21{\cdot}4}-\dfrac{0{\cdot}001196}{8{\cdot}5}}\right]=71{\cdot}27291=\text{wt. of}$$

platinum dish at 22° and 760 m.m.

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* Contribution from the John Harrison Laboratory of Chemistry No. 13 From the author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Ph.D.—From the *Journal of the American Chemical Society*, xviii., p. 990.

$$71{\cdot}47104 - 71{\cdot}27291 = 0{\cdot}19813 = \text{weight of deposit at } 22^\circ \text{ and } 760 \text{ m.m.}$$

$$0{\cdot}19813\left(1 + \frac{0{\cdot}001196}{10{\cdot}5} - \frac{0{\cdot}001196}{8{\cdot}5}\right) = 0{\cdot}19812 = \text{weight of deposit } \textit{in vacuo}.$$

Taking O = 16 and N = 14·04, the atomic mass of silver

$$= \frac{0{\cdot}19812 \times 62{\cdot}04}{(31202 - 19812)} = 107{\cdot}914.$$

Ten observations on silver nitrate computed in the foregoing manner are as follows:—

	Weight of $AgNO_3$. Grms.	Weight of Ag. Grm.	Atomic mass of silver.
1	0·31202	0·19812	107·914
2	0·47832	0·30370	107·900
3	0·56742	0·36030	107·923
4	0·57728	0·36655	107·914
5	0·69409	0·44075	107·935
6	0·86367	0·54843	107·932
7	0·86811	0·55130	107·960
8	0·93716	0·59508	107·924
9	1·06170	0·67412	107·907
10	1·19849	0·76104	107·932

Mean .. .. = 107·924
Maximum .. = 107·960
Minimum .. = 107·900

Difference .. = 0·060
Probable error = ±0·005

Computing the atomic mass of silver from the total quantity of material used and metal obtained, we have 107·926.

(To be continued).

INTERNATIONAL EXHIBITION AT BRUSSELS' 1897.

The rage for those displays known as "international expositions" still continues. Regardless of the fact that few persons are benefitted by such gatherings, except railways, hotel proprietors, and the small but noisy class who might be called professional exhibitionists, most States still think it their duty or their policy to challenge the world to an industrial competition. This season Belgium holds the arena. Its Exhibition will include a section of the Sciences divided into the following seven classes: Mathematics and astronomy, physics, chemistry, geology and geography, biology, anthopology, and bibliography. Participators will have nothing to pay for space, and will have to pay reduced freights for the conveyance of their exhibits.

We cannot, however, here refrain from reminding ourselves that any and every advance or improvement in any science will not fail to have become known to the world through the scientific and technical press, so that the communications and exhibits at such gatherings will have lost much of their novelty. We have much pleasure in admitting that there is here no class for political economy, which, whenever tolerated, slides inevitably into party politics with its usual amenities. The Belgian Government proposes a series of questions, and offers for the best solutions prizes amounting to the modest aggregate of 20,000 francs. Pamphlets giving full particulars may be obtained on application to the General Commissariat of the Government, at 17, Rue de la Presse, Brussels.

Among the problems to be solved in the chemical class must be mentioned—

To establish the constitution of camphor by means of reactions, both analytical and synthetic, to differentiate the optical isomers by means of new *chemical* reactions.

A practical method for transforming without great expense atmospheric nitrogen into ammonia.

A practical method for the preparation of chlorine from CaCl, more economical than those already in use.

A new process for fixing the azo-colour upon the various textile fibres preferable to those hitherto known.

The acid HI being not easy to prepare, to find an essentially practical method for its production.

An improvement in the procedures of fractionated distillation.

Under biology there is the demand for new researches of living beings by means of the X rays.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending December 31st, 1896.

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

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

London, January 11th, 1897.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Dec. 1st to Dec. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined all were found to be clear, bright, and well filtered.

Rain has fallen at Oxford on almost every day during the month, there being but nine days when none was recorded; the average fall for the month of December is 2·10 inches, the actual fall this month has been 3·13 inches, giving an excess of 1·03 inches. The deficiency for the whole year amounts to 3·53 inches, or 13·3 per cent, on a thirty years' average of 25·72 inches.

The details of the rainfall are shown in the following table:—

Rainfall in Inches at Oxford, Month by Month, during the Year 1896.

	Actual fall.	Mean of 30 years.	Difference from the mean.	
January ..	0·63	2·16	−1·53	—
February ..	0·36	1·76	−1·40	—
March ..	2·45	1·50	—	+0·95
April ..	0·58	1·66	−1·08	—
May	0·20	1·83	−1·63	—
June	2·42	2·11	—	+0·031
July	1·40	2·68	−1·28	—
August ..	2·01	2·32	−0·31	—
September ..	5·47	2·43	—	+3·04
October ..	2·85	2·75	—	+0·10
November ..	0·79	2·42	−1·63	—
December ..	3·13	2·10	—	+1·03
	22·29	25·72	−8·86	+5·43

Month.	Thames, unfiltered.	Five Thames-derived Companies filtered.	New River unfiltered.	New River filtered.	River Lea, unfiltered.	River Lea (East London), filtered.
January	1824	36	1525	31	2005	24
February	1453	26	1368	29	1109	28
March	2160	41	1938	27	1900	29
April	1833	33	1501	17	1643	34
May	1301	21	950	25	1216	73
June	2081	32	836	35	1729	28
	1775	31	1353	27	1600	36 Mean of 1st 6 months.
July	2731	21	1886	22	2859	33
August	1133	17	361	3	537	5
September	1331	11	709	4	1642	14
October	2691	19	671	4	742	14
November	2223	21	1054	20	1178	6
December	4613	60	2729	57	1825	15
	2453	24	1235	18	1464	14 Mean of 2nd 6 months.
	2114	27	1294	22	1532	25 Mean of 12 months.

It will be seen that the large excess of 3·04 inches in September has been mainly instrumental in reducing a deficiency which was becoming very serious.

Our bacteriological examinations of the waters during the month of December give the following results:—

	Colonies per c.c.
Thames water, unfiltered	4613
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	248
Ditto ditto .. .. lowest	6
Ditto ditto .. (13 samples) mean	60
New River water, unfiltered	2729
New River water, from the Company's clear water well	57
River Lea water, unfiltered	1825
River Lea water from the East London Company's clear water well	15

The accompanying table shows the bacterial variations during the year.

These results show that, taking the whole year's bacteriological examinations, the high efficiency of the filtration and the excellent character of the London waters have been uniformly maintained.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 17th, 1896.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Messrs. Alexander Scott, Frederick B. Power, W. W. Cobb, and Claude M. Thompson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Alfred Cartmell, Alexandra Road, Burton-on-Trent; William Diamond, Pye Bridge, Alfreton; William Buckland Edwards, 5, Garlinge Road, Brondesbury, N.W.; Vaughan Harley, M.D., 25, Harley Street, W.; Fred Ibbotson, B.Sc., 9, Melbourn Road, Spring Vale, Sheffield; David Smiles Jerdan, M.A., B.Sc., 68, Union Street, Greenock; Edward Rosling, Melbourne, Chelmsford; Henry Potter Stevens, B.A., 14, Lower Sloane Street, Chelsea, S.W., Harry Thompson, Walton House, West Parade, Anlaby Road, Hull.

The certificate of the following candidate, recommended by the Council, under Bye-law I., par. 3, was also read:—Jyoti Bhusan Bhaduri, Presidency College, Calcutta.

Of the following papers those marked * were read:—

*165. "*On the Experimental Methods employed in the Examination of the Products of Starch-hydrolysis by Diastase.*" By Horace T. Browne, F.R.S., G. Harris Morris, Ph.D., and J. H. Millar.

The paper is divided into the following sections: (1) the determination of solids from solution-density; (2) determination of specific rotary power; (3) the relation of $[\alpha]_j$ to $[\alpha]_D$; (4) determination of cupric reducing power; (5) limits of accuracy of the methods.

The authors state that this account is a preface to a series of papers dealing with the question of starch-hydrolysis, and is a critical review of the experimental methods which have been employed by different observers who have approached this subject. An attempt has also been made to remove the misunderstanding which still exists as to the relations of the different systems of notation.

The determination of the total solids from the density of the solution by the employment of the "divisor" method admits of great accuracy if the solution-densities of the pure substance have been previously determined.

The "divisors" at varying concentration have been determined for cane sugar, maltose, dextrose, levulose, soluble starch, and the mixed products of starch-hydrolysis of various grades, and the results have been plotted out in the form of curves whose equation is given in each case. The pure substances used in constructing these curves were dried in a vacuum over phosphoric pentoxide at temperatures from 100° to 130°.

For mixed starch hydrolytic products the divisor for equal concentrations increases with the specific rotatory power, and in such a regular manner that when the value of R is known, the divisor at any given concentration can be calculated. From the relation which this divisor bears to the divisor of the apparent maltose present in the mixed hydrolytic products, it is deducible that the divisor for the amylin constituent is constant for equal concentrations, even in starch products of very different grades of hydrolysis.

In the section on specific rotary power, the methods of exact determination are discussed, and the relations of $[\alpha]_j$, $[\alpha]_{j3\cdot86}$, and $[\alpha]_D$ are defined for substances of equal dispersive power. As the dispersive power of cane sugar is sensibly different from that of dextrose and starch hydrolytic products obtained by diastase, the factors for the conversion of $[\alpha]_J$ into $[\alpha]_D$ are not identical in these cases. Much confusion of these relations has also been introduced by the unrecognised fact that $[\alpha]_J$ has been referred to two distinct rays in the yellow of different refrangibility.

The cupric-reduction of maltose and of the products of starch transformation is constant only when the conditions of experiment are identical. These are exactly defined for the authors' method of procedure, and the reducing values are given in tabular form, and are compared with those of other observers.

*166. "*On the Specific Rotation of Maltose and of Soluble Starch.*" By Horace T. Brown, F.R.S., G. Harris Morris, Ph.D., and J. H. Millar.

The authors' determinations of the specific rotatory power of maltose at a temperature of 15·5° do not confirm the statement of Meissl that the values of $[\alpha]_D$ vary with the concentrations between 2 and 20 per cent, but confirm the general statement of Ost that between these limits the specific rotatory power is constant. At higher concentrations than 20 per cent the specific rotatory power diminishes slightly.

The actual results point to a value of $[\alpha]_D = 137{\cdot}93°$, which is sensibly greater than Ost's value of 137·46° at 15·5°.

This discrepancy is due to the fact that Ost employed weighed quantities of hydrated maltose which had been dried in a desiccator over sulphuric acid. The authors find that even after six weeks' drying in this manner, hydrated maltose contains 0·46 per cent more water than corresponds to $C_{12}H_{22}O_{11}{\cdot}H_2O$. If Ost's numbers are corrected for this they give values, up to 20 per cent concentrations, of $[\alpha]_D = 138{\cdot}12°$ at 15·5°, a result almost exactly identical with that of the authors.

The specific rotatory power of soluble starch for concentrations of 2·5 to 4·5 per cent is at 15·5°, $[\alpha]_D = 202{\cdot}0°$.

*167. "*On the Relation of the Specific Rotatory and Cupric-reducing Powers of the Products of Starch-hydrolysis by Diastase.*" By Horace T. Brown, F.R.S., G. Harris Morris, Ph.D., and J. H. Millar.

When starch is transformed by diastase, a certain relation is always found to subsist between the cupric reduction and specific rotatory power of the hydrolytic products. This relation can be expressed in such a manner as to be entirely independent of any view we may hold as to the true nature of the transformation products, and it is of so exact a nature that if one property is known the other can be predicted with certainty. This is true not only for the mixed hydrolytic products, but for any fractionated portion of them.

The authors regard this fact as lying at the root of the whole question of starch hydrolysis, and, as it is still not admitted by most continental workers, they bring forward a large amount of fresh evidence which they regard as absolutely conclusive.

The results of the examination of 70 different starch transformations are given, some of them mixed products, others fractionated products, the specific rotatory and cupric-reducing powers being given in the various notations in use. When the experimental results are plotted on a system of rectangular co-ordinates, the degrees of specific rotation between soluble starch and maltose being represented on the line of ordinates, and the cupric reducing powers from soluble starch to maltose on the line of abscissæ, the values all fall practically on a straight line joining the points of intersection of the co-ordinates corresponding to the optical and reducing properties of soluble starch and of maltose respectively.

The properties of soluble starch being $R = 0$, $[\alpha]_D = 202°$, and of maltose, $R = 100$ and $[\alpha]_D = 138{\cdot}0°$, then the relation of specific rotation and cupric reduction for any mixture or fractionation of the starch-hydrolytic products will be expressed by $[\alpha]_D = 202 - 0{\cdot}64\ R$.

The differences in the calculated and observed values for the 70 cases of hydrolysis examined are given, and are shown to be very small indeed.

The authors have examined the published results of C. J. Lintner and of Ost, both of whom have denied the existence of any relation between $[\alpha]_D$ and R, and find that, when rightly interpreted, they, for the most part, strictly conform to the law of relation expressed above.

Discussion.

Dr. Armstrong, after commenting on the value of the information brought under the notice of the Society by Mr. Horace Brown and his co-workers, and on the remarkable accuracy with which starch could now be estimated, expressed the hope that it would be possible ere long to determine what really took place when starch was hydrolysed; he thought it was time that we should no longer be content merely to determine certain analytical factors; we ought rather to seek for chemical methods which would render it possible to separate and isolate the products.

Mr. A. R. Ling asked what value the authors found for the cupric reducing power of maltose when Wein's method was used.

Dr. G. H. Morris, in reply, said that they found that Wein's tables give results about 5 per cent too low when the cupric reduction of maltose is estimated by Wein's method, and the copper obtained calculated into maltose by the table; in other words, perfectly pure maltose gives $R = 95$—96 instead of 100.

*168. "*The Action of Hydrogen Peroxide and other Oxidising Agents on Cobaltous Salts in presence of Alkali Bicarbonate.*" By R. G. Durrant, M.A.

Similar green solutions may be obtained by adding hydrogen peroxide, sodium hypochlorite, chlorine, bromine, or ozone to cobaltous salts in presence of alkali bicarbonates—or by adding a cobaltous salt to the anode of previously electrolysed potassium carbonate.

The green colour is not destroyed by excess of cold acetic acid, but is rendered rather bluer in tint. This acetic solution is reduced by hydrogen peroxide.

The evidence so far obtained shows (1) that the cobalt is in the "cobaltic state." This is proved by the results of three volumetric methods—in which standard sodium hypochlorite, hydrogen peroxide, and sodium sulphite are respectively employed—green precipitates, produced from the green solutions, gave results showing that the available oxygen closely approximates to that to be expected from cobaltic hydrate.

(2) That the green colour of the solutions and of the precipitates appears not to be due to a particular alkali, since (i.) identical tints were obtained with the five different alkali bicarbonates, (ii.) potassio-cobaltic nitrite gives no green colour with bicarbonates, (iii.) green precipitates washed free from all alkali, and digested with cold weak acetic acid, give green filtrates.

(3) That carbon dioxide is necessary both for the formation and preservation of the green colour. The green colour of the acetic solution remains only so long as carbon dioxide is present. The green precipitates (free from alkali) retain carbon dioxide so long as they remain green, and lose it when they become brown. It is, therefore, possible that the green cobaltic compound is of the nature of a carbonate.

Discussion.

Several speakers, including the President, expressed the view that whilst the author had made it clear that the green substance was a cobaltic compound, further proof was needed of the suggestion that the salt formed was a cobaltic carbonate.

Dr. Rideal mentioned that sodium peroxide, as well as hydrogen peroxide, gave rise to the green colour, provided that an alkali bicarbonate was also present.

Dr. Armstrong said that he would like to give expression to the opinion that the time was come to determine what should be their course of action with regard to the publication of the discussions that took place at the meetings; of late there had been an almost entire absence from the Proceedings of reports of the remarks made in the room, although these had often been of a nature which made it desirable that they should be brought under the notice of the Fellows generally. If the secretaries could not undertake the work, steps should be taken to procure a proper report. Personally he had had no difficulty in obtaining reports during the nine years in which he had charge of the Proceedings, and he did not believe that there would be any difficulty. Without such reports the Proceedings were of little value.

Professor Dunstan said that Fellows attending the meetings were aware that it was not often that a comprehensive discussion followed the reading of an ordinary paper. All important remarks and suggestions made at the meetings had been recorded in the Proceedings, and although no attempt had been made to record everything, and there might occasionally be room for difference of opinion as to what was important, he was always glad to receive from speakers, after the meeting, reports of their remarks, which he believed had been in nearly every case inserted in the Proceedings. He had, however, not thought it desirable to print Dr. Armstrong's remarks, of the omission of which Dr. Armstrong now complained, made on two recent occasions, proposing to record the time occupied by readers of papers. The method adopted by the speaker's predecessor in office in reporting discussions had given rise to much dissatisfaction. If the present plan was not thought sufficient, then a shorthand report of the discussions could be taken. As a matter of fact, however, the main value of the Proceedings lies in its being the means of bringing at an early date under the notice of the Fellows, not merely remarks and suggestions made at the meetings, but concise abstracts of the papers read, the full publication of which could not take place in the Journal until much later.

The President remarked that if a full report of the proceedings were considered desirable, its preparation could not be included in the duties of the Honorary Secretaries. He was disposed to think, however, that if it were generally known that the Secretaries were ready to receive from speakers after the meeting a few sentences giving the substance of their remarks, that this would meet the case in nearly every instance.

169. "*Electrical Conductivity of Diethylammonium Chloride in Aqueous Alcohol.*" By James Walker, Ph.D., D.Sc., and F. J. Hambly, F.I.C.

The authors have determined the conductivity of diethylammonium chloride dissolved in pure water, and in 10·1, 30·7, 49·2, 72·0, 90·3, and 99·0 per cent alcohol, by volume, at dilutions ranging from 10 litres to 8000 litres. Tables and curves have been constructed, showing the variation of the molecular conductivity and the degree of dissociation with varying dilution and varying proportions of alcohol.

170. "*Formation of Substituted Oxytriazoles from Phenylsemicarbazide.*" By George Young, Ph.D., and Henry Annable.

The action which takes place when a mixture of phenylsemicarbazide and benzaldehyde is oxidised, has been re-investigated, and the views expressed by one of the authors in a previous paper (*Trans.*, 1895, lxvii., 1063) have been confirmed. The following aldehydes yield oxytriazoles by this action: metanitrobenzaldehyde, paranitrobenzaldehyde, metatoluic aldehyde, terephthalic aldehyde, cinnamic aldehyde.

The authors have failed to obtain oxytriazoles from formaldehyde, acetaldehyde, paraldehyde, isobutyric aldehyde.

171. "*α-Bromocamphorsulpholactone.*" By C. Revis and F. Stanley Kipping, Ph.D., D.Sc.

When α-bromocamphor is treated with anhydrosulphuric acid, or with chlorosulphonic acid, it is converted into α-bromocamphorsulphonic acid (*Trans.*, 1893, lxiii., 548). In the course of some experiments on the preparation of this sulphonic acid, it was found that when 70 per cent anhydrosulphuric acid is added to a solution of α-bromocamphor in chloroform, the product consists, to some extent, of a crystalline compound which is insoluble in water.

This substance has the composition $C_{10}H_{13}BrSO_4$ (found C=38·8, H=4·3, Br=25·1, S=9·7 per cent.; calculated C=39·0, H=4·2, Br=25·8, S=10·3 per cent). It appears to be a bromocamphorsulpholactone, and its formation is doubtless due to the oxidation of hydrogen to hydroxyl accompanying sulphonation, water being then eliminated from the hydroxysulphonic acid; it is, probably, closely related to the dibromocamphorsulpholactone, $C_{10}H_{12}Br_2SO_4$, recently described (Lapworth and Kipping, *Proc.*, 1896, xii., 77), and it resembles the latter in ordinary properties. It crystallises from chloroform and ethylic acetate in lustrous transparent plates or prisms, melts at about 290°, and is moderately easily soluble in boiling acetic acid, chloroform, and ethylic acetate. It is very stable, and separates, unchanged, from a solution in nitric acid (sp. gr. 1·4), even after heating for some time; it seems not to be attacked by cold potash (sp. gr. 1·3), and, even on boiling, it is only slowly dissolved.

Dr. Lapworth has, independently, observed the formation of this lactone from α-bromocamphor and anhydrosulphuric acid.

172. "*Dimethylketohexamethylene.*" By F. Stanley Kipping, Ph.D., D.Sc.

In a recent paper on camphoric acid (*Amer. Chem. Journ.*, 1896, xviii., 685), Noyes describes the preparation, from dihydrocampholytic acid, of a ketone which forms an oxime melting at 112—113°, and possesses an odour similar to that of camphoroxime. On comparing the melting point of this oxime with that of the isomeric oxime of dimethylketohexamethylene, he found that, for the latter, the author had given the melting point 114—115° (*Trans.*, 1895, lxvii., 349), whereas Zelinsky had given it as 104—105° (*Ber.*, 1895, 28, 781). Noyes himself then prepared dimethylketohexamethylene oxime, and found the melting point to be 120—122°.

The possible identity of the two oximes in question being a matter of great importance—for, if their identity were established, much light would be thrown on the constitution of camphor — the author has prepared dimethylketohexamethylene by the improved method recently described (Kipping and Edwards, *Proc.*, 1896, xii., 188), and has made further experiments with this substance.

The oxime, prepared in the usual manner, is at first very oily, apparently from the presence of unchanged ketone, but it soon becomes a semi-solid crystalline mass; when freed from oil and re-crystallised once or twice, it melts quite sharply at about 114°, but further purification raises the melting point to 117·5° (uncorr.), at which point it remains, even after six successive crystallisations from different solvents. This melting point and that previously recorded were taken with an ordinary standard thermometer; observations made with a short thermometer, the thread of which was entirely immersed, gave a m. p. of 118·5—119°. Noyes does not state whether the m. p. 120—122°, is corrected, nor how the observation was made, and the range of 2° would seem to indicate that the substance did not melt sharply; he also leaves the identity of his dimethylketohexamethylene oxime with the oxime of the ketone which he obtained from camphor an open question.

Noyes suggests that the several preparations of the oxime obtained respectively by Zelinsky, by himself, and by the author, may be mixtures of stereoisomerides, and the latter has therefore directed attention to this possibility; there are certainly indications of the presence of more than one substance in the crude oxime, as a few crystals, melting not sharply at about 75°, have been separated; nevertheless, the only crystalline product which has yet been isolated in any quantity is that which melts sharply and constantly at 118·5—119° (corr).

This oxime crystallises from a mixture of chloroform and light petroleum in lustrous transparent prisms, which have been examined by Mr. Pope. "The crystals consist of monosymmetric prisms, which show the forms $\{100\}$, $\{001\}$, $\{110\}$, and $\{111\}$; the plane of symmetry is the optic axial plane, and an optic axis emerges normally to the face (100). Some faces give good reflections, but parallel faces do not give images at 180° to one another, a behaviour which is frequently observed in the case of mixtures." This indication that the oxime may be a mixture, in spite of its constant melting point, must be borne in mind, and if confirmed, the different melting points of the various preparations would be accounted for.

In order to facilitate the identification of dimethylketohexamethylene, the author has prepared the semicarbazone; this compound slowly separates in crystals on warming the ketone with a solution of semicarbazone hydrochloride and sodium acetate in dilute alcohol. After re-crystallisation it melts at about 196°, and further treatment does not seem to change its melting point. A sample dried at 100° gave $C = 59{\cdot}26$, $H = 9{\cdot}36$ per cent; calculated for $C_9H_{17}N_3O$, $C = 59{\cdot}02$, $H = 9{\cdot}29$ per cent.

Dimethylketohexamethylene semicarbazone is fairly soluble in cold chloroform, but less so in cold benzene and ethylic acetate, and crystallises best from methyl alcohol in the form of small translucent well-defined prisms. Heated slowly from about 175°, and using a short thermometer, it begins to sinter at about 190°, and melts completely at about 200—201°, effervescing, but not darkening; the m. p. depends on the size of the crystals and on the rate of heating. The crude semicarbazone seemed to be homogeneous, and the yield appeared to be good, but as, on re-crystallising the preparation from boiling acetic acid, most of it suffered decomposition, further experiments are necessary to prove that only one semicarbazone exists.

173. "*The Localisation of Deliquescence in Chloral Hydrate Crystals.*" By William Jackson Pope.

Chloral hydrate crystallises from solution in large monosymmetric plates, showing the forms $\{100\}$, $\{011\}$, and $\{\bar{1}11\}$, and having the axial ratios—

$$a : b : c = 1{\cdot}6369 : 1 : 1{\cdot}3951,\ \beta = 59^\circ\ 5';$$

these crystals consists of the same modification of chloral hydrate as was obtained in previous experiments (Pope, *Proc.*, 1896, xii., 142), and described as the biaxial modification, stable at ordinary temperatures. The crystals deliquesce in the air, but in a peculiar manner; the forms $\{011\}$ and $\{\bar{1}11\}$ rapidly absorb water vapour, and after a few minutes exposure become covered with a layer of solution, whilst the faces of the form $\{100\}$ remain perfectly bright during a considerable time. The attraction for moisture exercised by the pinacoïd $\{100\}$ is thus much less than that exhibited by the other two forms.

It is consequently concluded that crystal deliquescence, like crystal solubility and other properties, varies with the direction in the crystal perpendicular to which its intensity is measured.

174. "*Enantiomorphism.*" By William Jackson Pope and Frederic Stanley Kipping.

Crystals of the two enantiomorphous forms of a substance which exhibits circular polarisation only in the crystalline state, and in which the circular polarisation is an inherent property of the crystal structure, *i.e.*, of a substance belonging to Class 2*b* (Pope, *Trans.*, 1896, lxix., 971), should be deposited from the optically inactive solution in equal numbers, unless any disturbing factor is operative favouring the deposition of crystals of one particular enantiomorphous form, as, for example, contact of the slightly supersaturated solution with a crystal of that form. The truth of this statement can be demonstrated from our present knowledge of crystal structure, and is also evident from a consideration of the recent work of Landolt (*Ber.*, 1896, xxix., 2404), who showed that the crystalline powder of sodium chlorate, which rapidly separates from aqueous solution, consists of almost equal quantities of dextro- and lævo-rotatory crystals. The authors have extended these observations, and by taking a number of different crops of the large crystals deposited by spontaneous evaporation of sodium chlorate solution, have ascertained that the average numbers of dextro- and lævo-crystals deposited are the same, in absence of any disturbing factor.

It seemed probable that if a substance which is optically active in solution is introduced into an aqueous solution of sodium chlorate, the presence of the former would favour the deposition of chlorate crystals of one particular enantiomorph, and experiments were consequently made to test this view. About 5 per cent of some substance, such as dextrose, mannitol, and isodulcitol, was dissolved in a saturated sodium chlorate solution, and the crystals of the salt deposited on spontaneous evaporation examined; a great preponderance of lævo-crystals separated from the dextrose solutions whilst in the separation from the isodulcitol solutions the dextro-crystals were in excess. The mannitol solutions deposited rather more lævo than dextro-crystals; a number of crops from each solution were collected, and similar behaviour was noticed with each crop.

This selective deposition would seem to indicate, as would, indeed, be expected, from a consideration of the equilibria possible in such systems, that the solubility of a dextro-enantiomorph of Class 2*b* (see above) in a liquid containing an optically active substance, differs from the solubility of the lævo-enantiomorph in the same solvent. Solubility determinations, and also determinations of the rates of growth of dextro- and lævo-crystals of sodium chlorate in optically active solutions are in progress.

There would seem to be no *à priori* reason why a substance optically active in solution only and possessing a high specfic rotation, should exert more directive influence on the deposition of crystals of Class 2*b* than an optically active substance of very low specific rotation, the only condition necessarily favouring the deposition of crystals of a particular enantiomorph being that there should be an asymmetric compound in solution. Using methods such as those indicated above, it might, therefore, be possible to determine with ease and rapidity whether certain substances which, although containing asymmetric carbon atoms, are optically inactive in solution, are really asymmetric compounds, the inactivity in solution being due to a compensation brought about amongst the four different groups attaehed to one asymmetric atom. Experiments respecting this point are in progress.

Several cases, such as that of camphorsulphonic chloride (Kipping and Pope, *Trans.*, 1893, lxiii., 560), are known in which equal quantities of optical antipodes, when crystallised together, apparently do not form a racemic compound. In the light of the foregoing results it should be possible to effect a partial separation of such mixtures, and even of racemic compounds, by crystallising them from a solution containing an optically active substance. Experiments on the separation of a number of racemic compounds, and of inactive mixtures of optical antipodes by methods based on the above considerations, have been commenced, but the results are not yet sufficiently conclusive to warrant any definite statements respecting them.

Premising the truth of the considerations stated above, Eakle's observation (*Zeit. f. Kryst.*, 1896, xxvi., 562) that a sodium periodate solution containing sodium nitrate deposits more lævo- than dextro-crystals of the periodate, is quite incomprehensible.

Important Notice to Authors of Papers.

The attention of authors is directed to the following resolution of the Council.

"No title shall be included in the list of titles of papers to be brought before a Meeting of the Society, unless the paper and an abstract of it are in the hands of the Secretaries at least three days before the date of the Meeting; and no announcement of titles can be made in the Proceedings until the papers have been received by the Secretaries."

NOTICES OF BOOKS.

Register of the Associates and Old Students of the Royal College of Chemistry, the Royal School of Mines, and the Royal College of Science, with Historical Introduction and Biographical Notices and Portraits of Past and Present Professors. By Theodore G. Chambers, Assoc. R.S.M. London: Hazell, Watson, and Viney, Limited, 1896. 8vo., pp. 230.

The "Department," as it is often styled in brief, is not by any means sufficiently known either to its admirers or to its critics. Its origin, its development, its past history, and its future prospects are all debatable subjects.

The first step towards the formation of the establishment in question was taken in 1832 by Sir Henry de la Beche. He suggested that a collection should be formed and placed under the charge of the Office of Works. The institution thus founded was named the Museum of Economic Geology, and was to contain specimens of various mineral substances used for roads or constructing public works or buildings, employed for useful purposes or from which useful metals are extracted.

The building first occupied was No. 6, Craig's Court, and Richard Phillips, F.R.S., an eminent analyst, was appointed curator. In the laboratory of the Institution samples of ores, soils, and general minerals were analysed at a fixed moderate charge. The establishment was transferred from Craig's Court to Jermyn Street in 1849, and during the following years boxes and hampers which had been lying for years at Craig's Court were opened and their contents classified and arranged. In 1851 the formal opening of the museum took place under the chairmanship of Prince Albert. In 1854 Huxley was appointed Professor of Natural History, *vice* E. Forbes, who had accepted the Chair of Natural History at the University of Edinburgh. Robert Hunt resigned the lectureship on physical science, and Professor Sir G. G. Stokes was appointed in his stead. It must be mentioned that Prof. Forbes, F.R.S., in an introductory lecture on the "Educational Uses of Museums," commented rather sarcastically on the apathy evinced by the public.

With the inauguration of the "Department" a change ensued. Whereas the Director-General of the Geological Survey and Director of the School of Mines had hitherto reported direct to a Minister of State, he had now to conduct his communications through Mr. Henry Cole, who, in 1854, was constituted Inspector-General of Schools and Museums, his title being afterwards changed to Secretary of the Department of Science and Art and Director of the South Kensington Museum.

Lyon Playfair resigned his appointment in 1858, and Captain F. Donnelly virtually obtained the executive control of the Department of Science and Art, a striking feature being the preponderating military character of the "Department." It is sarcastically said abroad that Britain puts her army and navy under the chief control of civilians, and by way of compensation hands over the guidance of scientific education to soldiers.

Inorganic Chemical Preparations. By Frank Hall Thorp, Ph.D., Instructor in Industrial Chemistry in the Massachusetts Institute of Technology. Boston (U.S.A.) and London: Ginn and Co. 1896. Pp. 238.

This excellent work consists of two main sections:—An introductory or general portion, and a second or experimental part. The former contains general experimental directions, and is very judiciously drawn up. We find a simple precaution against the tiresome phenomenon known as "creeping." Dr. Thorp recommends the edges of the beaker and the evaporating dish to be smeared with a *very thin* layer of paraffin oil or vaseline.

On hydrometers the author speaks very sensibly and emphatically. For liquids heavier than water he pronounces Baumé's hydrometer an utterly unscientific instrument, whose readings bear no very direct relation to true specific gravity. An investigation made a few years ago reveals some thirty-four different scales none of which were correct; yet, in spite of its demonstrably fallacious character, it prevails largely in America and on the European Continent among people who are loud in their condemnation of Britain for her tardiness in adopting the decimal system of weights and measures. With us it is comparatively little used for liquids heavier than water.

An appendix shows the approximate atomic weights and valencies of the elements.

A Short Catechism of Chemistry arranged for Beginners, being an Introduction to the Study of the Science by means of Question and Answer. By Alfred J. Wilcox. London: Simpkin, Marshall, Hamilton, Kent, and Co. (Ltd.). Middlesbrough: T. Woolston. Entered at Stationers' Hall. Pp. 16.

If there is still room for another elementary work on chemistry, we may still ask whether the form of question and answer possesses any decided recommendations? The complaint is generally made that the pupil learns without understanding.

In the remarks on the word "Elements" we are told that four of them are gases,—oxygen, hydrogen, nitrogen, and chlorine. Now if the author does not recognise the elementary character of argon and helium, he must surely class fluorine among the gases. It is to be noted that the author, in his Preface, tells us that "his practice of frequently revising with his class the elements of the Science has — and especially before an examination — invariably given excellent results." This we do not in the least dispute; the catechetical system is likely to enable the pupil to answer questions whether he knows or not.

Catalogue of Books by Meyer and Müller, 51, Markgrafen-Strasse, Berlin, W. ("Wegweiser durch die Litterature der Chemischen Technologie").

A publishers' trade catalogue, containing not a few curious works, such as "Margarita Philosophica" (1583), by G. Reisch, "Pandora," the stone of the Muse, by means of which the old philosophi and also Theophrast Paracelsus ennobled the imperfect metals by the power of fire (1588); Helmont (Opera omnia, 1648); Guaita, St. de, "Essais de Sciences Maudites." II. Le Serpent de la Genèse. I. "Le Temple de Satan": this book is of as recent a date as 1891!

El Kamlic de Komposizion ke esperimenta el Aqua de "El Salto" durante el Imbierno. By K. Newman. Santiago de Chile. 1896.

The author's conclusions are:—The water of El Salto undergoes during the winter a chemical and bacteriological alteration, which causes it to lose its quality and potability. In June and July there existed in the water of El Salto a micro-organism with all the characters of *B. Coli communis*.

CORRESPONDENCE.

THE CYANIDE PROCESS FOR GOLD EXTRACTION.

To the Editor of the Chemical News.

SIR,—Kindly publish for me, as an old subscriber to the CHEMICAL NEWS, the singular and unexpected fact that aqueous solutions of cyanogen do not *exert the least* solvent action on gold or silver. Of course as the gas decomposes there is a slight solvent action, but even this is far too slow and destructive of the gas to make extraction of gold a commercial success. This must prove to be interesting to cyanide men.

I found this fact while engaged as an expert in the case Government *re* McDollin and Co., and published it here September 17th last, in a paper to our Philosophical Society.—I am, &c.,

WILLIAM SKEY,
Analyst to the Home Department, N.Z.

The Mines Department, Wellington, N.Z.,
December 5. 1896.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 1, January 4, 1897.

Position of the Academy of Sciences. — The following changes have taken place in the membership of the French Academy of Sciences:—Deaths since January 1st, 1896: Resol, Tisserand, Fizeau, Daubrée, Trécul, Reiset, Sappey. There have been elected: Bertrand, Michel Lévy (in the Section of Mineralogy); Muntz (Section of Rural Economy). Among the free Academicians, *i.e.*, those not attached to any especial section, Ronché. The following members have still to be replaced: Resol (Section of Mechanics), Tisserand (Astronomy), Fizeau (General Physics), Trécul (Botany), Sappey (Anatomy and Zoology), and Tchénichef (Foreign Associate). The following correspondents are deceased: Gylden and Gould (Astronomy), Prestwich (Mineralogy), Kékulé (Chemistry), Baron von Müller (Botany), Marquis de Menabree (Rural Economy). The correspondents elected (Section of Astronomy) are: Gill, *vice* Cayley, deceased; Van de Sande Bakhuyzen, *vice* Newcomb, elected Foreign Associate; Christie, *vice* Hind, deceased. The following correspondents have still to be replaced: Gylden and Gould, deceased (Astronomy); Kékulé, deceased (Chemistry); Prestwich, deceased (Mineralogy); Baron Müller, deceased (Rural Economy); Marquis de Menabrea, deceased (Rural Economy); Lovén, deceased (Anatomy and Zoology).

Effects of the Combined Variation of the Two Factors of the Expenditure of Muscular Energy on the Value of the Respiratory Exchanges.—A. Chauveau, with the assistance of J. Tissot.—This paper is too little and too doubtfully chemical in its character to merit insertion or abstraction in the CHEMICAL NEWS.

Action exerted upon the Alkaline Haloid Salts by the Bases which they contain.—A. Ditte.—The alkaline bases exert upon the alkaline haloid salts a precipitating action analogous to that produced by the corresponding acids.

Action of Ammonia upon Tellurium Bichloride.—René Metzner.—Ammonia acts upon tellurium bichloride in a manner which differs according to the temperature applied. At 200° to 250° the reaction, which is very slow, is represented by—

$$3TeCl_4 + 16NH_3 = 3Te + 12NH_4Cl + 4N.$$

At 0° the ammonia combines with tellurium chloride. At a lower temperature we may obtain combination of tellurium and nitrogen. When the operation succeeds the apparatus contains, after the washing is completed, a substance of a fine lemon-yellow colour, of the composition TeN. This nitride is friable and amorphous. It detonates with extreme violence if struck, producing a black vapour of tellurium in an impalpable powder. Tellurium nitride is not attacked either by water or dilute nitric acid. In contact with potassia it gives off all its nitrogen in the state of ammonia.

The Absorption of Hydrogen Sulphide by Liquid Sulphur.—H. Bélabon.—Liquid sulphur maintained at a temperature above 170°, in presence of sulphuretted hydrogen gas, absorbs a notable quantity of this gas. The quantity of gas absorbed is so much the greater as the temperature is higher, the pressure remaining the same. In all cases the gas escapes at the moment of the solidification of the sulphur; the gaseous liberation is a consequence of solidification. Pure hydrogen is not absorbed by liquid sulphur.

Production of Vanilline by means of Vanillo-Carbonic Acid.—Ch. Gassmann.—The author boils 1 part of this acid with 2 parts of aniline until the escape of carbonic acid has ceased. There is formed a substituted benzylidene-aniline, which is separated from excess of aniline by means of a current of steam. The vanilline-aniline is finally split up by a brief ebullition with dilute sulphuric acid at 50 per cent. The vanilline formed is isolated by extraction with ether, from which it easily crystallises.

The Transformation of Eugenol into Isoeugenol.—Ch. Gessmann.—Not adapted for useful abstraction.

A New Method for Determining Sulphur in Iron.—W. Schulte.—In order to evade the disadvantages of the bromine method and of working with barium sulphate the author dissolves the iron in dilute hydrochloric acid, conducts the gases evolved through a solution of cadmium acetate acidulated with acetic acid, and transforms the resulting cadmium sulphide in order to bring it into a state capable of easy determination into copper sulphide by the addition of an acid solution of copper sulphate. The copper sulphide is ignited and weighed as copper oxide. One atom of sulphur yields exactly 1 mol. of copper oxide; $31{\cdot}98\ S = 79{\cdot}14\ CuO$. It is not admissible to pass the gases evolved into the copper solution, since phosphorus and arsenic occasion separations. We prepare in the first place three solutions. I. 25 grms. cadmium acetate (or 5 grms. cadmium acetate + 20 grms. zinc acetate) and 200 c.c. glacial acetic acid per litre; II. dilute hydrochloric acid (1+2); III. 80 grms. copper sulphate and 175 c.c. concentrated sulphuric acid per litre. The apparatus consists of a boiling flask, into which are introduced 10 grms. comminuted iron, a funnel tube with a cock for the introduction of 200 c.c. hydrochloric acid, a bent glass tube as a reflux refrigerator, and a receiver with an appendix and a second safety receiver. Into the receiver there are introduced 40 to 50 c.c. of the cadmium solution. The development of gases is effected in the cold, heat is then applied with a Bunsen burner so as to complete the solution of 10 grms. iron in ninety minutes. The cadmium compound in the receiver is then transformed with 6—7 c.c. of the copper solution, the copper sulphide is then filtered off and ignited. If it is intended in this manner to determine zinc and manganese sulphides in iron sulphide, the portion operated upon must not exceed 0·15 grm. For 10 grms. iron the entire process requires two-and-a-half hours.—*Stahl und Eisen*

MISCELLANEOUS.

Mica.—Messrs. Wiggins and Sons, Mica Merchants, have, after rebuilding, returned to their old address, 102 and 103, Minories, both of which buildings are entirely devoted to their business.

Royal Institution.—On Saturday, Jan. 23, Mr. Carl Armbruster will deliver the first of three lectures on "Neglected Italian and French Composers" (with numerous vocal illustrations). The Friday Evening Meetings of the members will commence on Jan. 22, when Prof. Dewar will deliver a lecture on "Properties of Liquid Oxygen." Prof. J. C. Bose, Professor of Presidency College, Calcutta, will deliver his discourse on "The Polarisation of the Electric Ray" on Friday evening, Jan, 29th, and not on Feb. 5th as previously announced. The discourse on this night will be delivered by the Bishop of London, who will take as his subject "The Picturesque in History."

Sensitive Litmus-Paper.—Ronde.—The strong alkaline cubes occurring in commerce are covered with twelve to fifteen times their quantity of water, and allowed to stand for one day. The deep blue mixture is then treated with sulphuric acid until it becomes a light red, and heated on a steam-bath for fifteen minutes. To the liquid, which generally turns blue again, dilute sulphuric acid is added until the filter-paper becomes of a reddish-violet on immersion. When cold it is strained through a cloth, and the liquid is so adjusted, by the addition of drops of dilute sulphuric acid or traces of powdered litmus, that pieces of filter-paper, if immersed and quickly dried, take the desired red or blue tint. This method readily yields papers of a sensitiveness 1 = 150,000. —*Pharm. Zeitung* and *Chem. Zeitung*.

Royal Academy of Sciences of Turin. — From a courteous communication from the Academy we learn that from January 1st, 1897, to the end of December, 1898, this prize will be awarded to any scientific author or inventor, of whatever nationality, who, during the years 1895—98, shall, in the judgment of the Royal Academy of Sciences of Turin, have made the most important discovery or published the most valuable work on physical and experimental science. The prize (deducting income-tax !) will be 9600 francs. Candidates must send in this work (*in print*) to the President of the Academy within the stated time. MSS. will be disregarded. Unsuccessful work will not be returned. — Signed, G. Corb (President); E. D. Ondic (Secretary of the Commission); Turin, January 1st, 1897.

MEETINGS FOR THE WEEK.

Monday, 25th.—Society of Arts, 8. (Cantor Lectures). "Material and Design in Pottery," by Wm. Burton, F.C.S.

Tuesday, 26th.—Royal Institution, 3. "Animal Electricity," by Prof. A. D. Waller, F.R.S.

—— Society of Arts, 8. "The Artistic Treatment of Heraldry," by W. H. St. John Hope, M.A.

Wednesday, 27th.—Society of Arts, 8. "Voice Production," by William Nicholl.

Thursday, 28th.—Royal Institution, 3. "Some Secrets of Crystals," by Prof. H. A. Miers, F.R.S.

—— Society of Arts, 4.30 (at the Imperial Institute). "The Moral Advance of the Peoples of India during the Reign of Queen Victoria," by William Lee-Warner, M.A., C.S.I.

—— Society of Arts, 8. "The Mechanical Production of Cold," by Prof. James A. Ewing, M.A., F.R,S.

Friday, 29th.—Royal Institution, 9. "The Polarisation of the Electric Ray," by Professor Jagadis Chunder Bose, M,A., D.Sc.

Saturday, 30th.—Royal Institution, 9. "Neglected Italian and French Composers," by Carl Armbruster.

THE CHEMICAL NEWS
AND
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THE UNITY OF THE ATOMIC WEIGHTS.

By KARL SEUBERT.

IN a Report by F. W. Küster, on the Progress of Physical Chemistry in the year 1895, which lately appeared in the *Zeit. Anorg. Chem.*, it is mentioned that "all the more recent determinations of the atomic weight of hydrogen show in accordance that the relation O : H lies between 16 : 1·007 and 16 : 1·008 (or, in the old style, H : O between 1 : 15·87 and 1 : 15·88)." We read further that this result, which is not novel, will scarcely prevent the value H : O = 1 : 15·96 from being still quietly employed. I cannot share the apprehension of my colleague, Küster. I have at once, after Morley's great work had become known to me in its details, recognised the inadmissibility of the value 15·96, and have expressed this conviction on the next opportunity. The remaining adherents of the "old style" may probably think with me, since what formerly led us to the assumption of the value O = 15·16 is no longer valid, this number no longer presenting the result of the most trustworthy experimental determinations of the atomic weight of oxygen in reference to the atomic weight of hydrogen taken as unity. This result has seemed for some time probable, but the question was too much contested to admit of a full decision, and a certain reserve appeared to me the more imperative as now and then determinations spoke in favour of the older values 15·96 and 16. At present we may, however, admit that Morley's relation, O : H = 15·879 : 1, approaches so closely to the truth that it will not in future undergo any modification of importance. The uncertainty, in all probability, amounts to not more than a unit in the second decimal place, or about 0·06 per cent of entire value. Hence the atomic weight of oxygen now ranks among those most accurately determined, and its possible error becomes perceptible only in the higher values of atomic weights, and even there in decimal places which in any case must be held doubtful.

There is near at hand an expedient to avoid the unpleasantness involved in the uncertainty and the change in the atomic weight of oxygen by fixing this value arbitrarily, and thus rendering it independent of the issue of stöchiometrical determinations. This expedient must, however, be used with the utmost possible limitation. I should not delay for a moment to vote to-day for O = 16, if the result of the most recent investigations on the atomic weight of oxygen evinced considerable deviations and uncertainties which rendered a selection among the different values impossible; but, on the contrary, these researches, almost without exception, lead to a value derived from an experimental investigation conducted on a large scale and in an unexceptional manner, and invest it with a degree of probability which attaches to our best determinations of atomic weights. If, therefore, a number must be established for the atomic weight of oxgen, that value has the first claim which—according to our present experience—gives our atomic weights a rational unity, the atomic weight of hydrogen.

An advantage which has been put forward in favour of the assumption O = 16 is, that then a number of atomic weights can be reproduced with sufficient accuracy by whole numbers; but this plea is not sufficient to turn the scale in its favour. The new atomic weights are certainly less convenient in this respect.

They show that Prout's hypothesis, both in its original form and in the modification proposed by Dumas, is not refuted by experiment. The atomic weights of the elements—if we disregard desultory exceptions—are neither multiples of the atomic weights of hydrogen nor of 0·5 nor 0·25, therewith the conclusions attached to this supposed regularity become baseless.

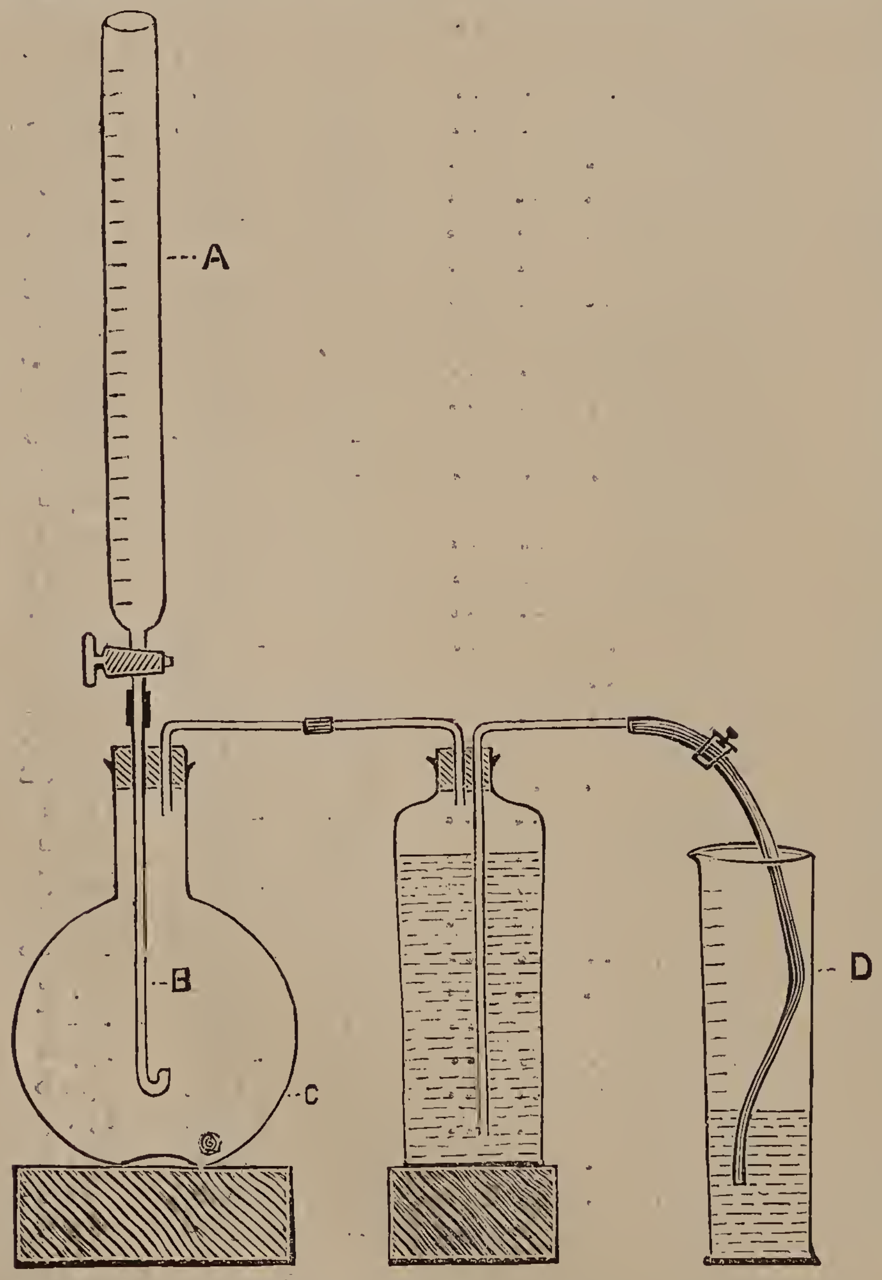
		O=16.	H=1.
Aluminium	Al	27·11	26·90
Antimony	Sb	119·9	119·0
Arsenic	As	75·1	74·5
Barium	Ba	137·43	136·40
Beryllium	Be	9·05	8·98
Bismuth	Bi	208·9	207·3
Boron	B	10·94	10·85
Bromine	Br	79·96	79·35
Cadmium	Cd	112·0	111·1
Carbon	C	12·00	11·91
Calcium	Ca	40·01	39·71
Cæsium	Cs	133·0	132·0
Cerium	Ce	140·3	139·2
Chlorine	Cl	35·46	35·19
Chromium	Cr	52·14	51·74
Cobalt	Co	59·6	59·1
Copper	Cu	63·60	63·12
Didymium	Di	142·5	141·4
Erbium	E	166·4	165·1
Fluorine	F	19·10	18·96
Gallium	Ga	70·1	69·6
Germanium	Ge	72·5	71·9
Gold	Au	197·2	195·7
Hydrogen	H	1·008	1·00
Indium	In	114·0	113·1
Iridium	Ir	193·0	191·5
Iron	Fe	56·02	55·60
Iodine	I	126·86	125·90
Lanthanum	La	138·3	137·3
Lead	Pb	206·91	205·35
Lithium	Li	7·03	6·97
Magnesium	Mg	24·26	24·18
Manganese	Mn	54·94	54·52
Mercury	Hg	200·3	198·8
Molybdenum	Mo	96·03	95·31
Nickel	Ni	58·9	58·4
Niobium	Nb	93·9	93·2
Nitrogen	N	14·04	13·94
Osmium	Os	190·8	189·3
Oxygen	O	16·00	15·88
Palladium	Pd	106·3	105·0
Phosphorus	P	31·03	30·80
Platinum	Pt	194·8	193·3
Potassium	K	39·12	38·83
Rhodium	Rh	103·0	102·2
Rubidium	Rb	85·4	84·8
Ruthenium	Ru	101·7	100·9
Scandium	Sc	44·05	43·75
Selenium	Se	79·07	78·47
Silver	Ag	107·92	107·11
Silicon	Si	28·38	28·16
Sodium	Na	23·05	22·88
Strontium	Sr	87·62	86·96
Sulphur	S	32·06	31·82
Tantalum	Ta	182·5	181·1
Tellurium	Te	127·5	126·6
Thallium	Tl	204·2	202·7
Thorium	Th	232·5	230·7
Tin	Sn	119·10	118·20
Titanium	Ti	48·1	47·8
Tungsten	W	184·1	182·7
Uranium	U	239·4	237·6
Vanadium	V	51·2	50·8
Ytterbium	Yb	173·0	171·7
Yttrium	Y	88·9	88·3
Zinc	Zn	65·41	64·91
Zirconium	Zr	90·6	89·9

If Küster further remarks that "the selection of hydrogen as the unit of the atomic weights has been often branded as illogical, and practically not to be upheld," I cannot share his opinion. It seems to me most natural and logical to refer the atomic weights to the smallest of all—that of hydrogen—as the unit. If this is not feasible from practical reasons, another unit must be selected out of the series of the atomic weights, as it has been done in the case of specific gravities. The unquestionably inconvenient numbers which result on referring to $O = 1$ have led to the expedient of taking the atomic weight of oxygen $= 16{\cdot}00$, and thus creating a unit identical with no known atomic weight, though it approximates to that of hydrogen. *Per se*, this choice is illogical, and the number 16 only obtains meaning with reference to hydrogen. It represents makeshift, founded on the idea that the reference to hydrogen as unit would be in principle more accurate. Practically we have obtained such a relation by assuming $O = 15{\cdot}879$, for which we may more briefly substitute 15·88, for in all probability future researches will modify this value so little that the influence of such a correction will be felt in most atomic weights only in places which are already uncertain. It is very questionable whether the advantages held out for the calculation $O = 16{\cdot}00$ will counterbalance the advantage of a really rational, logical unit.—*Zeit. Anorg. Chem.*

NOTE ON THE DETERMINATION OF EQUIVALENT OF SODIUM.

By WM. FRENCH.

For the determination of the equivalent of sodium by junior students I have adopted the following method, which I find has many advantages over the sodium amalgam method mentioned in most practical text-books.



I have not seen a notice of this modification in any of the numerous works on practical chemistry, and assume, therefore, that it is certainly not generally adopted. The accompanying sketch will explain the experimental part of the process. The tube B is completely filled by the stoppered burette, A, with dilute alcohol (of such strength that sodium dissolves in it at a gentle rate). A piece of sodium is quickly weighed and placed in the small dry flask, C, which is fitted on to the cork connected to a water syphon aspirator in the usual way. Dilute alcohol is then run on to the sodium from the burette, and the volume of water displaced after due cooling and levelling in the measuring cylinder, D, *minus* the volume of alcohol run in from the burette, gives the volume of hydrogen evolved, from which the equivalent of sodium can be calculated.

Grammar School, Bury.

THE TOXICOLOGIGAL BEHAVIOUR OF PICRIC ACID AND ITS SALTS, AND OF CERTAIN KINDRED SUBSTANCES.

By Dr. TH. BOKORNY.

Free picric acid is a powerful poison for algæ; in a 0·5 per cent solution they dried within fifteen minutes; in 0·1 and 0·05 per cent solutions within twenty-four hours. Many fungi are not quite so sensitive to picric acid.

Free picric acid is no powerful poison for fungi. With algæ a concentration of 0·05 per cent is sufficient for poisoning, whilst fungi require one of 0·1 per cent. Ammonium picrate is for low organisms a more powerful poison than potassium picrate.

In a solution of orthobenzoic acid of 0·2 to 0·1 and 0·65 per cent all life of algæ and low animals was extinguished in five hours.

Potassium nitrobenzoate in a 0·2 per cent solution destroys all animal and vegetable life within six hours.

According to Weyl, Martius yellow or dinitro-α-naphthol is a strong poison for dogs, the fatal dose being 0·3 grm. per kilo. living weight. Naphthol yellow S, a sulpho-acid of dinitro-α-naphthol, is harmless. A comparison between ortho- and para-nitrophenol shows that the para- compound is somewhat more poisonous to algæ and infusoria than the ortho-compound. It would be interesting to carry out a comparison between para- and ortho-compounds in an extensive series of organic compounds.—*Chemiker Zeitung.*

DETERMINATION OF BISMUTH.

By W. MUTHMANN and F. MAWROW.

The authors have shown some time ago that hypophosphorous acid is suitable for the determination of copper, and especially for its separation from cadmium and zinc. Experiments with bismuth have now shown that with suitable precautions it may be completely precipitated as metal by the reagent above named. Hence there results a method of separation and determination which in many cases surpasses in accuracy and expedition the methods hitherto known. We shall briefly describe it.

The solution of the bismuth salt, not too strongly acid, is mixed with an excess of hypophosphorous acid, and heated on the water-bath until the supernatant liquid has become perfectly clear, and a further addition of the reagent heated to ebullition produces no further colouration. The metal separates out in the form of a reddish-grey spongy mass, which can be easily filtered and washed. It is collected upon a weighed filter or in a Gooch crucible, washed with boiling water and then with absolute alcohol, and dried at 105°. The original solution is best used in a state of moderate concentration, and a few c.c. of hypophosphorous acid are forthwith added.

Our experiments have been carried out with bismuth oxychloride washed up in a little water and dissolved by the addition of a few drops of hydrochloric acid. The liquid after filtration was tested each time for bismuth by the introduction of hydrogen sulphide. There only appeared a faint brown colouration if heat had not been applied for a sufficient time. In four experiments there were used respectively—

BiOCl.	Obtained.	Bi per cent.
0·1158 grm.	0·0926 grm.	79·96
0·1559 ,,	0·1250 ,,	80·17
0·1201 ,,	0·0963 ,,	80·18
0·1068 ,,	0·0857 ,,	80·24

The average percentage being 80·13, and the calculated result 80·15.

The method is doubtless applicable for the separation of bismuth from metals which are not precipitated from their solutions by hypophorous acid, especially from zinc and cadmium.—*Zeit. Anorg. Chemie*, xiii., p. 207.

SÄRNSTRÖM'S METHOD OF DETERMINING MANGANESE IN IRON ORES.

By C. T. MIXER and H. W. DUBOIS.

About a year ago we had occasion to use a volumetric method which would allow the determination of manganese in iron ores ranging in amounts up to 15 per cent, and give results in half-an-hour which would check with gravimetric determinations within two-tenths per cent for ores as high as 15 per cent, and within a few hundredths of a per cent for ores under 1 per cent.

We found in use in a neighbouring laboratory a method which was generally known as the "Swedish Method." This method was found to fulfil the above conditions, and seems to have sufficient merit to be more widely known.

The first suggestion upon which the method is based was made by Guyard,* although his method of operating it did not give very satisfactory results.

The first description of the method in its present practicable form was made by C. G. Särnström, in the *Jernkontorets Annaler* (Sweden), 1881, p. 401.†

The principle upon which this method depends is the reaction which takes place when a manganese compound higher in oxygen than the manganous state, is dissolved in hydrochloric acid, forming a higher chloride, which is readily shown by the dark coloured solution. When this solution is boiled, it rapidly decolourises, being completely converted into manganous chloride, not easily oxidised by the air while in the acid solution.

In neutral or alkaline solutions the manganous compound has a slight tendency to oxidise in contact with the air, but we have never detected any appreciable oxidation under the conditions which we follow.

The separation of the iron and the manganese is effected in such a way that the iron is precipitated as hydroxide, and the manganese left in the manganous condition in solution. Sodium carbonate is used to precipitate the iron as hydroxide, and no trouble is experienced in the precipitation of the manganese as a carbonate, provided that only a very slight excess is employed beyond that necessary to completely precipitate the iron. It is advisable to add the sodium carbonate in the form of a solution, towards the completion of the precipitation of the iron, to avoid such an excess.

Särnström employs sodium bicarbonate, which has the advantage that a greater amount of carbon dioxide is generated, preventing subsequent oxidation of the manganous salt by the oxygen of the air. Manganese bicarbonate is formed, which is readily soluble in the solution containing carbon dioxide.

It is always desirable to test the sodium carbonate or bicarbonate for organic matter.

The results given below show the necessity of avoiding an excess of sodium carbonate (the same is true of the bicarbonate) in the precipitation of the iron. Aliquot portions of a solution of manganese containing 3·14 per cent manganese gravimetrically determined, gave only 2·61 per cent when treated with such an excess. Another ore giving 8·69 per cent under the proper conditions of this method, when treated with an excess of sodium carbonate gave 5·38 per cent.

After the precipitation of the iron in the hot solution, the manganese being in the manganous state, is oxidised by potassium permanganate, according to the following formula:

$$3MnO+2KMnO_4+H_2O=2KOH+5MnO_2,$$

which is the same reaction which takes place in Volhard's method. As the titration takes place directly, without filtering, the precipitate of ferric hydroxide is an advantage, especially in low manganese ores, as it serves to collect the fine precipitate of manganese dioxide and causes it to settle more rapidly.

In ores very low in iron it is desirable to add ferric chloride in order to obtain the requisite amount of the iron precipitate.

The Method.—Weigh half a grm. ore into a No. 0 beaker, add 15 c.c. of hydrochloric acid, 1·1 sp. gr., and boil until the residue is clear. If necessary fuse the residue with sodium carbonate. Add a few drops of nitric acid to oxidise any ferrous iron or organic matter. In magnetic ores more of course will be necessary. It is well to test for ferrous iron. Evaporate a short time to expel any nitrous acid that may have been formed. It is advisable to have a good amount of free hydrochloric acid present to generate carbon dioxide in the precipitation with sodium carbonate. The solution is then washed into a No. 3 beaker or a flask, which is then filled about two-thirds full with boiling distilled water, and solid sodium carbonate or bicarbonate added until the iron is completely precipitated, which is readily indicated by the characteristic spongy appearance of the precipitated ferric hydroxide. A solution of the salt is preferable for the final precipitation in order to avoid an excess.

The solution should be about 80° C. when it is titrated* with potassium permanganate directly, without filtering, and with intervals of vigorous stirring and settling of the iron and manganese precipitates, until the supernatant liquid shows a permanent faint pink colour. The first appearance of the pink colour must not be taken as an indication that the oxidation is complete, as gentle heating and vigorous stirring will allow more potassium permanganate to be added before the permanent pink appears.†

Multiplying the burette reading by two represents the equivalent for one grm., and this multiplied by the permanganate value in manganese, which is the iron value multiplied by 0·2946, gives the percentage of manganese.

In case of over-titration, it is practicable to titrate back with a carefully standardised solution of manganous chloride, which is prepared by evaporating 15 c.c. potassium permanganate down to 3 or 4 c.c., adding a few drops of hydrochloric acid and boiling as long as chlorine comes off. The solution should be neutralised with sodium carbonate, and diluted to 10 c.c., when 1 c.c. is equal to 1 c.c. of potassium permanganate.

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* Guyard, Chem. News, viii., 292; the following references relate to the subsequent modifications of the method; Habich, *Ztschr. Anal. Chem.*, iii., 474; Winkler, *Ztschr. Anal. Chem.*, iii., 423; Morawski und Stingl, *Journ. Prakt. Chem.* (N.F.), xviii., 96; Volhard, *Ann. Chem.* (Liebig), cxcviii., 318.

† Also published in Berg und Hüttenm., *Zeitung*, xl., 425. A review of the original article appears in the *Ztschr. Anal. Chem.*, xxii., 84. We are indebted to Mr. Hugo Carlsson, Chief Chemist of the Johnson Works of Lorain, Ohio, for calling our attention to Särnström's original publication and for furnishing us a translation of the same.

* Which should be done immediately after the neutralisation, in order to avoid any opportunity for oxidation.

† This is a very important point not only in relation to this method, but in all methods where potassium permanganate is used.

Särnström states that the method is reliable for high manganese ores and ferro-manganese "where it is not necessary to determine the manganese closer than a few tenths of 1 per cent."

Our experience does not confirm this. The results average from 1 to 2 per cent too low, so that we do not consider the method at all reliable for high percentages of manganese.

The following are some results which show this:—

	Särnström. Per cent.	Gravimetric (Ford's) Per cent.
Illinois ore	52·06 (1)	52·98
"	51·91 (2)	—
"	51·40 (3)	—
"	51·78 (4)	—
"	51·37 (5)	—
"	51·37 (6)	—
No. 595	42·07	—
"	42·35	44·3
"	42·90	—
"	42·60	—

In analyses from No. 1 to No. 4 sodium carbonate was used for the precipitation. To determine whether the employment of sodium bicarbonate would be advantageous, No. 6 was so treated, while at the same time No. 5 was precipitated with sodium carbonate, yielding the same result. We have tried sodium bicarbonate with low manganese ores, but have never noticed any practical advantages, while theoretically, as we have pointed out above, there should be an advantage in the employment of sodium bicarbonate.

This discrepancy with high percentages of manganese may possibly be accounted for by the fact that the large precipitate of manganese dioxide may act in a purely mechanical way in protecting the final amounts of the manganous chloride from being fully oxidised to dioxide by the potassium permanganate. It is to be noted in this connection that Volhard's method does not generally give reliable results with such high percentages of manganese.

The following are some results obtained by this and other methods:—

	Särnström.	Volhard.	Gravimetric.
A. Magnetic	0·07	0·10	0·07
Specular	—	0·08*	—
B. Mixture of blue granular and red hematite	0·30	0·31	0·29
	0·32	0·29	0·30
	0·28	—	—
C. Limonite	1·03	1·02	1·09
"	1·05	1·05	—
D. Silicious ore	2·98	3·08	2·93
" "	3·07	3·07	—
Cary Empire	3·93	T. V. Church	3·94
" "	3·88	Illinois Steel Co.	
Dexter No. 2	6·04	—	—
	6·02	6·02	6·01
	6·01	—	—
Davis ore	8·78	8·62	8·86
		A. G. McKenna,	(Ford's)
Newark ore	1·48	Duquesne Steel Works	1·50
No. 57	5·39	5·39	—
No. 218	5·59	5·59	—

In the determination of small amounts of manganese this method presents an advantage over Volhard's method in giving a more distinct end reaction.

The method can be used for iron and steel determinations if the usual precautions are taken to oxidise the carbon. But it is not so well adapted to these on account of the impracticability of taking large amounts for analysis. —*Journal of the American Chemical Society*, xviii., April, 1896.

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* This was so low as to necessitate filtering through asbestos in order to see end reaction by Volhard's method.

METAL SEPARATIONS BY MEANS OF HYDROCHLORIC ACID GAS.*

By J. BIRD MOYER.

Introduction.

THE action of gaseous haloid acids upon metallic oxides and their salts is a field of investigation which, though not of recent origin, has been but lately developed. It was Debray (*Comp. Rend.*, xlvi., 1098, and *Ann. Chem.* (Liebig), cviii., 250) who first called attention to the volatility of molybdic acid in a stream of hydrochloric acid gas, with the formation of $MoO(OH)_2Cl_2$.

E. Péchard (*Comp. Rend.*, cxiv., 173) applied this and showed that molybdic acid was completely eliminated and separated from tungstic acid by its volatility in a current of hydrochloric acid. Since that time nothing further has been done with single haloid acids, in gas form, until quite recently. Compounds have been decomposed, salts volatilised, and separations made, by means of other gases and mixtures, which may be as effective as hydrochloric acid, but are not devoid of trouble nor nearly so neat.

Smith and Oberholtzer (*Journ. Amer. Chem. Soc.*, xv., 1), repeated and confirmed Péchard's work in regard to the separation of molybdic acid from tungstic acid, and in addition showed that gaseous hydrobromic, hydriodic, and hydrofluoric acids acted similarly. Later, Smith and Maas (*Ztschr. Anorg. Chem.*, v., 280) made use of the volatilisation of molybdic acid for a close atomic mass determination of molybdenum.

Smith and Hibbs (*Journ. Amer. Chem. Soc.*, xvi., 578) showed that vanadium behaved like molybdenum. Hydrochloric acid gas completely eliminates vanadic acid from sodium vanadate. A little later they investigated the action of hydrochloric acid upon the members of Group V. of the periodic system (*Ibid.*, xvii., 682).

The sodium salts of nitric, pyrophosphoric, pyroarsenic, and pyroantimonic acids were used. They found nitrogen, arsenic, and antimony to be volatile in gaseous hydrochloric acid, and made it the basis of a separation of phosphoric acid from nitric acid. Lead arsenate changed completely to chloride, the arsenic being volatilised, thus affording a good quick separation. Smith and Meyer (*Ibid.*, xvii., 735) tried the action of all the haloid acids upon the elements of Group V. of the periodic system. They worked with sodium salts and observed:—I. That nitrogen was expelled completely by all the haloid acids. II. That phosphoric acid was not acted upon. III. That arsenic acid was fully expelled by hydrochloric, hydrobromic, and hydriodic acids, but only partially by hydrofluoric acid. IV. That antimony was completely volatilised by hydrochloric acid. There was no work done on bismuth. V. Vanadium went over completely in hydrochloric acid, but only partially in hydrobromic and hydrofluoric acids. VI. Columbium forms volatile products with hydrochloric and hydrobromic acids. No knowledge of didymium was obtained. VII. Tantalum is only slightly volatile in hydrochloric acid.

P. Jannasch and F. Schmidt (*Ztschr. Anorg. Chem.*, ix., 274) repeated some of the work of Smith and Hibbs, in which they confirmed the separation of arsenic from lead. They anticipated a slight portion of my work, and in addition separated arsenic acid from iron, tin from lead, tin from copper, and tin from iron, in a stream of hydrochloric acid gas.

The position of bismuth in the periodic system makes it natural to suppose that it too will be volatile in hydrochloric acid gas. This I have shown to be true, and was thus enabled to separate it from lead and copper. The action of hydrobromic acid on bismuth trioxide was also tried; it formed the bromide and then volatilised. It

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* From author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Ph.D., 1896. From the *Journ. Amer. Chem. Soc.*, xviii., December, 1896.

requires a higher temperature and longer action than with hydrochloric acid. Because of lack of time, I have been compelled to abandon the experiments instituted with a view of affecting separations, in atmospheres of hydrobromic acid and hydriodic acid gas, and have confined my labours to hydrochloric acid gas.

Method of Work.

The hydrochloric acid gas was generated by dropping concentrated sulphuric acid from a separatory funnel upon concentrated hydrochloric acid contained in a three litre flask. The gas evolved at the ordinary temperature was dried by passing it through two sulphuric acid drying bottles and then through a calcium chloride tower, when it was considered sufficiently dry for the purpose. The substance to be acted upon was weighed out in a porcelain boat, and the latter was placed in a combustion tube of hard glass.

The tube had previously been rinsed with alcohol and then with ether to remove all moisture. The ether was removed by drawing a current of dry air through the tube. This tube was connected to a two-necked bulb receiver containing about 300 c.c. of distilled water. When working with arsenic 10 c.c. of nitric acid were added. The connecting tube from the combustion tube to the bulb receiver was made to enter the receiver and dip below the surface of the water, thus catching all volatile products, as well as taking up the hydrochloric acid gas. To insure safety from the loss of volatile products, a small flask containing water was attached to the bulb receiver. The apparatus was controlled at both ends by stop-cocks. This is necessary to prevent backward suction on disconnecting the apparatus. After the reaction was completed the boat was removed to a sulphuric acid desiccator from which the air could be exhausted. In general, the procedure was similar to that employed by Hibbs (Thesis, 1896).

I.—*Behaviour of Antimony Trioxide.*

Antimony oxide, labelled chemically pure, was dissolved in hydrochloric acid and precipitated with a large amount of water. After washing by decantation it was re-dissolved and re-precipitated. This procedure was repeated several times, when it was precipitated by ammonium carbonate, washed, and ignited. The pure oxide obtained in this manner was subjected to the action of hydrochloric acid gas, and it was found to volatilise completely. In each trial a one-tenth grm. of the oxide was acted upon. The temperature varied between 150° and 190° C. It was determined in the following way:—The combustion tube was slipped through two holes made in the sides of a copper drying oven.

A very slow current of gas was used as the antimony seemed to volatilise more readily and completely if the current was slow and the heat gentle. This I attribute, on reflection, to the fact that I ignited the oxide too strongly (to a red heat) in its preparation. It dissolved with difficulty in concentrating hydrochloric acid. Lack of time prevented the repetition of this experiment and the separation of antimony from lead and copper, in which this substance was used. About eight hours was the time required for the volatilisation; very probably a shorter time would be required if the oxide had been obtained by gentle ignition.

II.—*Behaviour of Lead Oxide.*

Pure lead oxide was obtained from re-crystallised nitrate by careful ignition. This oxide changed completely into chloride at the ordinary temperature, and it was only necessary to apply a gentle heat to complete the change and entirely remove the water formed. No volatilisation was noticed until a temperature of 225° was reached; at this point the lead chloride slightly volatilised.

I think it possible to estimate lead as chloride, if the temperature is kept under 200°. A weighed amount of lead oxide was acted upon by hydrochloric acid gas in the cold for two hours, and then heated sufficiently to remove all the water formed.

The boat was cooled in the gas, and then placed in a sulphuric acid desiccator and allowed to stand one-half hour. It was then weighed.

Experiments.

	Lead oxide taken.	Lead chloride obtained.	Lead chloride required.	Difference.
	Grm.	Grm.	Grm.	Grm.
Experiment I.	0·1017	0·1267	0·1267	0·0000
,, II.	0·1015	0·1258	0·1265	−0·0007
,, III.	0·1169	0·1454	0·1447	+0·0007

The lead chloride dissolved in hot water without residue.

III.—*The Separation of Antimony from Lead.*

The oxides were carefully weighed and thoroughly mixed in a porcelain boat. Hydrochloric acid gas was passed over them in the cold, until the lead oxide had been entirely changed to the chloride. It was then heated with the smallest flame obtainable from a fish-tail burner, placed about two inches below the tube.

	Antimony trichloride taken.	Lead chloride taken.	Lead chloride obtained.	Lead chloride required.
	Grm.	Grm.	Grm.	Grm.
Experiment I.	0·1015	0·1189	0·1470	0·1482
,, II.	0·1090	0·1021	0·1266	0·1272
,, III.	0·1350	0·0852	0·1057	0·1062
,, IV.	0·1250	0·1671	0·2069	0·2083

The time required was seven hours. The lead chloride was immediately weighed. It dissolved completely in hot water, and this solution was tested by means of Marsh's apparatus for antimony, without finding the latter present. Experiment II. was slightly varied by first moistening the oxides with a drop of hydrochloric acid.

IV.—*Behaviour of Bismuth Oxide.*

Bismuth nitrate, as pure as could be obtained, was dissolved in nitric acid and then thrown down with a large quantity of water. The precipitate was carefully washed by decantation. This operation was repeated several times.

It was then dissolved in acidulated water and precipitated with ammonium hydroxide and ammonium carbonate. This, on ignition, gave pure oxide, which, heated in a stream of hydrochloric acid gas, completely volatilised as chloride. Here the same treatment is necessary as obtained for antimony. A slow current of gas and a low heat were best adapted for the volatilisation (a temperature of 130°, or roughly, the heat afforded by a fish-tail burner placed two inches below the combustion tube, with a flame an eighth of an inch high). The bismuth chloride sublimed nicely, forming a white crystalline mass beyond the boat, which could be readily driven along by a gentle heat.

V.—*The Separation of Bismuth from Lead.*

The same material was used as in the preceding experiments. The weighed oxides were thoroughly mixed in a porcelain boat. Usually the gas was allowed to act in the cold for an hour, which changed the oxides completely to chlorides.

The same conditions prevailed as under bismuth oxide alone. If an attempt was made to hasten the reaction by heating higher than 180°, a little lead would volatilise. This sublimate, slightly yellow in colour, would appear directly over the boat and could not be driven along the tube like bismuth; hence it was readily detected.

The separation of bismuth from lead requires much care, as it is not as sharp as could be desired. It is also difficult to tell exactly when the last traces of bismuth have been driven out of the boat, as there was no colour change to indicate it, both metals forming white chlorides. The separation is complete in from six to seven hours. At the end of the separation the position of the boat was changed and the action continued; if no further sublimation occurred it was cooled and removed to a desiccator. The weight was taken after standing one-half hour over sulphuric acid. With care bismuth can be separated from lead in this manner.

	Lead oxide taken.	Bismuth trioxide taken.	Lead chloride obtained.	Lead chloride required.	Difference.
	Grm.	Grm.	Grm.	Grm.	Grm.
Experiment I.	0·1014	0·2020	0·1261	0·1264	−0·0003
,, II.	0·1006	0·0642	0·1252	0·1254	−0·0002
,, III.	0·1038	0·1003	0·1294	0·1302	−0·0008
,, IV.	0·1412	0·1260	0·1759	0·1759	0·0000

The chloride of lead dissolved completely in hot water. It showed no bismuth. The sublimate contained no lead.

(To be continued).

THE DETERMINATION OF ATOMIC MASSES OF SILVER, MERCURY, AND CADMIUM, BY THE ELECTROLYTIC METHOD.*

By WILLETT LEPLEY HARDIN.

(Continued from p. 41).

Second Series.

Experiments on Silver Acetate.

The fact that silver forms well-crystallised salts with a number of organic acids makes the comparison of the atomic mass of silver with the combined atomic masses of carbon, hydrogen, and oxygen, a matter of no great difficulty. From certain preliminary experiments the acetate of silver seemed to fulfil the conditions necessary for accurate determinations.

Preparation of Silver Acetate.

The purest commercial sodium acetate was dissolved in water, the solution filtered and re-crystallised. After three crystallisations the material was dissolved in pure water, and to the rather concentrated solution was added a solution of silver nitrate, prepared in the manner already indicated. The white curdy precipitate which separated, after washing with cold water, was dissolved in hot water, the solution filtered and evaporated to crystallisation. The silver acetate separated in brilliant sword-shaped crystals. After pouring off the solution the crystals were quickly rinsed with cold water and placed between filters to remove the adhering moisture. The material was allowed to remain in contact with the filters only for a short time. It was then placed in a platinum dish, and when apparently dry the crystals were broken up into a finely divided condition and dried forty-eight hours in a vacuum desiccator. This work was carried on in a darkened room, and the silver acetate obtained was placed in a weighing tube, and kept in a desiccator in a dark place.

Mode of Procedure.

The method of operation was similar to that described under silver nitrate. After weighing the silver acetate its aqueous or cyanide solution was electrolysed and the weight of the resulting metallic silver determined. The results obtained from the aqueous solution were sometimes vitiated by the separation of silver peroxide at the anode. To prevent this, potassium cyanide was sometimes added. The results, however, from the two solutions were practically the same when no peroxide separated. From the aqueous solution the silver was deposited in a crystalline form. The strength of current and time of action were the same as for silver nitrate.

Ten observations on silver acetate reduced to a vacuum standard on the basis of—

3·241 = density of silver acetate,
10·5 = ,, metallic silver,
24·4 = ,, platinum dish,
8·5 = ,, weights.

and computed for the formula $AgC_2H_3O_2$, assuming the atomic masses of carbon, hydrogen, and oxygen to be 12·01, 1·008, and 16 respectively, are as follows:—

	Weight of $AgC_2H_3O_2$.	Weight of Ag.	Atomic mass of silver.
	Grms.	Grm.	
1	0·32470	0·20987	107·904
2	0·40566	0·26223	107·949
3	0·52736	0·34086	107·913
4	0·60300	0·38976	107·921
5	0·67235	0·43455	107·896
6	0·72452	0·46830	107·916
7	0·78232	0·50563	107·898
8	0·79804	0·51590	107·963
9	0·92101	0·59532	107·925
10	1·02495	0·66250	107·923

Mean .. .. = 107·922
Maximum .. = 107·963
Minimum .. = 107·896

Difference .. = 0·067
Probable error = ±0·005

Computing from the total quantity of material used and metal obtained, we have 107·918 for the atomic mass of silver.

Experiments on Silver Succinate.

Silver succinate was prepared in a manner similar to that of silver acetate. The commercial C. P. succinic acid was re-crystallised three times; the ammonium salt was then prepared and its aqueous solution precipitated with a solution of pure silver nitrates. The precipitate of silver succinate was thoroughly washed by decantation with pure water and carefully dried. After drying for several hours in an air-bath at 50°, the material was ground in an agate mortar to a finely divided powder, and was then re-dried for twenty-four hours in an air-bath at a temperature of 60°. The white powder obtained in this way was placed in a weighing tube and kept in a desiccator.

The method of analysis was similar to that of silver acetate. A weighed portion of the material was dissolved in a little potassium cyanide in a platinum dish. After diluting with pure water, the solution was electrolysed and the resulting deposit weighed. The strength of current and time of action were the same as for silver nitrate. The results computed for the formula $C_4H_4O_4Ag_2$ were not constant, and were invariably from one to two units lower than those obtained from silver nitrate and silver acetate. The material was then dried at a temperature of 75°, but the results obtained were not satisfactory.

The two most probable causes for these low results are:—

First, the difficulty of removing the last traces of impurities from a precipitate like that of silver succinate. The experience throughout this work has been, that to remove all the impurities from a finely divided precipitate by washing is almost impossible.

Second, the difficulty met in drying material of this kind. This same difficulty was met in the experiments on silver oxide which, as shown by Lea, retained moisture up to 165°.

Third Series.

Experiments on Silver Benzoate.

The preceding work on silver acetate and silver succinate shows the necessity of selecting compounds which form well-defined crystals. Perhaps no organic salt of silver fulfils the conditions necessary for accurate analysis better than silver benzoate.

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* Contribution from the John Harrison Laboratory of Chemistry No. 13. From the author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Ph.D.—From the *Journal of the American Chemical Society*, xviii., p. 990.

Preparation of Silver Benzoate.

The purest commercial benzoic acid was re-sublimed three times from a porcelain dish into a glass beaker. The product thus obtained was dissolved in pure aqueous ammonia, and the solution evaporated to crystallisation. The ammonium salt was then dissolved in distilled water, and to the solution was added a solution of pure silver nitrate. The white precipitate of silver benzoate which separated was washed with cold water; it was then dissolved in hot water, the solution filtered, and evaporated to crystallisation. The salt separated in fine needles, which clung together in arborescent masses. After removing the liquid from the beaker, the crystals were quickly rinsed with cold water and placed between filters to remove the adhering moisture. When apparently dry they were broken up into small fragments and dried forty-eight hours in a vacuum desiccator. The material was then placed in a glass-stoppered weighing-tube and kept in a dark place.

Mode of Procedure.

The details of the method of operation are the same as those given under silver nitrate. A weighed portion of the material was dissolved in a dilute solution of potassium cyanide in a platinum dish. The solution was then electrolysed and the resulting metal weighed. The strength of current and time of action were the same as for silver nitrate.

Before the results could be reduced to a vacuum standard it was necessary to determine the specific gravity of silver benzoate. This was done by means of a specific gravity bottle, the liquid used being chloroform. The mean of two determinations gave 2·082 for the specific gravity of silver benzoate.

Ten results on this compound, reduced to a vacuum standard on the basis of—

2·082 = density of silver benzoate,
10·5 = ,, metallic silver,
21·4 = ,, platinum dish,
8·5 = ,, weights,

and computed for the formula $C_7H_5AgO_2$, assuming 12·01, 1·008, and 16 to be the atomic masses of carbon, hydrogen, and oxygen, respectively, are as follows:—

	Weight of $C_7H_5AgO_2$. Grms.	Weight of Ag. Grm.	Atomic mass of silver.
1	0·40858	0·19255	107·947
2	0·46674	0·21999	107·976
3	0·48419	0·22815	107·918
4	0·62432	0·29418	107·918
5	0·66496	0·31340	107·964
6	0·75853	0·35745	107·935
7	0·76918	0·36247	107·936
8	0·81254	0·38286	107·914
9	0·95673	0·45079	107·908
10	1·00840	0·47526	107·962

Mean .. .. = 107·938
Maximum .. = 107·976
Minimum .. = 107·908

Difference .. = 0·068
Probable error = ± 0·005

Computing from the total quantity of material used and metal obtained, we have 107·936 for the atomic mass of silver.

Summary.

In discussing the work on the atomic mass of silver, two possible sources of error suggest themselves:—

First, the hydrogen which is continually being set free in the process of electrolysis may, in part, be occluded by the metallic silver. As already pointed out, the metallic deposits were washed several times with boiling water, with the hope of removing any occluded gases; but whether this effected a complete removal of all the occluded gases was not determined.

Second, the condensation of moisture on the platinum dish might be urged as a possible source of error. But it must be remembered that the dish was dried in the same manner each time and kept for several hours in a desiccator and that the atmosphere inside the balance was kept dry by means of several beakers of anhydrous calcium chloride, and that the temperature of the balance room throughout the work was almost constant. Under these conditions there is but little chance of error from different amounts of moisture condensed. Moreover, the variation in the different weighings of the same dish was very slight.

The advantages of the method are evident:—

First, the great advantage of the method is its extreme simplicity.

Second, the nature of the compounds used and of metallic silver renders them well adapted to weighing.

Third, the method was such as to eliminate the errors incident to the ordinary gravimetric methods of analysis.

Of the three series, the first is probably entitled to the greatest weight. That the silver nitrate was pure and free from moisture seems beyond question. However, the close agreement of the last two series with the first indicates that the acetate and benzoate of silver were also free from moisture.

Giving equal weight to each of the three series, we have the following as the general mean computed from the separate observation:—

	Atomic mass of silver.
First series	107·924
Second ,, ...	107·922
Third ,, ...	107·938

General mean = 107·928

Computing the general mean from the total quantities of material used and metal obtained, we have:—

	Atomic mass of silver.
First series	107·926
Second ,, ...	107·918
Third ,, ...	107·936

General mean = 107·927

Combining this with the first general mean we have 107·9275 as the final result for the atomic mass of silver.

(To be continued).

ALUMINUM ANALYSIS.*

By JAMES OTIS HANDY.

Although the aluminum industry is not a large one in the sense that the iron industry is, it is growing very rapidly. The output of the United States in 1894 was 550,000 pounds, and in 1895 it was about 850,000 pounds. The Pittsburg Reduction Company, with works at New Kensington, near Pittsburg, Pa., and at Niagara Falls, N. Y., is the only American producer of aluminum. The material is made by the electrolysis, in carbon-lined pots, of alumina dissolved in a fused bath of fluorides. The product of each pot is ladled out at intervals, and is graded according to the analyses of the Pittsburg Testing Laboratory, Limited. Some of the aluminum is sold as it is made, and some is alloyed to modify its physical properties. Alloys of aluminum with 3 per cent nickel, or with 3 to 7 per cent copper, or similar amounts of zinc, are very useful, on account of increased strength with only slightly increased specific gravity. The aluminum at present produced with the best ores available contains from—

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* From the *Journal of the American Chemical Society*, Sept., 1896.

99 to 99·9 per cent of aluminum.
0·3 to 0·05 per cent of silicon (combined and graphitic).
0·50 to 0·0 per cent of copper.
0·20 to 0·0 per cent of iron.
Carbon is sometimes present in aluminum.

Second grade aluminum contains 96 to 98 per cent aluminum, silicon and iron making up the remainder. Aside from analyses of metallic aluminum, there are required, in the pursuit of the aluminum industry, analyses of alloys of copper, nickel, manganese, chromium, tungsten, zinc, and titanium, with aluminum; aluminum solders, containing tin, zinc, and phosphorus; aluminum hydrate, bauxite, and electrode carbons; hydrofluoric acid and fluorides.

Analysis of Commercial Aluminum. (95 *to* 99·9 *per cent, pure*).

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

Solubility of aluminum:—Hydrochloric acid of 33 per cent (*i.e.*, 1 part of hydrochloric acid of 1·2 sp. gr. to 2 parts water) is a rapid solvent.

Sulphuric acid of 25 per cent dissolves aluminum completely on long boiling.

Nitric acid of $1\frac{7}{10}$ sp. gr. dissolves aluminum on prolonged boiling.

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

100 c.c. nitric acid of 1·42 sp. gr.
300 c.c. hydrochloric acid of 1·20 sp. gr.
600 c.c. sulphuric acid of 25 per cent.

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

Sodium hydroxide solution of 33 per cent is a useful solvent when it is desired to separate the metallic impurities from the bulk of the aluminum at once. Weaker solutions do not work as quickly or completely. Solution succeeds best in an Erlenmeyer flask.

Fifteen c.c. of the sodium hydroxide solution suffice for 1 grm. of aluminum.

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

Other Reagents and Standard Solutions used in Aluminum Analysis.

Sodium carbonate, chemically pure.

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

Powdered zinc: practically free from iron and copper.

Fifteen per cent nitric wash: (15 parts 1·42 nitric acid to 85 parts water).

Standard potassium permanganate: 5·76 grms. in 2 litres. One c.c. equals 0·005 grm. iron.

Standard potassium cyanide: 45 grms. in 2 litres. One c.c. is made to equal 0·005 grm. copper.

Special Apparatus.

Two narrow glass tubes, graduated roughly, one to hold 1 grm. of powdered zinc, and the other 1 grm. of chemically pure sodium carbonate.

The evaporating dishes which are used are, preferably, about 4½ inches in diameter, and are covered with 5-inch glasses.

The Erlenmeyer flasks are of about 12-ounce capacity, and furnished with porcelain crucible covers.

The Method.

Determination of Silicon, Iron, and Copper in Commercial Aluminum.—One grm. of aluminum drillings is dissolved in a 4½-inch evaporating dish in 30 c.c. of "acid mixture." If the drillings are thin it is best to add only 15 c.c. at first. Placing cold water on the cover-glass sometimes prevents loss from too energetic foaming. Solution having been completed by warming slightly, evaporate quickly to strong fumes of sulphuric acid, and continue heating for five minutes. Experience will show on what parts of the hot plate these solutions can be evaporated without spattering at the time when aluminum sulphate begins to crystallise out. Remove the dishes from the plate by means of an iron fork, and in a few moments add to the contents of each 75 to 100 c.c. of water and 10 c.c. of 25 per cent sulphuric acid, break up the residue in each dish with a short heavy glass rod, and place the dishes back on the hot plate. Boil until all aluminum sulphate dissolves. Add to each dish 1 grm. of metallic zinc powder, measured. Be careful to pour the zinc into the middle of the liquid. If it touches the sides of the dish it sometimes becomes firmly fixed there. Keep the dish contents at 60° to 70° C. until the zinc has dissolved, leaving the iron reduced and the copper precipitated. Filter and wash well with hot water. Cool, titrate the filtrates with standard potassium permanganate. One c.c. equals 0·50 per cent iron when 1 grm. of aluminum has been used. Placing new receivers under the funnels, treat each residue twice with hot 15 per cent nitric acid wash. Wash out with water, and in the solutions thus obtained titrate the copper with standard potassium cyanide, after adding saturated soda ash solution until the precipitated copper carbonate re-dissolves. The end point of the titration is very satisfactory. The cyanide solution should be standardised with copper of known purity in about the amount usually found, viz., 0·005 to 0·010 grm. The residue of silicon and silica are burned off in numbered crucibles, and each fused with 1 grm. of chemically pure sodium carbonate (measured). The crucible containing the fused mass is placed in 15 c.c. of water in the porcelain dish originally used, and 25 c.c. of 25 per cent sulphuric acid are added. Solution takes place quickly without separation of silica, and after rinsing out and removing the crucible, the solution is evaporated to five minutes fuming on the hot plate. After cooling add 75 to 100 c.c. of water, and boil to disintegrate the silica. Filter and wash well with water. Burn off and weigh silica and crucible, treat with hydrofluoric acid and a drop of sulphuric acid if impurity is suspected. Evaporate, ignite, and weigh again. Loss equals silica; calculate to silicon.

Determination of Crystalline (Graphitic) Silicon in Aluminum.—Dissolve 1 grm. of aluminum in 30 c.c. of 33 per cent hydrochloric acid (two parts of water to one of hydrochloric acid) in a platinum dish; add about 2 c.c. of hydrofluoric acid, stir, and filter at once through a No. 0 9 c.m. filter, contained in a funnel which has been thinly coated with paraffin. Wash with water and burn off in a platinum crucible. Fuse with 1 grm. of sodium carbonate, cool in 15 c.c. of water in a four-and-a-half-inch evaporating dish. Add 20 c.c. of 25 per cent sulphuric acid. Rinse out the crucible. Evaporate to fumes, cool, add 75 c.c. of water, boil up, and filter off the silica. Wash, ignite, and weigh. Calculate to silicon.

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

(To be continued).

The Chemical Society.—At the last meeting of the Chemical Society it was announced that Mr. J. J. Tustin had made a donation of one thousand guineas to the Research Fund of the Society.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, January 22nd, 1897.

Prof. Ayrton, Vice-President, in the Chair.

Mr. Croft gave an exhibition of some simple apparatus.

The exhibition included an ingenious form of clip to fit on an upright retort stand; a nicol used for projecting the rings and brushes in crystals, with which it is sufficient to use the ordinary condenser of the lantern, the source of light having been moved further away from the lens than is usual; some photographs showing caustics, conical refraction, and diffraction; a stand for magnets, &c., when demonstrating the attraction and repulsion of poles; a stand for the suspension of objects for experiments on diamagnetism; a holder for X ray tubes, consisting of a spiral of wire fitting round the exhaustion tube of the bulb; an X ray photograph taken by means of a Wimshurst machine; a model of Michelson's interference experiment; an arrangement to show subjective colours, in which a double lantern is arranged to give two partly overlapping discs. A sheet of green glass is placed before one lantern, and the light of the other decreased till the illumination of the two discs is the same. The overlap then appears white, while the remainder of the uncoloured disc appears red.

Prof. Silvanus Thompson said he was surprised that "patent plate" was sufficiently good for Michelson's experiment. Had the author tried illuminating the discs in his subjective effect experiment for a very short interval, so that the eye would not have time to wander from one disc to the other?

Mr. Griffith said that if you looked through a tube at one disc at a time, one appeared green and the other white.

The Chairman said the point seemed to be, could you fatigue the eye simultaneously, or must it be successive?

Prof. Silvanus Thompson said two common one-inch microscope objectives were very suitable for projecting rings and brushes.

Mr. E. C. Baly read a paper on the "*Passage of Electricity through Gases.*"

In this paper, which is of a purely controversial nature, the author brings forward as arguments that electrical conduction in gases is not of an electrolytic nature the following:—(1) That the sign of the supposed gaseous ion is variable. (2) The initial resistance of a gas. (3) The invalidity of Ohm's law. (4) The permanence of the supposed gaseous electrolyte. (5) That every mixture of gases must equally be an electrolyte. (6) That the potential gradient in a vacuum-tube when the current is passing has been shown to be very uneven. It is very steep in the cathode glow, and is by no means a regular decline between the electrodes.

Prof. Armstrong said it was difficult to know from what point of view the author had treated the question. The first part of the paper consisted almost entirely of a criticism of Prof. J. J. Thomson's theory and experiments. Prof. Thomson, however, is not the only observer who has dealt with this subject. The author's arguments seemed vitiated by the fact that he has looked upon the subject from one very narrow standpoint only, viz., the ionic hypothesis, and Lord Kelvin, for instance, does not believe in the truth of the ionic hypothesis even in the case of liquids. Prof. Thomson has shown that the phenomena depend on the dryness of the gas, so that the conduction cannot depend on the gaseous molecule alone. In the case of conduction induced by a neighbouring discharge, this might be due to the expulsion of condensed vapour from the walls of the vessel. It would appear that in the dry state gases are not electrolytes.

Mr. Enright said he thought it was not correct to say no work was done in electrolysis.

Prof. Silvanus Thompson said that the pursuit of the analogy between the conductivity in gases and liquids was apt to lead one too far. Thus, if you compare the conduction in a mixture of H and Cl with electrolysis, your analogy will be a false one unless you import into the term electrolysis the idea of chemical separation as taking place in the solution. If a current separated a mixture of powdered zinc and sulphur, it could not be called a case of electrolysis.

Prof. Armstrong said an experiment of Prof. Dewar's was very instructive. He had shown that if you cool the surface of a Crookes tube the discharge stops. It was quite inconceivable that at these low pressures the gas became liquefied, so that this experiment seemed to show that conductivity depends on the presence of a vaporous electrolyte.

Mr. Enright asked if Prof. Armstrong knew how the presence of an electrolyte assisted conduction.

In a communication Prof. J. J. Thomson said that in the decomposition of steam by a spark, the fact that in the tube as a *whole* the amount of steam decomposed is greater than the amount of gases liberated in a voltameter in series was no objection to the conductivity being electrolytic. The only condition imposed by the laws of electrolysis was that the excess of H or O at one terminal, and of O or H at the other, should correspond to the amount of electricity passing through the tube. Thus, suppose in a water voltameter a number of metal partitions are fixed so that the current has to pass across these plates. Then at each plate H will be given off on one side and O on the other, and by making the partitions sufficiently numerous the total quantity of gases given off for the passage of a given current may be made as large as we please. The excess at the terminals would not be affected at all by these partitions. In the experiments made by Mr. Rutherford and himself (Prof. Thomson), they did not observe any polarisation when the conductivity was produced by Röntgen rays. With reference to Mr. Baly's objections to the electrolytic theory, (1) There is no reason to think that under conditions other than in solution the atom of hydrogen may not have a negative charge. (2) The electrolytic theory leads us to expect that it would require a finite electromotive force to send a discharge through a gas. Before such a discharge can take place, the molecules must be split up, and this requires an electric field of finite strength. (3) In the case of a gas the electric field has to ionise the molecules, so that an increase in the strength of the field will not only (as in the case of a liquid electrolyte) increase the speed of the ions, but it will also increase their number, and thus the current will increase faster than the electromotive force. (4) The ion once used can again combine, and since the ionisation is done by the electric field it can be again split up and used again. If, however, the ionisation has been done by external sources, as, for example, by Röntgen rays, then we find that the conductivity decreases as the current passes. (5) There seems to be no reason on the electrolytic theory why in a mixture of HCl and Cl some of the current should not go through the chlorine. (6) A variable potential gradient would be produced if the ions moved with different velocities. Mr. Baly's process in the positive column appears to be the same as on the electrolytic theory, minus the atomic charges.

In a communication Prof. Schuster said: Mr. Baly criticises what he calls the electrolytic theory, but directs his arguments against a form of the theory which is, as far as the writer knows, upheld by no one. Mr. Baly appears not to have read the original papers in which the fundamental points of the theory upheld by J. J. Thomson and the writer (Prof. Schuster) are explained. If he had done so he could not have given as an objection to the theory that the conductivity of a gas increases with the E.M.F. The essential difference between a liquid and a gas is that in the liquid the number of ions is fixed by the chemical constitution of the liquid, while in a gas dissociation has first of all to be produced by the current itself, and hence the number of ions depends on the current. In the paper referred to by Mr. Baly, in which the fact that when a spark is passed through a gas the gas ceases to insulate for some distance round the spark is described, the explanation that this was due to a difficulty of passage of the electricity from the electrode into the gas was especially disclaimed, the explanation given being substantially the same as that now given by Mr. Baly. Mr. Baly asks what becomes of the ions that are set free? The answer, of course, is that they re-combine. The view that stratifications are due to compound molecules, and do not probably occur in pure gases, is not new. With reference to the author's statement about "measurements made by Wheatstone and J. J. Thomson prove that the electricity travels along the positive column from the anode to the cathode, and that its velocity is about half that of light," Prof. Thomson's results show that the breakdown of the insulating power of air takes place in the manner described, but this does not show anything as to what happens when the discharge has reached the steady state. Mr. Baly is quite wrong in the excess charges he assigns to different parts of the vacuum tube. Experiments on the excess charges can count for nothing unless they are done with continuous currents. Mr. Baly is further wrong in stating that the fall of potential is rapid in the glow; on the contrary, it is very small in the glow, being very rapid in the dark space between the glow and the cathode. Mr. Baly adopts Prof. Thomson's view as to the formation of molecular chains, but in a form very difficult to accept. The whole foundation of Mr. Baly's theory is upset by his wrong assumptions as to the excess charges in different parts of the tube.

The Author, in his reply, said, that on some points he had been misunderstood. He thought that the increase in conductivity could not be due to vapour driven off from the sides, for ultra-violet light also produced such an increase. If Röntgen rays produce ionisation, then there ought to be a reduction in the density of the gas.

NOTICES OF BOOKS.

Röntgen Rays, and Phenomena of the Anode and Cathode. By Edward P. Thompson, M.E., E.E. With concluding Chapter by Prof. William A. Anthony. New York: D. Van Nostrand Company.

This book is really a collection of abstracts from papers dealing with electrical discharges generally, and with the production of X rays in particular; it is well printed, and the illustrations are good, but there seems to be an idea in the mind of the printer that these latter need to be uniformly distributed through the book, with the result that within the first 70 pages or so we have no less than seven illustrations all referring to matter beyond pages 100. The first 60 pages are occupied with details of experiments on anodic and cathodic phenomena made long previous to Röntgen's discovery, the reason for this being, as the author points out in his preface, "that the student and general reader, whose object is to become acquainted with the properties of cathodic and X rays, might better understand them." This is very commendable, only we are rather afraid that the general reader will be in danger of confusion, while for the student the abstracts are far too meagre to be of much value beyond that of an index to the publications.

The book contains far too much of the sensational newspaper character that seems quite out of place; for instance, a whole-page illustration of "Edison's beneficent X-ray exhibit" at the Electrical Exposition in 1896 is given on page 37, and is referred to on page 71 as an instance when "thousands of people, through the beneficence of Dr. Edison, were permitted to see the shadows of their bones surrounded by living flesh!"

How this will enable either students or general readers to become better acquainted with X rays is difficult to comprehend.

Another personal illustration, given on page 122, seems equally superfluous; in this a Sprengel pump is shown of such an obsolete form, that if the physicist in question really used such an apparatus the wonder is that he ever produced any successful results at all.

The abstracts of the most important papers are good. The review of Spottiswoode and Moulton's paper on Sensitive Discharges, Mr. Crookes's on Radiant Matter, and Lenard's Experiments, show that the author has thoroughly investigated the subject; but again we must point out that they seem too technical for the general reader, and the student had far better refer to original papers for an intelligent knowledge of the experiments and the conclusions drawn from them. This cannot be got from an abstract, no matter how carefully it may have been made.

In several places there are statements that cannot fail to mislead an uninformed reader. For instance, on page 47 Perrin's experiment to find out if the cathodic rays carry negative charges is given with illustrations, but it is not stated that this was fully demonstrated five years previously by Mr. Crookes in his Address before the Institute of Electrical Engineers.

On page 96 a standard X-ray tube is shown with two concave cathodes, one at either end, and this is stated to have been "first proposed by Prof. Elihu Thompson." As this form of tube immediately suggested itself to many workers on the subject, it was proposed by numbers of people in the early days of X-ray work, and it is difficult to see the value of a claim to priority, especially in view of the fact that it does not appear to have fulfilled the hopes of those who proposed it. With regard to the so-called "focus tube," which is really an unimportant modification of Mr. Crookes's incandescent platinum tube, it is said that King's College published a description of it, and that Mr. Shallenberger was the first, as far as the author knew, to originate it. It is perfectly well known in England, at least, that the use of this tube was fully described by Mr. Jackson, of King's College, to whose energy much of the subsequent success of practical skiography is due, and it seems a pity that his name is not given.

Great prominence is given to the calcium-tungstate screen for X-ray work. This material, although it possesses the advantage of cheapness, is much inferior to barium or potassium platinocyanide.

On the whole, we cannot but feel disappointed that the book, which, as the author says, is got up regardless of expense, should be of no more use than a compilation of abstracts.

CORRESPONDENCE.

REPORT OF COMMITTEE ON THE PROXIMATE CONSTITUENTS OF COAL.

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lxxiv., p. 292) there appeared a letter from Messrs. Cross and Bevan relating to the above report. To this I should have replied before had not my vacation intervened, during which I was unable to refer to the papers cited in the letter.

As Secretary of the Committee, and mainly responsible for the drawing up of the Report, I would wish, in the first place, to take the onus of the shortcomings of the Report on my own shoulders, and, secondly, to disavow entirely any intention to disparage or belittle in any way the work of Messrs. Cross and Bevan on this subject. That the scope of their investigations had not been properly appreciated by me arose entirely from the fact that I was not—as I ought certainly to have been—aware of the extent of their investigations. The perusal of their papers published in 1881, and in the *Philosophical Magazine* of 1882, has led me to realise something of what they have done toward furthering our knowledge of the relations of coal. I wish, therefore, to acknowledge the justice of their claim to priority for the method of attacking this problem by the action of chlorinating agents.—I am, &c.,

P. Phillips Bedson.

The Durham College of Science,
Newcastle-upon-Tyne, January 20, 1897.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 2, January 11, 1897.

Obituary.—M. Loewy gave an account of the career and researches of Prof. B. A. Gould, the illustrious astronomer, of Cambridge (U.S.A.), who died on November 26th last. The deceased was one of the first who successfully applied photography to the determination of the positions of the stars.

The Academy proceeded to nominate a Commission charged with the appointment of a young French *savant*, to whom will be granted the "encouragement" founded by the Royal Society of London in memory of the eminent physicist Joule.

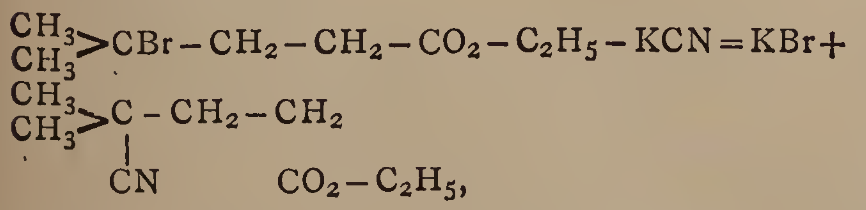
M. Berthelot presented to the Academy a volume entitled "Seriæ intorne alla Teorie Moleculare ad Atomica ad alla Notazone Chimica," by S. Cannizzaro. This volume has been printed by occasion of the 70th anniversary of the birth of the eminent chemist, at the expense of an international subscription (July 13, 1896).

Density of Ozone.—Marius Otto.—The density is 1½ times that of oxygen, *i.e.*, 1·6584.

Decomposition of Metallic Sulphates by Hydrochloric Acid.—Albert Colson.—If the action of hydrochloric acid upon sulphates is assimilable to heterogeneous dissociations two conclusions are necessary:—1. Sulphuric acid at about 15° will not attack lead chloride placed in an atmosphere of hydrochloric acid gas. The attack takes place only if the pressure is sufficiently reduced. Not merely is the principle of mechanical equivalence applicable to these phenomena of displacement, but Carnot's principle intervenes in a decided manner.

Polymerisation of some Cyanic Compounds, being a Rectification of some of the Author's former Paper on Cy_3Cl_3.—Paul Lamoult.—A thermo-chemical paper.

Action of Potassium Cyanide upon the Olides 1—4.—Edmond Blaise.—The author is seeking to effect the synthesis of dimethyl 2-2 pentanedioic acid by the action of potassium cyanide upon bromo –2–, ethyl –α–, pentanoate—



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CBr-CH_2-CH_2-CO_2-C_2H_5-KCN=KBr+$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\underset{\displaystyle CN}{\underset{|}{C}}-CH_2-\underset{\displaystyle CO_2-C_2H_5,}{CH_2}$$

and saponification of the nitrile ether obtained.

Phosphoric Ethers of Allylic Alcohol.—J. Cavalier.—The author is studying the monoallyl-phosphoric, diallylic and triallyl-phosphoric acids.

A Difference between the "Top" and "Bottom" Yeasts.—P. Petit.—Top yeast consumes more than double the amidic nitrogen of bottom yeast, and, on the contrary, much ammonial nitrogen.

MEETINGS FOR THE WEEK.

Monday, Feb. 1st.—Society of Arts, 8. (Cantor Lectures). "Material and Design in Pottery," by Wm. Burton, F.C.S.
Tuesday, 2nd.—Royal Institution, 3. "Animal Electricity," by Prof. A. D. Waller, F.R.S.
—— Society of Arts, 8. "The Progress of the British Colonial Empire during the past Sixty Years of Her Majesty's Reign," by the Right Hon. Sir Charles W. Dilke, Bart., M.P.
Wednesday, 3rd.—Society of Arts, 8. "The Recommendations of the Recess Committee for the Development of Ireland's Industrial Resources," by The Right Hon. Horace Plunkett, M.P.
—— Society of Public Analysts, 8. "The Composition of Meat Extracts and similar Products," by Otto Hehner. "The Distillation of Formaldehyd from Aqueous Solution," by Norman Leonard, B.Sc., Harry M. Smith, and H. Droop Richmond. "Some Analyses of Water from an Oyster Fishery," "Remarks on Formaldehyd" (postponed from last meeting), by Charles E. Cassal.
Thursday, 4th.—Royal Institution, 3. "Some Secrets of Crystals," by Prof. H. A. Miers, F.R.S.
—— Society of Arts, 8. "The Mechanical Production of Cold," by Prof. James A. Ewing, M.A., F.R.S.
—— Chemical, 8. "The Oxidation of Nitrogen," by Lord Rayleigh. "Researches in the Stilbene Series, I.," by J. J. Sudborough, Ph.D. "Diortho-substituted Benzoic Acids. III. Hydrolysis of Substituted Benzamines," by J. J. Sudborough, Percy G. Jackson, and L. L. Lloyd. "Apparatus for Steam Distillation," by F. E. Matthews, Ph.D. "Oxidation of Sulphurous Acid by Potassium Permanganate," by T. S. Dymond and F. Hughes.
Friday, 5th.—Royal Institution, 9. "The Picturesque in History,' by The Right Rev. The Lord Bishop of London.
Saturday, 6th.—Royal Institution, 9. "Neglected Italian and French Composers," by Carl Armbruster.

THE CHEMICAL NEWS.

Vol. LXXV., No. 1941.

ON SOME CHROMATIC REACTIONS PRODUCED BY ORGANIC ACIDS, PRINCIPALLY TARTARIC, CITRIC, AND MALIC ACIDS.

By E. PINERNA,
Professor of Chemistry in the University of Valladolid.

THE reagent employed by me contains of a fresh solution of naphthol-β in concentrated sulphuric acid (β-napthol-sulphuric acid). It is prepared with 0·02 grm. of naphthol-β and 1 c.c. of sulphuric acid, 1·83.

Five centigrms. of each of the organic acids, or the residue left on the evaporation of their solutions, gradually heated in a little porcelain capsule with a spirit flame, after having added from 10 to 15 drops of the reagent, produce the following tints:—

Tartaric acid, pure, gives at first a blue colour, and on continuing gradually to heat, it produces a very decided green colouration. On adding water to the liquid resulting from the reaction, after it has cooled (15 to 20 times its volume), the colour changes to a persistent reddish-yellow.

Citric acid, pure, gives an intense blue colour which does not change to a bright green even when it is heated gently for a long time. On pouring fifteen or twenty times its bulk of water on the liquid after cooling, the solution remains colourless or takes a light yellow colour. A small quantity of tartaric acid added to the citric acid is sufficient to produce the above-mentioned indigo-green colour.

With pure citric acid we never obtain the strong green colouration so characteristic of tartaric acid. A dull blue-green corresponds to the presence of 10 or 12 per cent of tartaric acid.

Malic acid, pure, first gives a greenish yellow colour, and on continuing the gradual action of heat a bright yellow colour. When the amount of acid is very small the colouration is well seen by shaking the capsule so that the liquid resulting from the reaction moistens the interior side, and the portion which remains on the sides is of a very perceptible yellow colour. The addition of water changes the colour to a bright orange.

All the reactions of these organic acids are characteristic, and can be produced with great facility.

It is only necessary to pay great attention to the employment of heat, and to notice the moment when any colouration commences, and then to remove the capsule from the fire, waiting till the change has terminated before re-commencing to heat (if necessary) until there appear the colours corresponding to each of the acids indicated above.

The reactions produced by other organic acids are different in colour and tint, but are not so characteristic or brilliant as those already pointed out. One must proceed to separation by solvents of the colouring matters produced. Other coloured reactions are produced with nitrites, nitrates, and chlorates. On adding ten drops of the above described reagent to five centigrms. of sodium nitrite with three or four drops of water, a very strong red colouration is produced, and the addition of water does not change it.

On pouring ten drops of a solution of resorcin in sulphuric acid (0·1 grm. of resorcine in 1 c.c. of sulphuric acid at 66°) on five centigrms. of sodium or potassium nitrate, there is produced at first a red-brown colouration, and then a very intense violet, changing to orange on the addition of water.

With potassium chlorate (two centigrms. of chlorate suffices) a very intense green colour is produced, changing to brown on the addition of water.

THE DETERMINATION OF ATOMIC MASSES OF SILVER, MERCURY, AND CADMIUM, BY THE ELECTROLYTIC METHOD.*

By WILLETT LEPLEY HARDIN.

(Continued from p. 55).

PART II.

Determination of the Atomic Mass of Mercury.

From all the earlier determinations Clarke gives 200 as the most probable value for the atomic mass of mercury, assuming oxygen equal to 16.

Experiments on Mercuric Oxide.

A large number of experiments were made with a view of determining the ratio of mercury to oxygen in mercuric oxide. The method proved to be unsatisfactory, although apparently very good results were obtained in some preliminary experiments. The cause of this close agreement of results will be explained in the details of the work.

Preparation of Pure Mercuric Oxide.

The purest commercial mercuric chloride was carefully sublimed from a porcelain dish into a glass funnel. The sublimed portion was dissolved in water, the solution filtered, and evaporated to crystallisation. The crystals were then thoroughly dried and carefully re-sublimed. The product obtained in this way consisted of white crystalline leaflets which dissolved completely in water. Pure sodium hydroxide was then prepared by throwing pieces of metallic sodium on pure water contained in a platinum dish. To the pure sodium hydroxide was added a solution of mercuric chloride, the former always being in excess. The yellow mercuric oxide which separated was washed for several days by decantation with hot water. The material was then dried twenty-four hours in an air bath at 105°.

Mode of Procedure.

In a series of preliminary experiments made in the spring of 1895, a weighed portion of mercuric oxide prepared in the above manner was dissolved in a dilute solution of potassium cyanide in a platinum dish. The solution was then electrolysed and the weight of the resulting metallic mercury determined. Inasmuch as the results obtained in these preliminary experiments were not reduced to a vacuum standard, it was thought advisable to weigh the empty platinum dish after removing the metallic deposit in order that the two weighings might be made under approximately the same conditions. The results for the most part agreed very closely and differed very little from the results obtained by other methods. Six observations computed for the formula HgO, assuming the atomic mass of oxygen to be 16, are as follows:—

Atomic Masses of Silver, Mercury, and Cadmium.

	Weight of HgO. Grm.	Weight of Hg. Grm.	Atomic mass of mercury.
1	0·26223	0·24281	200·05
2	0·23830	0·22065	200·02
3	0·23200	0·21482	200·06
4	0·14148	0·13100	200·00
5	0·29799	0·27592	200·03
6	0·19631	0·18177	200·02

Mean=200·03.

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* Contribution from the John Harrison Laboratory of Chemistry No. 13. From the author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Ph.D.—From the *Journal of the American Chemical Society*, xviii., p. 990.

These results were selected from a larger series. After making the above observations it was noticed that the platinum dish had gradually decreased in weight throughout the work. This decrease in weight indicated that the mercury deposit had formed an amalgam with the platinum dish, which was soluble in hot nitric acid. To ascertain whether such was the case or not the platinum dish, after weighing, was filled with a solution of the double cyanide of mercury and potassium and the solution electrolysed. On dissolving the mercury deposit in cold nitric acid a dark coloured film remained on the sides of the dish. The dish was then carefully washed, dried, and re-weighed, and found to be heavier than at the beginning of the operation, showing that the mercury had not been completely removed. The dark film was then dissolved in hot nitric acid and the dish again weighed. This last weight being less than that at the beginning showed that some of the platinum had been dissolved from the dish. The nitric acid solution of the dark film was evaporated to dryness and ignited to remove the mercury. The residue was dissolved in aqua regia, the solution evaporated to dryness, and enough water added to dissolve the small residue. A little concentrated ammonium chloride was then added to the solution, and the double chloride of ammonium and platinum separated as a yellow crystalline powder. This proved conclusively that the mercury deposit had united with the platinum dish to form an amalgam which was soluble in hot nitric acid. Hence the results given for mercuric oxide are of no value in determining the atomic mass of mercury.

A series of careful experiments was then made on the oxide dried at different temperatures. To avoid any error from the amalgam which formed with each deposit, the platinum dish was weighed at the beginning of each observation, the temperature and barometric pressure being noted at the same time. The results obtained from the oxide dried at a temperature of 105° gave from 180 to 185 for the atomic mass of mercury. The material was then dried at a temperature of 125°, but the increase in the amount of mercury obtained was very slight. Finally, with material dried at 150°, the results obtained for the atomic mass of mercury were all below 195°.

The most probable causes for these low results are:—

First, the difficulty of removing the last traces of alkalies from the mercuric oxide.

Second, the difficulty met in the complete removal of the moisture from an amorphous precipitate. This difficulty as well as the first was referred to in the experiments on silver oxide.

Third, mercuric oxide does not form a clear solution with potassium cyanide. There seems to be a slight reduction of the oxide to the metallic state. It is difficult to determine whether this reduced portion unites completely with the metallic deposit or is partially removed in the process of washing. The latter is probably true, and it may be that a different method of analysis would give more accurate results for this compound.

First Series.

Experiments on Mercuric Chloride.

The material used in this series of experiments was prepared from the commercial C. P. mercuric chloride. The product was first dissolved in water, the solution filtered and evaporated to crystallisation. The crystals were dried and carefully sublimed from a porcelain dish into a glass funnel. The sublimed portion was dissolved in water, the solution filtered and evaporated to crystallisation. These crystals were dried as before and carefully re-sublimed. The material was then placed in a weighing tube and kept in a desiccator.

Mode of Procedure.

The method of operation was similar to that already described under the different compounds of silver. A weighed portion of the mercuric chloride was dissolved in a little potassium cyanide and the solution electrolysed. The deposit was washed and dried and handled in every way like the deposits of silver. The strength of the current and time of action were as follows:—

Time of action.	Strength of current.
4 hours	$\mathrm{N.D}_{100}=0{\cdot}02$ amperes.
6 "	$\mathrm{N.D}_{100}=0{\cdot}05$ "
6 "	$\mathrm{N.D}_{100}=0{\cdot}10$ "
6 "	$\mathrm{N.D}_{100}=0{\cdot}30$ "

A current of gradually increasing strength deposits the mercury in extremely small globules, which can be washed and handled more easily than the larger globules obtained by using a strong current at first. In cases where more than one-half grm. of metal was deposited the strong current was allowed to act two hours longer.

Ten results on mercuric chloride reduced to a vacuum standard on the basis of

5·41 = density of mercuric chloride,
13·59 = " " metallic mercury,
21·4 = " " platinum dish,
8·5 = " " weights,

and computed from the formula $HgCl_2$, assuming 35·45 to be the atomic mass of chlorine, are as follows:—

	Weight of $HgCl_2$. Grms.	Weight of Hg. Grm.	Atomic mass of mercury.
1	0·45932	0·33912	200·030
2	0·54735	0·40415	200·099
3	0·56002	0·41348	200·053
4	0·63586	0·46941	199·947
5	0·64365	0·47521	200·026
6	0·73281	0·54101	199·988
7	0·86467	0·63840	200·838
8	1·06776	0·78825	199·946
9	1·07945	0·79685	199·917
10	1·51402	1·11780	200·028

Mean .. .. = 200·006
Maximum .. = 200·099
Minimum .. = 199·917

Difference .. = 0·182
Probable error = ± 0·011

Computing from the total quantity of material used and metal obtained we have 199·996 for the atomic mass of mercury.

Second Series.

Experiments on Mercuric Bromide.

The bromine used in these experiments was prepared by distilling the commercial C. P. bromine twice over manganese dioxide. Any trace of chlorine which might be present would be removed by this method.

Preparation of Mercuric Bromide.

Fifty grms. of metallic mercury were placed in a beaker and covered with water. Pure bromine was then added until the mercury was completely saturated. The contents of the beaker were then digested with hot water until the mercuric bromide dissolved; the solution was filtered and evaporated to crystallisation. The white crystals of mercuric bromide which separated were thoroughly dried and carefully sublimed from a porcelain dish into a glass funnel. Only the middle portion of the sublimate was used in the experiments. The product obtained in this way consisted of brilliant crystalline leaflets which dissolved completely in water. The material was kept in a weighing tube in a desiccator.

Mode of Procedure.

The method of analysis was exactly like that described under mercuric chloride. A weighed portion of the mercuric bromide was dissolved in dilute potassium cyanide in a platinum dish. The solution was then electrolysed and the resulting metal weighed. The strength of current and time of action were the same as for mercuric chloride.

Ten results on mercuric bromide reduced to a vacuum standard on the basis of

5·92 = density of mercuric bromide,
13·59 = „ metallic mercury,
21·4 = „ platinum dish,
8·5 = „ weights,

and computed for the formula $HgBr_2$, assuming 79·95 to be the atomic mass of bromine, are as follows :—

	Weight of $HgBr_2$.	Weight of Hg.	Atomic mass of mercury.
	Grms.	Grm.	
1	0·70002	0·38892	199·898
2	0·56430	0·31350	199·876
3	0·57142	0·31750	199·938
4	0·77285	0·42932	199·832
5	0·80930	0·44955	199·814
6	0·85342	0·47416	199 911
7	1·11076	0·61708	199·869
8	1·17270	0·65145	199·840
9	1·26186	0·70107	199·899
10	1·40142	0·77870	199·952

Mean .. .. = 199·883
Maximum .. = 199·952
Minimum .. = 199·814

Difference .. = 0·138
Probable error = ± 0·010

Computing from the total quantity of material used and metal obtained, the atomic mass of mercury is 199·885.

(To be continued).

METAL SEPARATIONS BY MEANS OF HYDROCHLORIC ACID GAS.*

By J. BIRD MOYER.

(Continued from p. 54).

VI.—*Behaviour of Cupric Oxide.*

Pure copper nitrate was made by re-crystallisation. It was then ignited in a porcelain crucible at a dull red heat, until it became constant in weight. The pure black oxide was then subjected to the action of hydrochloric acid gas. In Experiment I., the boat containing the oxide was heated at the outset to 175°. It was taken out after two hours, placed over sulphuric acid for half-an-hour, and weighed. The weight showed that the copper oxide had hardly been acted upon. It had only been superficially changed to chloride. It was then moistened with two or three drops of hydrochloric acid, dried in a rapid current of the gas, and heated two hours longer. This resulted in the complete transformation into chloride. The anhydrous chloride thus obtained, liver brown in colour, was placed in a desiccator from which the air was exhausted. This was done to remove all the gas that might be retained, and prevented a too rapid absorption of moisture.

Copper chloride absorbs moisture, but not so rapidly as to prevent weighing in this form :—

	Copper oxide taken.	Copper chloride obtained.	Copper chloride required.	Difference.
	Grm.	Grm.	Grm.	Grm.
Experiment I.	0·1011	0·1708	0·1713	−0·0005
„ II.	0·1025	0·1726	0·1736	−0·0010
„ III.	0·1034	0·1756	0·1752	+0·0004

In Experiment II. the change was completed in the cold by prolonged action through four hours. It was then heated about ten minutes at the end to drive out the moisture that had formed. In all the experiments cited, the copper chloride, after weighing, was found to dissolve completely in cold water.

VII.—*The Separation of Antimony from Copper.*

The same material was used as in the preceding experiments.

The weighed oxides were thoroughly mixed. The antimony was completely volatilised, leaving copper chloride which was weighed as such. The volatile antimony chloride was caught in the bulb receiver at the end of the tube. The bulb and tube were washed out with acidulated water into a beaker, and the antimony thrown down with hydrogen sulphide. The antimony sulphide was filtered, thoroughly washed, and while moist dissolved in strong hydrochloric acid. The hydrogen sulphide evolved was conducted into bromine water and oxidised to sulphuric acid, which was estimated as usual and the antimony calculated.

The length of time required was eight hours. On several occasions the experiment was interrupted at the end of four hours, but invariably the separation was incomplete, and on dissolving out the copper chloride formed, black copper oxide and white antimony oxide were plainly evident. In some cases the mixture of oxides was moistened with a couple of drops of hydrochloric acid, and then evaporated down in a stream of acid gas by heating the tube over a water-bath. This treatment seemed to facilitate matters, but it is not altogether advisable, because the copper chloride has a tendency to creep over the sides of the boat. It is quicker in the end to separate them in the dry condition, allowing plenty of time for the reaction. The copper chloride obtained was perfectly soluble in cold water and contained no antimony. It could readily be changed to oxide and weighed if thought necessary.

	Antimony trioxide taken.	Copper oxide taken.	Copper chloride obtained.	Copper chloride required.	Difference.
	Grm.	Grm.	Grm.	Grm.	Grm.
Experiment I.	0·1068	0·1040	0·1750	0·1745	+0·0005
„ II.	0·1062	0·1053	0·1774	0·1784	−0·0010
„ III.	0·1022	0 1020	0·1726	0 1728	−0·0002
„ IV.	0·1198	0·1020	0·1722	0·1728	−0·0006

	Antimony trioxide taken.	Antimony trioxide found.	Difference.
	Grm.	Grm.	Grm.
Experiment I.	0·1068	0·1059	+0·0009

VIII.—*The Separation of Bismuth from Copper.*

The pure oxides were mixed and treated as directed under bismuth and lead.

	Copper oxide taken.	Bismuth trichloride taken.	Copper chloride obtained.	Copper chloride required.	Difference.
	Grm.	Grm.	Grm.	Grm.	Grm.
Experiment I.	0·1030	0·1069	0·1738	0·1745	−0·0007
„ II.	0·1004	0·1077	0·1701	0·1713	−0·0012
„ III.	0·1026	0·1060	0·1741	0·1738	+0·0003
„ IV.	0·1019	0·1058	0·1718	0·1726	−0·0008

	Bismuth trioxide obtained.	Bismuth trioxide required.	Difference.
	Grm.	Grm.	Grm.
Experiment I.	0·1076	0·1069	+0·0007

The time required in each of these trials was seven hours. It seemed to be advantageous to raise the temperature and heat sharply for about ten minutes at the end, to insure the complete removal of the bismuth.

Moistening with acid helped the reaction, but subjected it to the same danger of creeping as noted under antimony and copper.

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* From author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Ph.D., 1896. From the *Journ. Amer. Chem. Soc.*, xviii., December, 1896.

The bismuth was estimated as follows: It was washed out of the tube and bulb with acidulated water, and then precipitated as sulphide. The bismuth sulphide was filtered, washed, and dissolved in nitric acid. It was thrown out of the solution with ammonium hydroxide and ammonium carbonate as hydrated oxide, and then filtered, dried, and ignited. It was weighed as oxide. The residue of copper chloride in the boat dissolved in cold water and showed no bismuth.

IX.—*Action of Gaseous Hydrochloric Acid on Sodium Pyroarsenate.*

Hibbs (*Journ. Amer. Chem. Soc.*, xviii., 1044) showed that arsenic was completely volatilised from sodium pyroarsenate, leaving weighable sodium chloride. In fact, so clean was the elimination of arsenic that he made it the basis of an arsenic atomic mass determination, with admirable success.

In working up the separation of arsenic from other metals it was necessary to start with the pure sodium salt. After purification I decided to test it, by weighing the salt produced by the action of the acid gas upon it. Several determinations gave close results, proving the salt pure.

Chemically pure arsenate was procured. It was re-crystallised and then ignited (not too strongly) for an hour. The pyroarsenate obtained was used in precipitating the various arsenates investigated.

	Sodium pyroarsenate taken.	Sodium chloride obtained.	Sodium chloride required.
	Grm.	Grm.	Grm.
Experiment I.	0·2021	0·1330	0·1335
,, II.	0·1039	0·0691	0·0686

X.—*The Separation of Arsenic from Copper.*

Pure sodium pyroarsenate was used to precipitate the copper salt.

Copper sulphate was re-crystallised five times, a few good crystals were dissolved and the two solutions mixed. A green copper arsenate was precipitated. It was washed and dried at 100°. Salkowski (*Journ. Prakt. Chem.*, civ., 129) observes that copper arsenate still contains water above 130°. My salt had the composition—

$$Cu_3As_2O_8 + 2H_2O.$$

Hydrochloric acid gas completely changes it in the cold to chloride. A slight heat drives out the arsenic and water and leaves a brown anhydrous copper chloride, which can be weighed as such. Care was taken to remove all the acid gas before weighing.

The arsenic was washed out of the bulb into a beaker; this was warmed with nitric acid to insure oxidation, and then it was precipitated from an ammoniacal solution with "a magnesia mixture." It was weighed as $Mg_2As_2O_7$.

	Copper arsenate taken.	Copper chloride obtained.	Copper chloride required.	Difference.
	Grm.	Grm.	Grm.	Grm.
Experiment I.	0·1067	0·0850	0·0851	−0·0001
,, II.	0·1240	0·0998	0·0991	+0·0007
,, III.	0·1072	0·0860	0·0856	+0·0004
,, IV.	0·1155	0·0924	0·0923	+0·0001
,, V.	0·1042	0·0832	0·0833	−0·0001

Experiment I. As_2O_5 obtained, 0·0498 grm.; As_2O_5 required, 0·0487 grm.

The residue of copper chloride completely dissolved in water. It showed no arsenic when tested in a Marsh apparatus.

XI.—*The Separation of Arsenic from Silver.*

Silver arsenate was made by precipitating silver nitrate with sodium arsenate. Care was taken to have the nitrate in excess. The reddish-brown arsenate of silver was washed with boiling water, until the washings no longer showed silver when tested with hydrochloric acid. It was dried at 110°.

As was expected, the acid gas attacked it even in the cold. In fact the action was so vigorous that a couple of analyses were spoiled by spattering. The trouble arose from the fact that the arsenate was not finely powdered. Heat was generated in the reaction sufficiently to send over a portion of the water formed. Experiment I. was run in the cold for one hour and then heated sharply for a few minutes to expel the arsenic and water. The result was only 0·46 per cent too high, but indicated that the salt should be heated longer, and not necessarily as high to remove all the arsenic.

The succeeding experiments were heated from one to two hours at 150° with better results:—

	Silver arsenate taken.	Silver chloride obtained.	Silver chloride required.	Difference.
	Grm.	Grm.	Grm.	Grm.
Experiment I.	0·2542	0·2381	0·2363	+0·0018
,, II.	0·2325	0·2163	0·2161	+0·0002
,, III.	0·2084	0·1952	0·1938	+0·0014
,, IV.	0·2070	0·1927	0·1924	+0·0003

Experiment I. Ag obtained = 70·45 per cent; Ag required = 69·99 per cent.

The residues in Experiments II., III., and IV. were dissolved and tested for arsenic. None was found.

XII.—*The Separation of Arsenic from Cadmium.*

Chemically pure cadmium sulphate was precipitated by a solution of sodium pyroarsenate. Stirring brought out a gelatinous arsenate, which changed by additional stirring to a granular salt. This was thoroughly washed and dried at 110°. It had the composition $Cd_3As_2O_8 + 2H_2O$. Salkowski (*loc. cit.*) observes that a red heat is necessary to fully dehydrate this salt.

The moisture and arsenic were completely expelled at 150°, leaving a uniform mass of cadmium chloride. It was weighed as such after standing over sulphuric acid for one-half hour. The arsenic was determined as usual.

	$Cd_3As_2O_8 +$ $2H_2O$ taken.	Cadmium chloride obtained.	Cadmium chloride required.	Difference.
	Grm.	Grm.	Grm.	Grm.
Experiment I.	0·2359	0·1965	0·1977	−0·0012
,, II.	0·1166	0·0968	0·0968	0·0000
,, III.	0·1030	0·0857	0·0855	+0·0002
,, IV.	0·1138	0·0947	0·0946	+0·0001
,, V.	0·1043	0·0870	0·0867	+0·0003

	$Cd_3As_2O_8 +$ $2H_2O$ taken.	As_2O_5 obtained.	As_2O_5 required.	Difference.
	Grm.	Grm.	Grm.	Grm.
Experiment I.	0·2359	0·0813	0·0822	0·0009

The cadmium chloride dissolved perfectly in water, and showed no arsenic when tested in a Marsh apparatus.

XIII.—*The Action of Hydrochloric Acid Gas on Ferric Oxide.*

Pure oxide of iron was heated in a stream of acid gas. The behaviour of iron is rather peculiar, as it very readily changes into chloride, and then only partially volatilises On heating to 200° the greater part is driven over as flaky crystals of ferric chloride. The remainder consists of a white mass, which refuses to go over on prolonged action and also on raising the temperature.

This residue was soluble in water and did not react with potassium thiocyanate, but immediately gave a blue precipitate with ferricyanide. Reduction was therefore evident; this is also noted by Jannasch and Schmidt (*loc. cit.*). The temperature at which ferric chloride usually goes into the ferrous condition is above 1000°.

Care was taken to prepare perfectly pure hydrochloric acid gas. Chemically pure acids were used to this end. The action, however, was the same in all cases.

XIV.—*The Separation of Arsenic from Iron.*

Chemically pure ferrous ammonium sulphate was carefully oxidised with nitric acid, it was taken up in water, filtered, and then crystallised several times. The best crystals were selected, and a solution made to precipitate the arsenate. A white precipitate tinged with yellow was formed. It was washed by decantation and then filtered and washed until the washings no longer gave Prussian blue with ferrocyanide. It was then dried and gently ignited.

The acid gas acts on it quickly in the cold, and it becomes a light green liquid. In evaporating off the moisture the chloride of iron was carried over with the arsenic.

In a second trial, with the temperature lower and occasionally removing the source of the heat altogether, when ebullition threatened to cause spattering, ferric chloride was obtained without loss. This was gradually heated a little higher to remove all the arsenic.

The chloride of iron was dissolved, oxidised, precipitated with ammonium hydroxide, and estimated as usual. The result was fair, and the product tested showed the absence of arsenic, but all succeeding experiments failed. Either the substance spattered or the iron went along with the arsenic.

Jannasch and Schmidt (*loc. cit.*) separated arsenic from iron by placing their material in a large hard glass bulb and evaporating down to dryness with nitric acid in an air current. This is not applicable when a porcelain boat is employed. They then volatilised the arsenic in hydrochloric acid gas at 120°.

(To be continued).

NICKELO-NICKELIC HYDRATE, $Ni_3O_4.2H_2O$.

By WILLIAM L. DUDLEY.

In studying the action of fused sodium dioxide on metals, I have obtained interesting crystalline compounds, some of which at least have never been described. Only one of them has been carefully investigated, and it proves to be nickelo-nickelic hydrate, having the formula $Ni_3O_4.2H_2O$.

It is prepared by fusing sodium dioxide in a nickel crucible with metallic nickel at a cherry-red heat. The action of the oxide upon the nickel proceeds with moderate rapidity, and in a few minutes scaly crystals appear floating in the fused mass. The crystals multiply steadily until, in the course of an hour, the contents of the crucible is thick with them, and comparatively little liquid remains. After cooling, the crucible is submerged in a beaker of distilled water, and the undecomposed sodium dioxide, together with the sodium oxide, dissolves out, leaving the crystals which rapidly settle to the bottom of the liquid. The crystals should be washed several times with boiling water by decantation, and finally thrown in a filter. It is quite difficult to wash out all the alkali, which adheres with unusual persistence. Probably the best plan to adopt is to put the crystals in a Soxhlet extraction apparatus, and wash with water until no colouration is obtained with phenolphthalein. This requires about fifty hours of continuous washing. The crystals should then be dried at 110° C., and a magnet passed carefully through them to remove any particles of metallic nickel which may have eroded and not been completely acted upon.

The crystals are lustrous and almost black, with a slight brown-bronze hue. They are soft, and grind in a mortar much like graphite. The crystals seem to be hexagonal plates, but measurements of the angles have not been made. They dissolve slowly in acids, forming nickelous salts. Hydrochloric acid evolves chlorine; sulphuric and nitric acids, oxygen. They are insoluble in water and in solutions of the alkalies. The compound is not magnetic. The specific gravity is 3·4115 at 32° C. At 130° C. the compound does not undergo decomposition, but at about 140° C. it begins to lose weight; at 240° C. the weight remains constant. At a red heat further loss is sustained and the residue remaining is nickelous oxide. The loss from 130° C. to 240° C. is due to water driven off, and at a red heat this loss is due to the evolution of oxygen.

The compound proved to be $Ni_3O_4.2H_2O$, as is shown by the results of the analysis:—

Loss of H_2O on heating from 130° C. to 240° C.:—

	Per cent.
First determination	13·00
Second ,, ...	13·13
Theory for $Ni_3O_4.2H2O$	13·06

The residue remaining after heating to 240° C. is Ni_3O_4. On heating this residue to redness the loss of oxygen was found to be:—

	Per cent.
Loss of oxygen	6·63
Theory	6·67

The total loss of water and oxygen obtained on heating the compound from 130° C. to redness was:—

	Per cent.
First determination	18·91
Second ,, ...	18·88
Theory for $Ni_3O_4.2H_2O$	18·86

The oxygen given off on heating to redness was determined by calcining the compound in an atmosphere of carbon dioxide, and collecting in Schiff's apparatus over potassium hydroxide solution. The result gave:—

	Per cent.
Oxygen	5·93
Theory for $Ni_3O_4.2H2O$	5·84

The nickel was determined and found to be:—

	Per cent.
Nickel	63 67
Theory	63·72

In all of the calculations the atomic weight of nickel was taken to be 58·56, and oxygen 16.

The compound made in a nickel crucible of commerce is not perfectly pure, as the sample obtained was found to contain 0·71 per cent of cobalt, the presence of which, however, would make no appreciable difference in the results of the analyses. No method has been found for freeing the compound from this impurity, and it appears at present as if the only plan would be to use a chemically pure nickel crucible in making it, for no crucible will withstand the action of fused sodium dioxide. Porcelain, iron, silver, gold, and platinum crucibles are rapidly attacked.

The presence of water in this compound seems curious, but it may be due to the presence of sodium hydroxide in the sodium dioxide. Again it may be due to the water added to dissolve the soluble residue from the crystals. The first explanation seems to be the more plausible since the crystals are formed in the mass while it is fused, and they are not produced upon the addition of the water. If such is the case it would seem that the water driven off between 130° C. and 240° C. is from the breaking down of a true hydrate, rather than the expulsion of water of crystallisation.

A cobalto-cobaltic hydrate, $Co_3O_4.2H_2O$, has been described (Genth and Gibbs, *Amer. Journ. Sci.*, xxiii., 257), but it was obtained by exposing to moist air, Co_3O_4, prepared by heating cobalt carbonate. Ni_3O_4, prepared by heating nickelo-nickelic hydrate to 240° C., is hygroscopic, and absorbs about $7\frac{4}{10}$ per cent of water from the air at 30° C., which is completely lost at 110° C., showing that no hydrate is formed under these conditions.

The study of the action of fused sodium dioxide on the metals will be continued here, and it is hoped that some more data can be contributed soon.—*Journal of the American Chemical Society*, xviii., October, 1896.

ALUMINUM ANALYSIS.*

By JAMES OTIS HANDY.

(Continued from p. 56).

Determination of Sodium in Aluminum.

One grm. of drillings is dissolved in a porcelain evaporating dish in 50 c.c. of 1·3 sp. gr. nitric acid and sufficient hydrochloric acid to effect solution. Boil down until all hydrochloric acid has been removed. Rinse the solution into a large platinum dish and evaporate to dryness. Heat over a good Bunsen burner until nitric oxide fumes cease to be evolved. Grind the residue finely. Mix it by grinding with 1 grm. of chemically pure ammonium chloride and 8 grms. of chemically pure calcium carbonate. Heat the mixture in a large covered platinum crucible. For the first fifteen minutes have a Bunsen burner flame just touching the bottom of the crucible, and for the next forty-five minutes have the whole crucible heated bright red by a full Bunsen burner flame. Cool, and treat the residue with hot distilled water until it becomes just friable under pressure. Avoid adding an excess of water beyond that necessary to make the sintered mass just friable. Grind it in a Wedgwood mortar, and rinse out with hot distilled water. Filter, rejecting the well-washed residue, and treat the filtrate at the room temperature with saturated ammonium carbonate solution in slight excess. Stir very thoroughly. The precipitated calcium carbonate is at first flocculent, but on standing for about ten minutes it becomes crystalline. Filter into a platinum dish; reject the residue, and evaporate the solution on the water-bath to dryness. Heat carefully to dull redness to expel ammonium salts. Dissolve the residue in a little water, and add a few drops of ammonium carbonate solution. If this produces a precipitate, add sufficient ammonium carbonate solution to precipitate all of the remaining lime. Stir well, wait ten minutes, filter, evaporate to dryness, heat to dull redness, and weigh sodium chloride. Deduct any sodium chloride found in a blank determination, using acids, &c., as above, and finally 8 grms. of calcium carbonate and 1 grm. of ammonium chloride.

$$\mathrm{NaCl} \times 0{\cdot}39316 = \mathrm{Na}.$$

Care should be taken when heating up the residue of sodium chloride, &c., after evaporating on the water-bath. If the platinum dish and contents are heated for a few minutes on sheet asbestos on the hot plate before placing over the lamp, spattering may be avoided. Sodium is generally absent from aluminum, but it has been found in amounts as high as 0·20 per cent, and is considered a cause of the occasional deterioration of the metal in water.

Determination of Carbon in Aluminum. (Moissan's Method Modified).

Triturate 2 grms. of drillings in a Wedgwood mortar with 10 to 15 grms. of mercuric chloride, powdered and dissolved, or partly dissolved, in about 15 c.c. of water. Reaction takes place rapidly, and a heavy grey residue is left. Persistent trituration removes the last particles of metallic aluminum. Evaporate on the water-bath to dryness. The dry residue is heated in a current of pure hydrogen to expel mercuric compounds. The remaining material is then placed in a boat in a combustion-tube and burned off as in carbon determination in steel. The carbon dioxide is caught as barium carbonate, and the excess of barium hydroxide determined by means of standard acid. We are working on a more generally applicable method for carbon in aluminum.

Determination of Nitrogen in Aluminum.

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

Determination of Aluminum in Metallic Aluminum.

Dissolve 1 grm. of metal in 30 c.c. of 33 per cent hydrochloric acid in a porcelain dish and evaporate cautiously to complete dryness. Re-dissolve, by boiling with 10 c.c. of concentrated hydrochloric acid and 75 c.c. of water. Wash into a 12-ounce beaker; dilute to 250 c.c., and pass hydrogen sulphide until saturated. Filter into a beaker and boil off hydrogen sulphide. Oxidise by adding 1 c.c. of concentrated nitric acid and continuing to boil for ten minutes. Cool, and make the solution up to 500 c.c. Remove 50 c.c. of the solution, and, having diluted to 250 c.c. and heated to boiling, add ammonium hydroxide in slight excess and boil well for twenty minutes. Let settle; filter, and wash thoroughly with hot water. It is necessary to wash the precipitate off from the filter, break it up, and wash it back again. Finally burn off in a thin-walled platinum crucible, igniting most intensely, and weighing the instant the crucible and contents are cool. We have found that alumina is one of the most difficult oxides to dehydrate completely, and when dehydrated it absorbs atmospheric moisture even more rapidly than calcium oxide does. Moissan prefers to precipitate aluminum by ammonium sulphide. Having prepared a solution in hydrochloric acid, he takes an amount equal to 0·15 grm. of aluminum, neutralises it in the cold with ammonia, and precipitates it by ammonium sulphide which has been recently prepared. He then digests for one hour, filters, washes with hot water, ignites, and weighs.

Analysis of Alloys of Aluminum with Smaller Amounts of other Metals.

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

Dissolve ½ grm. or 1 grm. in 15 c.c. of 33 per cent sodium hydroxide solution in an Erlenmeyer flask of 12-ounce capacity. If the flask is covered and set in a warm place, solution is complete in a few minutes, even if the drillings are quite coarse. Dilute to 30 c.c. with hot water, and filter through a coarse lintless filter-paper (Whitall, Tatum, and Co.'s 5-inch). Wash well with hot water. Dissolve residue, after washing it off the filter-paper into a 12-ounce beaker, by warming with 5 c.c. of concentrated nitric acid. Cool, add saturated commercial sodium carbonate solution until re-solution occurs. Titrate with standard potassium cyanide solution to the disappearance of the blue colour. Standardise the cyanide for about the same amount of copper.

For commercial reasons 20 per cent alloys are made in the reduction pots, and these alloys are subsequently used for making copper alloys of low percentage.

Determination of Nickel in Aluminum Alloys.

The 3 per cent nickel alloy is now used. The addition of 3 per cent of nickel increases the tensile strength of aluminum by several thousand pounds per square inch.

One grm. of drillings is dissolved in 15 c.c. of 33 per cent sodium hydroxide solution in a 12-ounce Erlenmeyer flask. Dilute to 50 c.c., and filter through a 5-inch lintless paper, washing the residue thoroughly with hot water. Rinse the residue back into the flask, and add 3 to 5 c.c. of concentrated nitric acid, and a drop of concentrated hydrochloric acid. Boil, and when dissolved cool, and make up to 250 c.c. In 100 c.c. determine the copper by neutralising with ammonia, adding 2 c.c. of concentrated hydrochloric acid, warming, and passing hydrogen sulphide. Filter and wash with ammonium sulphide. Burn it off carefully in a porcelain crucible, and, having weighed, dissolve in 5 c.c. of concentrated nitric acid.

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* From the *Journal of the American Chemical Society*, Sept., 1896.

Then dilute to 20 c.c., add excess of sodium carbonate solution, and titrate with standard potassium cyanide. Boil the filtrate from the cupric sulphide, oxidise with 1 c.c. of nitric acid, and precipitate with ammonium hydroxide. Do not boil, but digest for a few minutes just below the boiling-point. Filter, wash, re-dissolve in hot 15 per cent nitric acid wash. Dilute to 150 c.c., and again precipitate with excess of ammonium hydroxide, being careful to avoid boiling or prolonged digestion. Filter and wash. Burn off and weigh ferric oxide, &c. In a second 100 c.c. of the main solution, precipitate nickel hydroxide, cupric oxide, ferric hydroxide, &c., by 33 per cent chemically pure sodium hydroxide solution, added in slight excess to the boiling solution. Boil for fifteen minutes, filter, and wash most thoroughly with hot water. Burn off and weigh nickel oxide, cupric oxide, and ferric oxide. Deduct cupric oxide and ferric oxide already found. Calculate nickel oxide to metallic nickel.

Analysis of Aluminum-Manganese Alloys.

Determination of Manganese.—Place 1 grm. of drillings in a 12-ounce beaker. Add 30 c.c. of 33 per cent hydrochloric acid (one part of concentrated hydrochloric acid to two parts of water). When dissolved add 25 c.c. of nitric acid (1·42), and boil down to 10 c.c. Add 50 c.c. of colourless nitric acid (1·42), and boil. Precipitate the manganese with powdered potassium chlorate, added cautiously, and proceed as described under manganese in steel by Williams's method (Blair's "Chemical Analysis of Iron").

Analysis of Chromium-Aluminum Alloy.

Determination of Chromium. — Dissolve 1 grm. in a 12-ounce beaker in 30 c.c. of 33 per cent hydrochloric acid, and when dissolved add 50 c.c. of sulphuric acid (1·84), and evaporate carefully until fumes of sulphur trioxide escape. Cool, add 60 c.c. of water, and boil. After five minutes, if all aluminum sulphate has been dissolved, add powdered potassium permanganate until the solution has a distinct pink colour. Boil until the excess of potassium permanganate is decomposed. Filter through washed asbestos, and determine the chromium in the filtrate as in chrome steel (Galbraith's method. See Blair's "Chemical Analysis of Iron").

Analysis of Tungsten-Aluminum Alloy.

Determination of Tungsten.—Dissolve 1 grm. in 33 per cent hydrochloric acid in a 4½-inch evaporating dish. Add 30 c.c. of nitric acid (1·42), and evaporate to dryness. Re-dissolve in 30 c.c. of hydrochloric acid (1·20), dilute to about 90 c.c., and boil for two hours. Filter and wash thoroughly. Burn off and weigh $Si + SiO_2 + WO_3 +$ crucible. Treat with 3 drops of 25 per cent sulphuric acid and about 2 c.c. of hydrochloric acid. Evaporate carefully over an Argand burner, re-ignite, and weigh crucible and silicon and tungstic oxide. Fuse with 1 grm. of sodium carbonate, cool, place in dish, and add 15 c.c. of water and 20 c.c. of 25 per cent sulphuric acid, remove crucible, and evaporate until white fumes escape. Cool, re-dissolve in about 50 c.c. of water. Filter, wash, ignite, and weigh silica (from silicon), tungstic oxide, and crucible. Treat with sulphuric acid and hydrofluoric acid, evaporate, ignite, and re-weigh. Loss equals silica. Calculate to silicon, and add to the weight of silica lost by treatment of first insoluble residue. Deduct this sum from the weight of silicon, silica, and tungstic oxide first found, and the remainder equals tungstic oxide. Calculate to tungsten.

Analysis of Aluminum-Titanium Alloy.

Determination of Titanium.—Two grms. of the alloy in a 12-ounce Erlenmeyer flask are dissolved by addition of 50 c.c. of 10 per cent potash solution. Dilute with distilled water to about 125 c.c., boil up, and filter as quickly as possible. Wash ten times with boiling water. Burn off the residue in a porcelain crucible, crush it in a Wedgwood mortar, fuse in a large platinum crucible with 10 grms. of potassium bisulphate. Conduct the fusion exactly as follows:—Choose a good Bunsen burner, and protect it from draught by a sheet-iron chimney; make the flame 1½ inches long, and place the triangle carrying the upright crucible just at the point of the flame. Increase the heat gradually until in ten minutes the lower fourth of the crucible is red hot. Allow it to remain at this temperature ten minutes, moving the lid slightly to one side every two minutes, and giving the crucible (held firmly in the tongs) a gentle rotating movement, then turn up the light until the flame reaches the top of the crucible and envelopes it. Five minutes of this treatment melts down any potassium bisulphate, &c., which have risen on the sides. The flame is lowered and the lower fourth heated for ten minutes longer. Cool, dissolve in about 200 c.c. of water; filter, rejecting the residue, if ignition and treatment with hydrofluoric acid show it to be only silica. If it contains anything more, fuse with 4 grms. of potassium bisulphate again. The filtrate contains all the titanic oxide and the ferric oxide. Add ammonia until a slight permanent precipitate is formed, then add dilute sulphuric acid from a pipette or burette until this precipitate just re-dissolves. Finally add 1 c.c. more of 25 per cent sulphuric acid, and dilute to 300 c.c. If the solution is high in iron (which will be indicated by its distinct yellow colour) sulphur dioxide gas must be run into it until it is decolourised and smells strongly of sulphur dioxide; but if the solution is nearly colourless, indicating a low percentage of iron, only sulphur dioxide water need be added for the reduction. Boil well for one hour, adding water saturated with sulphur dioxide occasionally. Filter off the titanic oxide through double filters, and wash well with hot water. Burn off and weigh as titanic oxide. If the precipitate is yellow, indicating the presence of iron, it may be fused with 1 grm. of potassium bisulphate, the fusion dissolved in 10 c.c. of dilute sulphuric acid, and the iron determined in this solution by reducing with 1 grm. of zinc, and titrating with permanganate. This is not often necessary. Calculate titanic oxide to titanium. $TiO_2 \times 0{\cdot}6 = Ti$.

Determination of Zinc in Zinc-Aluminum Alloys. First Method.

Dissolve 1 grm. in 30 c.c. of 33 per cent hydrochloric acid in a 12-ounce beaker. Dilute to 200 c.c., and heat nearly to boiling. Pass hydrogen sulphide till all copper is precipitated. Filter and boil off hydrogen sulphide, oxidise with 1 c.c. nitric acid by boiling ten minutes. Add sodium hydroxide solution until neutral, then make barely acid with hydrochloric acid, and stir until the aluminum hydroxide all dissolves. Add 10 grms. of sodium acetate and 500 c.c. of water, boil up, and filter at once. Dissolve the washed precipitate in hydrochloric acid, and repeat the acetate separation. Heat the united filtrates to boiling and pass hydrogen snlphide. Filter off the zinc sulphide on double filters, wash thoroughly with hot water. Burn off in a porcelain crucible, and weigh zinc oxide. Calculate to zinc. This method may be used when only a small quantity of the sample is available; but when this is not the case, it is better to use the method given below.

Determination of Zinc in Zinc-Aluminum Alloy. Second Method.

Dissolve 1 grm. of drillings in 33 per cent sodium hydroxide solution in a 12-ounce Erlenmeyer flask. Filter as soon as dissolved through a 4-inch lintless filter-paper. Wash thoroughly with hot water. Rinse the residue of zinc, iron, copper, silicon, &c., back into the flask. This may require 25 c.c. of water. Add 5 c.c. of hydrochloric acid and boil. Dilute to 150 c.c. with hot water and pass hydrogen sulphide. Filter and boil off hydrogen sulphide, re-oxidise by adding 1 c.c. nitric acid and boiling ten minutes. Add sodium hydroxide till neutral, then add dilute hydrochloric acid till just acid, and then 10 grms. of sodium acetate, and 300 c.c. of boiling water, and boil for five minutes. Wash well. If the precipitate is small re-solution and re-precipitation are not necessary. Pass hydrogen sulphide through the filtrate. Filter off zinc sulphide through double filters. Wash well. Ignite in a porcelain crucible, heating finally over the blast to zinc oxide. $ZnO \times 0\cdot8032 = Zn$.

Analysis of Aluminum Solders.

Determination of Tin, Phosphorus, and Zinc.—Aluminum solders generally contain phosphor-tin and zinc. As presented for analysis they usually consist of a soldered joint, from which the solder must be scraped and analysed. The analysis, therefore, involves a separation of the elements aluminum, zinc, tin, and phosphorus. It is a difficult matter to determine whether aluminum was a constituent of the solder when only a soldered joint is available for examination. It is best to dissolve all adhering aluminum from the pieces chosen for analysis by treatment with 33 per cent sodium hydroxide solution, after which the residue is filtered off, dried, and weighed out for analysis. Dissolve or decompose three-tenths to five-tenths grm. in a twelve-ounce beaker by means of 20 c.c. of nitric acid (1·42). If necessary, 5 c.c. of hydrochloric acid (1·2) may be used to effect complete decomposition. Evaporate to complete dryness on a hot plate. Cool, add 25 c.c. of nitric acid (1·13), and boil thoroughly. Filter. The residue contains all of the tin, most of the phosphorus, and possibly some zinc. Burn it off in a porcelain crucible, and, after pulverising the residue in an agate mortar, mix it with 2 grms. of sodium carbonate and 2 grms. of sulphur, fuse it in a covered porcelain crucible over a Bunsen burner for about half-an-hour. Give it three minutes of gentle blast flame at the last. Cool, boil out with 150 c.c. of water in a twelve ounce covered beaker. Filter and wash. Extract any possible zinc sulphide, &c., from the residue by dissolving in nitric acid, boiling off hydrogen sulphide, and adding this to the first filtrate obtained after evaporating to dryness with nitric acid. The sodium sulphide solution contains the tin and phosphorus. Add it to hydrochloric acid until just acid. Warm slightly and pass hydrogen sulphide. Filter off stannous sulphide and wash thoroughly with hot water. Burn off in a porcelain crucible and weigh stannic oxide. Calculate to metallic tin. The filtrate from the stannous sulphide is boiled to expel hydrogen sulphide, and then oxidised by adding 2 c.c. of nitric acid and boiling for fifteen minutes more. Filter off any sulphur which separates, and in this filtrate, which should amount to only about 100 c.c., precipitate the phosphorus by adding pure sodium hydroxide solution till alkaline, then nitric acid till distinctly acid, heating to 85° C., and adding 50 c.c. of filtered molybdate solution. Stir or shake well for five minutes, filter on a weighed filter paper, and after washing with one per cent nitric acid wash, dry at 100° C., and weigh. Yellow precipitate multiplied by 0·0163 equals phosphorus. The nitric acid solution obtained after evaporating the first solution to dryness, &c., is now neutralised with sodium hydroxide solution, and then made just acid with hydrochloric acid. Ten grms. of sodium acetate are now added, and 300 c.c. of water (hot). Boil up for five minutes, then filter and wash. If the precipitate is of considerable size, it is probable that aluminum was a constituent of the solder. Re-dissolve it in a little hydrochloric acid, neutralise, acidify, and make a basic acetate separation as before. Precipitate the zinc in the acetate solutions by hydrogen sulphide. Filter, wash, ignite in a porcelain crucible, and weigh as zinc oxide. Calculate to metallic zinc. Dissolve the precipitate of aluminum acetate in hydrochloric acid, dilute to 250 c.c., and precipitate with ammonia. After filtering, washing, igniting, and weighing as alumina, calculate to metallic aluminum. Solders containing lead are sometimes met with. In such cases, evaporate the nitric acid filtrate from the metastannic acid to small bulk, add 25 c.c. of 25 per cent sulphuric acid, and evaporate until white fumes escape. Cool, add 100 c.c. of water, stir, and let stand for an hour in a warm place. Filter and wash with water containing 5 per cent sulphuric acid. Burn off in a porcelain crucible at a low temperature. Re-oxidise any reduced lead oxide, and restore its sulphur trioxide by adding a few drops of nitric acid and sulphuric acid and evaporating. Finally weigh lead sulphate. Calculate to metallic lead. Zinc is determined in the lead sulphate filtrate.

Analysis of Alumina.

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

(To be continued).

PROCEEDINGS OF SOCIETIES.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

At a meeting of the Edinburgh University Chemical Society on the 11th January, a paper was read by Dr. Macdonald on the "*Constitution of Benzene.*"

The different formulæ from time to time proposed for benzene were discussed and criticised. It was pointed out that for the study of all ordinary benzene derivatives, Kekulé's hexagonal formula had proved the most serviceable. The identity of 3- and 5-methylpyrazole is much akin to the benzene tautomerism, and points more clearly to re-arrangement of single and double bonds such as proposed in Kekulé's oscillation hypothesis. This hypothesis is difficult to accept in detail, but for a working hypothesis it is sufficient to assume that in certain peculiar conditions of ring symmetry double linkings are not fixed. The disturbing agent might be found in the intra-molecular energy. Assuming this to take the form of energy of motion round the ring, the single and double bonds would then represent something like the phases of a wave motion.

At the Fourth Ordinary Meeting, held on Monday, Jan. 25th, 1897 (Dr. Macdonald in the chair), Dr. Dobbin read a paper on the subject—"*Who Introduced the Use of the Balance into Chemistry?*"

After quoting a variety of statements from current text-books, which more or less emphatically attributed to Lavoisier the discovery of the law of the conservation of matter, and the first employment of the balance in investigating theoretical questions in chemistry, the author of the paper remarked upon the startling character of these statements to any person who had read Black's research on "Magnesia Alba," and quoted a few passages from Black in support of the statement that every step in his investigation has been made good by appeal to direct quantitative experiments. He next quoted a passage from "La Révolution Chimique," showing that Berthelot was well aware of the fact that these views regarding Lavoisier were entirely at variance with the true state of matters.

Dr. Dobbin then went on to mention that, so far as he was aware, the well known and often quoted experiment of van Helmont upon the supposed formation, from water only, of 164 pounds weight of the substance of a willow tree—the weight of the earth in which this willow grew having varied only by about two ounces in five years—was the earliest attempt to determine the accuracy of a view concerning a matter of scientific fact by appeal to quantitative experiment. It was further pointed out that Boyle made very frequent use of the quantitative method of investigation in dealing with the most diverse subjects, and that his inspiration in this direction was very probably derived from van Helmont.

The author concluded his paper by pointing out, with regard to Lavoisier's examination of the alleged conversion of water into earth, that every essential point in the investigation, and in the mode of carrying it out, was to be found discussed or suggested in the works of Boyle, of which we know that Lavoisier was an attentive student. So far as he had been able to ascertain, attention had not previously been called to this fact by the historians of chemistry.

NOTICES OF BOOKS.

The Manufacture and Properties of Structural Steel. By Harry Hume Campbell, S.B. New York and London: The Scientific Publishing Co. 8vo., pp. 397. 1896.

If we were called upon to classify this valuable work we should feel at a loss. A chemical treatise it certainly is not, seeing that the metal which it discusses is characterised not by its chemical composition, qualitative or quantitative, and is hence named "structural steel." Chemical considerations are certainly not overlooked, but they play here a relatively less weighty part than they do, *e.g.*, in tissue-printing or in alkali-making. If we bear in mind that steel and iron works are in the hands of engineers, and that the authorities here quoted are the proceedings of societies for civil and mechanical engineering we must place this work under the category of "engineering."

The author in his first chapter brings forward the "errancy" of scientific records—a painful subject under a strange name. Errors are shown in Howe's "Metallurgy of Steel."

These variations in the results of experiments are due to the accumulation of petty errors. It is of some consolation to find that the variations here cited are not in chemical composition, but in physical properties, such as ultimate strength, elastic limit, percentage of elongation, reduction of area, and percentage of elastic ratio. But variations in chemical composition are also quoted. The different methods of determining carbon vary to an extent unexpected as unsatisfactory.

The author remarks—as it might be fairly expected—that the comparison of miscellaneous records is perfectly useless and misleading. "Even the results of two different well-conducted laboratories may not be trustingly placed together. This may be done if the two works in question exchange samples and find that both obtain similar results from the same metals, but under no other circumstances is the comparison valid."

In the determination of phosphorus similar but more important errors are committed.

The author concludes this chapter with the pithy dictum: "The making of steel was once a trick; it was then an art; it is now a business."

Chapter IV. leans to the definition of steel, a task which though apparently simple has never yet been accomplished to the satisfaction of all concerned. "A true formula," says an author, "must apply not only to all the metals commonly designated by the term, but to all compounds which ever have been or ever will be worthy of the name, including the special alloys made by the use of chromium, tungsten, nickel, and other elements introduced to give peculiar qualities for special purposes."

After criticising various proposed definitions the author gives the following standards as embodying current usage in America, and become universal also in Britain and in France. In other lands the authority of famous names, backed by conservatism (word wrongly used!) governmental prerogative, has fixed for the present in metallurgical literature a list of terms which I have tried to show is not only difficult but fundamentally false.

The author understands therefore by the term wrought iron the product of the puddling furnace or the sinking fire. On the other hand, "by the term steel is meant the produce of the cementation process, or the malleable compounds of iron made in the crucible, the converter, or the open-hearth furnace."

In subsequent chapters we have accounts of the acid and the basic Bessemer processes, as also the open-hearth process in its acid and basic modifications.

In Chapter XVII. follows an investigation of the influence of certain elements on the physical properties of steel, the pre-eminence in injurious effects being ascribed to phosphorus. "Safety increases as phosphorus decreases," and the engineer may calculate just how much he is willing to pay for greater protection from accident.

A relatively high proportion of copper has in certain experiments given a slightly higher elastic ratio and a better elongation and reduction of area. These results are scarcely to be viewed as conclusive.

Aluminium has little effect upon tensile strength, while it does not injure the ductility in proportions under 2 per cent.

Notes on the Qualitative Analysis arranged for the Use of Students of the Rensselaer Polytechnic Institute. By W. P. Mason, Professor of Chemistry. Third Edition. Easton, Pennsylvania, Chemical Publishing Co. 1896. 12mo., pp. 56.

In the Preface to this little book we find the admission that "the market is unquestionably much overstocked with books upon this subject," and the author puts forward as his only excuse that it meets the requirements of his own classes. He further expresses the opinion that, were it not for the "expense of printing, every teacher of chemistry would use a text-book made by himself with either pen or scissors." Sad, indeed, if true! He hopes that those who use the matter here given may be led so to think for themselves as to "create a desire to know rather than an anxiety to pass." This is a very laudable aspiration, but we doubt if there is anything calculated to create this desire in this book rather than in not a few others. In the recognition of certain elements the author makes use of the spectroscope and of blowpipe reactions.

An Introduction to the Study of Chemistry. By W. H. Perkin, Jun., Ph.D., F.R.S., Professor of Organic Chemistry in the Owens College, Manchester; and Bevan Lean, D.Sc., B.A., Assistant Lecturer and Demonstrator, and late Berkely Fellow of the Owens College, Manchester. London: Macmillan and Co., Ltd. New York: The Macmillan Co. 1896. Pp. 399.

This is a gratifying book. The student is trained to rediscover, or, as the case may be, to re-demonstrate for himself, the cardinal factor and laws of chemical science. Hence, instead of—as is too generally the case—closing the book with the sad reflection that the contents, how true soever, are a mere *rechauffée* of what has been many times said before, we are in a position to congratulate the authors and still more their pupils and readers. They are reminded in the Preface, according to a quotation from Prof. H. A. Miers, that "the order in which problems have presented themselves to successive generations is the order in which they may be most naturally presented to the individual."

In carrying out this plan the author gives an abstract of the birth of chemistry drawn fron the invaluable work of Berthelot. The passages cited fully support the maxim that conclusions must be tested by experiment and by measurement. Virgil's strange recipe for generating a swarm of bees from the putrid carcase of a bullock may be traced to the inability of the classical world to distinguish bees from certain carrion-hunting Diptera.

In the chapter on the metric system the authors do not overlook its occasional inconveniences, *e.g.*, its unsuitableness to retail trade. They do not mention the pedantic refusal of French and other instrument makers to admit of any weights except the multiples and submultiples of 10. Had they been willing, instead of the French arrangement of 5, 5, 2. 2, 1, to adopt the English scale, 6, 3, 2, 1, they would have found the metric system gain in popularity.

We are most favourably impressed with Messrs. Perkin and Lean's book, and hope that it may be widely appreciated.

The Progress of Medical Chemistry, comprising its Application to Physiology, Pathology, and the Practice of Medicine. By J. L. W. Thudichum, M.D., F.R.C.S.L. London: Baillière, Tindall, and Cox. 1896. Pp. 212.

We have here a handy book, which will prove of great value to the earnest student of animal chemistry, in perhaps its most complicated region. The character of the work is decidedly controversial, and it possesses a not unpleasant acidulous flavour.

The controversy is mainly directed against the shade of the late Professor F. Hoppe-Seyler, Brücke, E. Salkowsky, Kossel, Freitag, &c. We must not, however, suppose that Dr. Thudichum's hand and pen are raised against all his contemporaries engaged in the same class of researches.

The author commences his work by comments on the "Rise of Specialism, Limited." In a succeeding paragraph he enlarges on the reign of the phagocyte, and the astonishing feats of this creature of the bacteriological imagination, "among which none was more surprising than that by which it put all chemistry to shame—namely, chemotaxis."

We have an elaborate discussion of the protagon question, which we hope after all its changing phases may now be considered as definitively settled. Dr. Thudichum tells us that the effect of the analytical operations of Kossel and Freytag is entirely retrograde, as they "carelessly repeat indecisive data, ignore facts which have been proved for many years, iterate refuted errors, try to displace proved facts, substitute erroneous names and dates for true ones, and in the only part of their operation which might have furnished something original and new fail in a manner which is the necessary result of disregard for the accepted principles of scientific research."

Towards the end of the book we have a very interesting chapter on "Shady Side of Biological Science," otherwise the ghosts of spurious researches. Following the example of Babbage, he divides spurious researches into four groups — forgeries, hoaxes, cooked and trimmed results.

In addition come the *blunderings*, made not necessarily in bad faith.

We may thank Dr. Thudichum for some innovations in nomenclature which are decided improvements. For alcohols in its generic sense he would say "cohols." "Quantation" is a convenient abbreviation for quantitative determination.

Dimorphism of the Succinates of the Camphols $+\alpha$ and $-\alpha$; Isomorphism of the Succinates of the Camphols $+\alpha$ and $-\alpha$, and of the Succinates of the Isocamphols $+\beta$ and $-\beta$.—J. Minguin.—As the crystalline form of the succinates approximates decisively to that of borneol and that of camphor, it should seem that a transformation of CO into the CHOR of camphor does not sensibly affect the crystalline form, whilst a transformation effected in CH_2 makes itself more felt.—*Comptes Rendus*, cxxiv., No. 2.

CORRESPONDENCE.

ON THE RELATION OF THE SPECIFIC ROTATORY AND CUPRIC REDUCING POWERS OF THE PRODUCTS OF STARCH HYDROLYSIS BY DIATASE.

To the Editor of the Chemical News.

Sir,—The paper by Messrs. Brown, Morris, and Millar, read before the Chemical Society on December 17th, 1896, and subsequently abstracted and appearing in the Chemical News, lxxiv., 43, confirms my own experience in starch estimation in various products by the O'Sullivan process. I have found that, without exception, there is a constant relation between the cupric reducing power and the specific rotatory power, and am, therefore, glad to see a confirmation of my own work by such eminent chemists as the authors of the above paper.—I am, &c.,

J. Arthur Wilson.

Newchurch, Rossendale,
Jan. 27, 1897.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Zeitschrift fur Analytische Chemie.
Vol. xxxvi., Part 1.

A Contribution to the Chemistry of Animal Fats. — Carl Amthor and Julius Zinc. — An elaborate paper, not admitting of abstraction.

Determination of Formaldehyd.—Dr. G. Romijn.—For the examination of pure solutions of formaldehyd the iodometric method is to be preferred, on account of its great accuracy and convenient execution. The methods of Brochet and Cambier and the potassium cyanide method may also be recommended. But if the presence of other aldehyds is to be feared the potassium cyanide method is suitable, and, along with the iodometric method, will in many cases permit of the entire analysis of the mixture. Legler's method will never bear a comparison with the other three methods.

Behaviour of the Shellac Acids in the Separation of Fatty Acids and Resin Acids, according to Gladding and Twitchell. — F. Ulzer and Rudolf Defris.—It appears that samples are sold under the name of shellac which consist of a mixture of shellac and ordinary colophonium.

Determination of Thoria in Thorin.—E. Hintz and H. Weber.—This memoir will be inserted in full.

Determination of Fatty Matter in Milk.—H. Fresenius.—The author evaporates the sample over purified quartz-sand, and extracts the dry residue with ether in a suitable apparatus. After distilling off the ether, the residual fat is dried for one hour in a weighing-glass at 100°, and weighed.

A Simple and Universally Applicable Method for Determining the Water in Silicates.—P. Jannasch and P. Weingaten (*Zeit. Anorg. Chem.*).—This paper requires the accompanying illustration.

A Technical Pyrometer.—W. C. Heräus and Keiser and Schmidt.—This instrument depends on the same principle as that of Le Chatelier, and is described in the *Zeit. fur Instrumentenkunde.*

Determination of Arsenic.—R. Engel and J. Bernard.—From the *Comptes Rendus.*

Production of Chlorine for Laboratory Purposes. — F. A. Gooch and D. A. Kreider (*Zeit. fur Anorg. Chemie*).

Analysis of Purified Zinc. — F. Mylius and O. Fromm (*Zeit. fur Anorg. Chemie*).—This memoir will be inserted in full.

Quantitative Determination and Separation of Copper. — F. Mawrow and W. Muttmann (*Zeit. fur Anorg. Chemie*).—This memoir will be inserted *in extenso.*

Detection of Formaldehyd.— G. Romijn (*Nederland Tijdschrift voor Pharm. Chem. en Toxicologie*). — The author is of opinion that formaldehyd may best be recognised by conversion into hexamethylamin by means of ammonia. At ordinary temperatures this transformation is effected in eighteen to twenty hours. At higher temperatures the conversion is very rapid. The addition of formaldehyd to ammoniacal liquids as a disinfectant is therefore of little value. Romijn gives a number of reactions for the identification of hexamethylamin.

Determination of Nitrogen in presence of Nitrates. — H. C. Sherman. — From the *Journal of the American Chemical Society.*

Execution of the Gravimetric Determination of reducing Sugar by means of Fehling's Solution.— Abstracts are here given of recent papers by Nihoul, Grünhut, Killing, Prager, Farnsteiner, and Hefelmann.

Occurrence and Determination of Copper in Organic Substances, especially in Foods.—From the *Archiv fur Hygiene*, *Chemiker Zeitung*, and *Kaiserlich Gesundheits amte.*

Normal Constituents of Beerwort which may be supposed to be Abnormal. — J. Brand (*Zeit. fur Brauwesen* and *Dingler's Polyt. Journal*, also *Berichte*, xxvii., 3115). — Of these substances the principal is maltol, $C_6H_6O_3$. It is probably a methyl-pyromeconic acid.

Examination of Mace.—E. Spaeth.—The fat of genuine mace is yellowish brown, while that of Bombay mace is light yellow.

Volumetric Determination of Lead. — A. C. Beebe. From the Chemical News.

Determination of Dry Matter in Peat.—H. Puchnor (*Lonw. Versuchstationen*).—Not suitable for abridgment.

Behaviour of Stannous Chloride with Essential Oils.—E. Hirschsohn.—The author has previously observed that the ethereal oil obtained from Gurgun balsam by means of watery vapour, if boiled with stannous chloride, gives a red colour passing into violet and blue. He proposes examining a series of ethereal oils by this reaction.—(*Pharm. Zeitung Russland*).

Alkaloidal Stearates and their Therapeutic Application. — F. Zonandi. — The author has examined the preparation and properties of the morphin, atropin, and cocain stearates.

Action of Morphine and of Acetanilide upon Mixtures of Ferric Salts and Potassium Ferricyanide.— E. Schaer (*Archiv der Pharmacie*).—This paper is more of theoretical than analytical importance.

Detection and Determination of Sodium Salicylate in presence of Ichthyol (*Journ. de Pharmacie*).— Vissen dries the mixture with fine sand on the water-bath, and extracts in the Soxhlet apparatus with anhydrous ether.

Testing the Purity of Apiol.—G. Francois (*Journal de Pharmacie* and *Pharm. Central-Halle*).

Atomic Weight of Tungsten.—R. Schneider. — The mean from all the author's experiments is 184·01.

Atomic Weight of Helium. — M. A. Langlet (*Zeit. Anorg. Chemie*).—The mol. of helium, like that of argon, contains only one atom, and its atomic weight must be taken as = 4.

MISCELLANEOUS.

Harben Gold Medal.—At a meeting of the Harben Nomination Committee held last month in connection with the British Institute of Public Health, Professor Max von Pettenkofer, Scientific Director of Liebig's Extract of Meat Company, was nominated Harben Gold Medallist for 1897. The medal was founded in 1895 by Henry Harben, Esq., J.P., for the recognition of eminent service to the public health, and one presentation is made every year.

Institute of Chemistry.—January Examinations, 1897 —Candidates who passed the practical examination for the Associateship :—Walter Harry Barlow, Finsbury Technical College; Charles Beavis, Ph.D. (Würzburg), Universities of Bonn and Würzburg, and with Dr. Quirin Wirtz, F.I.C. (for Fellowship); Cecil Joslin Brooks, King's College, London; Ernest Mostyn Hawkins, Finsbury Technical College, London; Charles J. S. Makin, Royal College of Science, London, and the Fresenius Laboratory, Wiesbaden; William Moore, Laboratories of the Pharmaceutical Society, University College, London, and with Professor John Attfield, F.R.S., F.I.C.; Sigmund Salomon G. Rosenblum, University of Warsaw, Fresenius Laboratory, Wiesbaden, and with Dr. Samuel Rideal, F.I.C. *Intermediate Examination.*—Reginald Arthur Berry, Cambridge University; John Alfred Foster, under the late Dr. A. Norman Tate, F.I.C, Professor V. B. Lewes, F.I.C.; Robert Dexter Littlefield, University College, London, and also with Dr. John Muter, F.I.C., and Mr. W. A. H. Naylor, F.I.C. *Final Examination for the Associateship* (In Branch A., Mineral Analysis).—Frank Collingridge, B.Sc., (Lond.), University College, London (passed "Intermediate." July, 1896); William Ranson Cooper, M.A., B.Sc., (R.U.I.), Royal University of Ireland, and King's College, London; John Allsopp Walker, B.A. (Oxon.), Oxford University. (In Branch E., Analysis of Water, Food, and Drugs).—Raymond St. George Ross, Owens College, Manchester, and Dresden Polytechnic (for Fellowship). Examiners: Professor Percy F. Frankland, F.R.S., F.I.C., and Otto Hehner, Esq., F.I.C.

City and Guilds of London Institute for the Advancement of Technical Education.—The following is the Scheme for the Leathersellers' Company's Research Fellowships in Chemistry, founded 2nd December, 1896, during the Mastership of Dr. W. H. Perkin, F.R.S. :—

I.—*Number and Amount of Fellowships.*

1. The Grant of £150 a year offered by the Leathersellers' Company shall be applied in founding one or more Fellowships, entitled "Leathersellers Company's Research Fellowships," for the encouragement of Higher Research in Chemistry in its relation to Manufactures.

2. The amount of the grant attached to each Fellowship shall be determined by the Executive Committee of the Institute, regard being had as far as practicable to the nature of the Research, the time required to complete it, and the merits of the candidate; subject in all things to the approval of the Company.

II.—*Conditions of Eligibility.*

1. Applications for Fellowships shall be made in writing, addressed to the Honorary Secretary of the Institute, at the Head Office, Gresham College, E.C., and shall state the name of the proposed research and the qualifications of the candidate.

2. The Fellowships shall be open to natural born British subjects, who are—

a. Students of the Institute who have completed a full three years' course of instruction in the Chemical Department of the Central Technical College, or

b. Candidates duly qualified in the methods of Chemical Research in its relation to manufactures, without restriction as to age or place of previous study, but preferably to class (*a*).

III.—*Award.*

1. The Fellowships shall be awarded by the Executive Committee with the consent of the Company in accordance with this Scheme, or with such modifications as the Company may from time to time approve.

2. The Executive Committee shall appoint a special Committee to receive applications, and select candidates, and to report thereon, and upon the progress of researches; and such Committee shall include the representative or representatives for the time being of the Company on the Executive Committee.

3. The Executive Committee shall report to the Company the award of each Fellowship, and at the close of each session shall report the results or progress of the Research or Researches undertaken during the session.

IV.—*Tenure.*

1. Every Fellowship shall be tenable for part of a year or for one year, and may be renewed for a second or third year, but in no case shall be held for a further period.

2. Holders of Fellowships shall devote their whole time to the prosecution of research, unless otherwise sanctioned by the Executive Committee, and shall report as required on their work.

3. The Researches shall be carried out at the Central Technical College, and the holders of Fellowships shall be subject to the regulations of the College and the supervision of the Board of Studies.

4. The Company reserve to themselves the right at any time to modify this Scheme, or to withdraw all or any of the Fellowships.

F. A. Abel, Chairman of the Executive Committee.
John Watney, Honorary Secretary.

MEETINGS FOR THE WEEK.

Monday, 8th.—Society of Arts, 8. (Cantor Lectures). "Material and Design in Pottery," by Wm. Burton, F.C.S.

Tuesday, 9th.—Royal Institution, 3. "Animal Electricity," by Prof. A. D. Waller, F.R.S.
—— Society of Arts, 8. "Lithography as a Mode of Artistic Expression," by George McCulloch.

Wednesday, 10th.—Society of Arts, 8. "The Chemistry of Tea," by David Crole.

Thursday, 11th.—Royal Institution, 3. "The Problems of Arctic Geology," by J. W. Gregory, D.Sc., F.R.S.
—— Society of Arts, 4.30 (at Imperial Institute). "The Progress of Science Teaching in India," by Prof. J. C. Bose.
—— Society of Arts, 8. "The Mechanical Production of Cold," by Prof. James A. Ewing, M.A., F.R.S.

Friday, 12th.—Royal Institution, 9. "Recent Advances in Seismology," by Professor John Milne, F.R.S., F.G.S.

Saturday, 13th.—Royal Institution, 9. "The Growth of the Mediterranean Route to the East," by Walter Frewen Lord.

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PATENTS, DESIGNS, AND TRADE MARKS ACTS, 1883 TO 1888.

NOTICE IS HEREBY GIVEN, that HENRY ROBERT ANGEL, of 7, St. Helen's Place, London, E.C., has applied for leave to amend the Specification filed in pursuance of the Application for Letters Patent, No. 335, of 1896, for "Improvements in the Manufacture of Caustic Soda, Carbonate of Soda, and Sulphide of Sodium."

Particulars of the proposed amendments were set forth in the Illustrated Official Journal (Patents), issued on the 27th January, 1897.

Any person, or persons, may give notice of opposition to the amendment (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date of the said Journal.

(Signed) H. READER LACK,
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THE CHEMICAL NEWS.

Vol. LXXV., No. 1942.

NOTE ON THE LIMIT OF ACCURACY ATTAINABLE IN COLORIMETRY.

By CHARLES W. FOLKARD.

As the result of a large number of experiments in 1893 and 1896, the author has come to the conclusion that analytical processes depending on the exact imitation of the colour of a solution of unknown strength by another solution containing a known amount of the substance (as in Nesslerising, &c.), are capable of affording results of far greater accuracy than has been generally supposed.

By taking proper precautions it is possible to work colorimetrically to within one-fortieth or one-fiftieth (say, 2 per cent), and by averages to within 1 per cent of the quantity of substance present (*e.g.*, copper in ammoniacal solution).

This was at first so startling that publication was deferred, but further experience has afforded ample confirmation as regards azure blue, yellow, and red solutions, and the object of this note is to ascertain if other observers (more particularly works' chemists) have been led to a similar conclusion in the course of their daily practice.

Ealing, February 5, 1897.

THE EFFICIENCY OF THE HERMITE BLEACHING SOLUTION.

By CLAYTON BEADLE.

As far as I am aware there are no published results of experiments upon the bleaching efficiency of the Hermite bleaching solution in comparison with that of a solution of bleaching-powder upon the bleaching of cotton and linen fibre. All the published results—viz., those of Messrs. Cross and Bevan, and Professor Pictet—are, I believe, upon the bleaching of wood pulp.

I made a series of experiments to determine whether the Hermite solution still gave the same efficiency when used for bleaching cotton and linen rags and rag half-stuff. For this purpose a small beater was used, similar in construction to the paper-maker's hollander. I took half-stuff produced from second quality linen rags and from second quality cotton rags. Before doing experiments in the small beater, I mixed a known weight of each of the half-stuffs with a carefully ascertained volume of Hermite solution, also with bleaching-powder solution, the chlorine strength of each having been carefully ascertained.

The time required to bleach the materials to a full white was noted, and when the bleaching was complete the available chlorine in the residual liquors was determined, and the amount of chlorine consumed by the fibre calculated. The following are the results:—

	Put in.					Consumed.		
	Half-stuff.	Dry weight. Grms.	Liquor.	Strength per litre. Grms.	Per cent on fibre.	Chlorine. Grms.	Chlorine. P.c. on fibre.	Time of bleaching.
1.	Linen ..	162·6	Hermite ..	2·8	17·2	2·44	1·5	30 mins.
2.	,, ..	162·6	Bleaching pd.	3·16	19·4	3·72	2·29	4 hrs.
3.	Cotton ..	176·2	Hermite ..	2·8	15·9	4·0	2·27	2 hrs.
4.	,, ..	176·2	Bleaching pd.	3·16	18·0	6·49	3·68	10 hrs.

The efficiency of chlorine in the Hermite liquid as compared with that of chlorine in ordinary bleaching-powder is claimed by the inventors to be as 5 is to 3. This has been substantiated by the results of Messrs. Cross and Bevan, and Professor Pictet.

3 : 5 :: 1 : 1·66.

Comparing this with the experiments above,—

	Hermite.		Bleaching powder.				
1 and 2.	1·5	:	2·35	::	1	:	1·54
3 and 4.	2·27	:	3·68	::	1	:	1·65

These results therefore confirm fairly closely those of other observers. The next two experiments were done with a view of finding how long the Hermite solution took to exhaust itself if the chlorine put in was the exact amount necessary, according to the above experiments, to do the bleaching. The rate of bleaching was much slower than if the chlorine had been used greatly in excess. After three days, however, the liquid only contained the least possible trace of chlorine, and the fibre appeared to be perfectly bleached.

The preceding experiments were all done with "still" liquor. In the following experiments the half-stuff was put into the small beater, and the Hermite liquor allowed to flow round the beater, and washed out again by means of a washing drum, from whence it was delivered to a store tank and then again to the beater. The total amount of liquor was first of all measured both into the beaker and into the store tank, from which a sample was taken and tested for chlorine. This experiment was not done under the most favourable circumstances, as the liquor was drawn from the store tank and not from the electrolysing tank whilst the electrolysis was going on, which I think would have made a considerable difference to the results.

	Put in.			
Half-stuff.	Weight dry fibre. Grms.	Volume of liquid.	Strength per litre. Grms.	Per cent on fibre.
Linen	542	56·12	2·64	27·3
Cotton	470	56·12	2·64	31·5

Consumed.		
Weight of chlorine.	Per cent on fibre.	Time.
5·6	1·03	40 mins.
5·6	1·20	60 ,,

It is evident that the circulating liquor is more economical than the non-circulating.

Half-stuff.	Non-circulating chlorine consumed.	Circulating chlorine consumed.	Saving by circulating over non-circulating.
Linen ..	1·5	1·03	30 p.c.
Cotton ..	2·27	1·20	47 ,,

My results confirm those of other observers as regards the rapidity of bleaching by the Hermite solution, which I found to bleach very rapidly, doing as much work in thirty minutes as bleaching-powder solution of the same strength would do in three hours. I also found that Hermite solution will bleach in one treatment, when any amount of bleaching-powder will fail to do so without an intermediate acid treatment. It can be used either circulating or stored in tanks for use like ordinary bleaching-powder, but the latter, as we have seen, does not give such good results.

Laboratory, West Street, Erith,
January 23, 1897.

VISCOSE AND VISCOID.*

By CLAYTON BEADLE.

In August, 1894 (*Journal of the Franklin Institute*, cxxxviii., No. 824), I had the honour of reading a paper before the Franklin Institute upon some new cellulose derivatives which had been discovered and partly worked out by my colleagues, Messrs. C. F. Cross and E. J. Bevan, and myself. Mr. Arthur D. Little, of Boston, took up the subject on this side of the water, and the samples which we showed you at that time were produced by him. Since then we have added considerably to our knowledge of these derivatives. The basis of these products is a substance to which we have given the name "Viscose." Viscose is chemically cellulose xanthate, the preparation and constitution of which is fully explained and set forth in my previous paper (*vide ut supra*).

The dry regenerated cellulose obtained from the viscose solution we have named "Viscoid."

It is impossible, in a paper of this length, to give a history of all the work ws have done in the last two years in connection with viscose; so I have chosen to confine myself to certain branches of the work, the description of which, I trust, will prove interesting to the members of the Institute.

Manufacture of Alkali Cellulose.

In the manufacture of viscose on a large scale, we first endeavoured to discover what materials could be utilised, and in the course of our work we found that any kind of cellulose could be used, provided that it was fairly pure. The fibres, however, should be very short indeed; the process depends as much upon the length of the fibre as upon the purity of the cellulose. As an instance of this, if raw cotton be used without any disintegration it is almost impossible to mercerise it and convert it into viscose; but if the fibre be disintegrated so as to break up the ultimate fibre into pieces of about one-twentieth of the length of the original, the mercerisation and conversion into viscose is rapid and complete. With regard to the purity of the fibre, bleached wood generally yields a better viscose than unbleached wood, but it is next to impossible to convert mechanical wood (*i. e.*, wood disintegrated by mechanical means, and containing a large amount of resin and other impurities) into viscose. The alkali cellulose often requires to be kept for several days before treatment with carbon bisulphide; but when the disintegration of the fibre is thorough, and the mixture with caustic properly effected, the maturing of the alkali cellulose is almost unnecessary.

One great precaution, which at first we lost sight of, was to prepare the alkali cellulose without contact with the atmosphere.

This we discovered by analysing a number of samples. We found that on an average about 50 per cent of the alkali had been carbonated during mercerisation, and thus rendered useless for the reaction. Alkali cellulose is converted by the action of the CO_2 of the atmosphere into sodium carbonate and cellulose without our knowing it. This change was the cause of a large number of failures, which necessitated conducting a series of trials under varying conditions, in which we determined the amount of alkali carbonated.

At last we arrived at a method of producing the alkali cellulose by which only 5 per cent to 10 per cent of the total soda is converted into carbonate.

Yield of Viscoid.

A great deal of work has been done upon the amount of viscoid yielded by different celluloses. Pure cotton yields somewhat more than its own weight. This is due to a change in the cellulose molecule (*vide* Beadle, *Journ. of the Franklin Inst.*, cxxxviii., No. 824). Wood, on the other hand, even when thoroughly bleached and pure, undergoes a considerable loss, which amounts often to 20 per cent. This is due to the formation of soluble products during mercerisation.

We have followed this very carefully, and it appears that bleached wood pulp contains oxycellulose, which is largely dissolved by caustic soda. Under certain conditions the regenerated cellulose has no strength, as when films made from viscose solution are found to be rotten. Very great care has to be taken in the manufacture of viscose to insure that the regenerated cellulose is not injured by the treatment. A knowledge of this can be acquired only by experience, and those who are thoroughly acquainted with the manufacture of viscose can often tell at a glance, from the appearance of the alkali cellulose or the viscose solution, whether a satisfactory product will be obtained. These conditions are now well understood by us, so that we can insure that the cellulose is always regenerated in the proper physical condition required for the particular purpose to which it is to be applied.

Production of Veneers.

Mention was made in my previous paper (*Journal of the Franklin Institute*, vol. cxxxviii., No. 824) of cutting pieces from the coagulum and annealing them under pressure for the production of sheets. This has been worked at on a larger scale. The viscose has been run into rectangular moulds, and the coagulation of the mass has been effected by exposure to a hot damp atmosphere. These masses, weighing from 250 to 400 pounds, have been dehydrated by exposing them to an atmosphere which is gradually raised in temperature. When the blocks have been sufficiently hardened, they are cut into sheets about 24 × 18 inches, by a guillotine specially constructed for the purpose. By an automatic gear the bed on which the guillotine rested was made to travel forward at every stroke of the knife, and the amount of travel could be regulated at will, so that sheets of any thickness could be cut. By this means we were able to cut about twenty sheets per minute.

The sheets were deprived of the chemical by-products, and then submitted to heavy pressure, by means of which the cellulose hydrate was dehydrated down to a compact sheet of cellulose. We had a difficulty by this method in obtaining our dehydrated sheets free from structure. They had a tendency to split in laminæ. The fracture had every appearance of slaty cleavage (Chemical News, vol. lxx., p. 139), and the planes of cleavage were found always to be at right-angles to the direction in which the pressure was applied. With thin sheets we had less trouble, and I believe the reason of this was that the sheet was thinner than the laminæ. In order to avoid this difficulty with thicker sheets, we were obliged to dehydrate the coagulum to a greater extent, by exposure to a hot atmosphere of steam before applying the pressure. The fact of pressure on the coagulum giving rise to slaty cleavage, prevented us from applying pressure for moulding solid articles from the coagulum. This is obvious when we take into consideration the fact that the dehydrated laminæ formed on the outer surfaces by the first application of pressure, prevents the egress of moisture from the interior, and, as it were, seals the interior from further dehydration. We found it next to impossible to mould articles of any thickness under pressure from the coagulum for this reason, even on the application of a pressure of several tons to the square inch. When, however, the sheets are almost dried by exposure to warm air, or by one of the processes described subsequently for the production of solids, they can be embossed and

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* *Journal of the Franklin Institute*, January, 1897.

stamped into small articles, such as buttons, which are sufficiently structureless for all practical purposes.

When the sheets are completely dried they offer too great a resistance for moulding under pressure. Viscoid sheets can be produced by the above process in almost any colour, either translucent or opaque, and they can be prepared in such a way that they are either soft and pliable, or stiff and horny like celluloid. Under pressure they can be embossed in various patterns.

(To be continued).

THIRD ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS.

RESULTS PUBLISHED DURING 1895.*

By F. W. CLARKE.

TO THE MEMBERS OF THE AMERICAN CHEMICAL SOCIETY.

YOUR committee upon atomic weights respectfully submits the following report, summarising the work done in this branch of chemistry during 1895—a year which may be well called eventful in the history of the science. Two new elements, argon and helium, have been made known to the world, and from the most unexpected sources; the collective works of Stas have been published by the Belgian Academy, as a monument to his memory; Prof. Morley's great research upon oxygen is at last finished; and a goodly number of other important determinations have appeared. Incidentally, but pertinently, I may also call attention to the Marignac memorial lecture by Clève (*Journ. Chem. Soc.*, June, 1895), in which the atomic weight researches of the former chemist are well outlined; and to the extraordinary number of papers upon the periodic law, which have been called out by the discovery of argon and helium. These papers fall outside the scope of this report, and they are numerous enough to almost warrant a bibliography of their own.

The H : O *Ratio.*—Prof. Morley's work upon this fundamental constant has been published in full by the Smithsonian Institute,† and divides itself naturally into four parts:—First, the density of oxygen; second, that of hydrogen; third, the volumetric composition of water; and fourth, its gravimetric synthesis.

For the density of oxygen, or rather the weight of 1 litre at 0°, 760 m.m.. at sea-level, and in latitude 45°, three sets of measurements are given, with the following mean values in grms.:—

Series 1	1·42879 ± 0·000034
,, 2	1·42887 ± 0·000048
,, 3	1·42917 ± 0·000048

As the third series, on experimental grounds, is regarded by Morley as the best, he assigns it double weight, and on this basis the general mean of all three becomes—

1·42900 ± 0·000034.

For the weight of a litre of hydrogen under similar standard conditions, five series of determinations are given, as follows:—

Series 1	0·089938
,, 2	0·089970
,, 3	0·089886 ± 0·0000049
,, 4	0·089880 ± 0·0000088
,, 5	0·089866 ± 0·0000034

The hydrogen of the first and second series was probably contaminated by traces of mercurial vapour, and these results are therefore rejected by Morley. For the third, fourth, and fifth series the electrolytic gas was occluded in palladium and transferred to the measuring globes without the intervention of stopcocks; thus avoiding contact with mercury and leakages of external air. Their general mean is—

0·089873 ± 0·0000027.

Dividing the weight found for oxygen by this value for hydrogen the ratio becomes—

15·9002.

For the volumetric ratio O : 2H, Morley finds the value 1 : 2·00269. Applying this as a correction to the density ratio, we have for the atomic weight of oxygen—

O = 15·879.

In his synthesis of water Morley differs from all of his predecessors in that he weighed both constituents separately, and also the water formed. In other words, his syntheses are complete, and take nothing for granted. The weights in grms. are as follows:—

	O used.	H used.	Water found.
1	25·9176	3·2645	29·1788
2	25·8531	3·2559	29·1052
3	30·3210	3·8193	34·1389
4	30·5294	3·8450	Lost
5	30·4700	3·8382	34·3151
6	30·5818	3·8523	34·4327
7	30·4013	3·8297	34·2284
8	30·3966	3·8286	34·2261
9	30·3497	3·8225	34·1742
10	30·3479	3·8220	34·1743
11	29·8865	3·7637	33·6540
12	30·3429	3·8211	34·1559

From these data two sets of values for the atomic weight of oxygen are derivable; one from the ratio H : O, the other from the ratio H : H_2O. These sets are subjoined.

	H : O.	H : H_2O.
1	15·878	15·877
2	15·881	15·878
3	15·878	15·873
4	15·880	—
5	15·877	15·881
6	15·877	15·876
7	15·877	15·875
8	15·878	15·879
9	15·879	15·881
10	15·881	15·883
11	15·881	15·883
12	15·882	15·878
Mean.. ..	15·8792	15·8785

From the density work the value found was 15·879, and the mean of this with the two synthetic results is—

O = 15·8789.

Hence, for all practical purposes, the atomic weight of oxygen may be put at 15·88, with an uncertainty of less than one unit in the second decimal.

It is impracticable, in a report of this kind, to go into the details of so elaborate an investigation as this of Morley's, and a bare statement of results must suffice. The research, however, is one of the most perfect of its kind, every source of error having been considered and guarded against, and it will doubtless take its place in chemical literature as a classic. Independently of its main purpose, the book is almost a manual on the art of weighing and measuring gases, and no experimenter who engages upon work of that kind can afford to overlook it.

More recently still, a new determination of the atomic weight of oxygen has been published by Julius Thomsen (*Ztschr. Anorg. Chem.*, xi., 14), whose method is quite novel. First, aluminum, in weighed quantities, was dis-

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* Read at the Cleveland Meeting, December 31, 1895. From the *Journal of the American Chemical Society*, xviii., No. 3.

† "On the Density of Oxygen and Hydrogen, and on the Ratio of their Atomic Weights." By Edward W. Morley. Smithsonian Contributions to Knowledge, 1895. 4to. xi. + 117 pages. 40 cuts. Abstract in *Am. Chem. Journ.*, xvii., 267 (gravimetric); and *Ztschr. Phys. Chem.*, xvii., 87 (gaseous densities); also note in *Am. Chem. Journ.*, xvii., 396.

solved in caustic potash solution. In one set of experiments the apparatus was so constructed that the hydrogen evolved was dried and then expelled. The loss of weight of the apparatus gave the weight of the hydrogen so liberated. In the second set of experiments the hydrogen passed into a combustion chamber in which it was burned with oxygen, the water being retained. The increase in weight of this apparatus gave the weight of oxygen so taken up. The two series, reduced to the standard of a unit weight of aluminum, gave the ratio between oxygen and hydrogen.

The results of the two series, reduced to a vacuum and stated as ratios, are as follows:—

First, $\frac{\text{Weight of H}}{\text{Weight of Al}}$. Second, $\frac{\text{Weight of O}}{\text{Weight of Al}}$.

First.	Second.
0·11180	0·88788
0·11175	0·88799
0·11194	0·88774
0·11205	0·88779
0·11189	0·88785
0·11200	0·88789
0·11194	0·88798
0·11175	0·88787
0·11190	0·88773
0·11182	0·88798
0·11204	0·88785
0·11202	
0·11204	0·88787 ± 0·000018
0·11179	
0·11178	
0·11202	
0·11188	
0·11186	
0·11185	
0·11190	
0·11187	
0·11190 ± 0·000015	

Dividing the mean of the second column by the mean of the first, we have for the equivalent of oxygen:—

$$\frac{0·88787 \pm 0·000018}{0·11190 \pm 0·000015} = 7·9345 \pm 0·0011.$$

Hence,—

$$O = 15·8690 \pm 0·0022.$$

The details of the investigation are somewhat complicated, and involve various corrections which need not be considered here. The result as stated includes all corrections and is evidently good. The ratios, however, cannot be reversed and used for measuring the atomic weight of aluminum, because the metal employed was not absolutely pure.

The Stas Memorial.—As a monument to the memory of the late Jean Servais Stas, more appropriate than statue or column of stone, the Belgian Academy has published his collected works in three superb quarto volumes.* All of his great investigations are here gathered together, and in the third volume, entitled "Oeuvres Posthumes," some hitherto unpublished data are given for the important ratio between potassium chloride and silver. These data are represented by two series: one made with a uniform sample of silver, and chloride from various sources; the other with constant chloride, but with silver of diverse origin; the aim being to establish experimentally the fixed character of each substance. The first series is complete; of the second series only one experiment was found recorded among Stas's papers.

The quantity of potassium chloride equivalent to 100 parts of silver was found to be as follows:—

69·1227
69·1236
69·1234
69·1244
69·1235
69·1228
69·1222
69·1211
69·1219
69·1249
69·1238
69·1225
69·1211

Mean of first series	69·1229
Second series . ..	69·1240

These results give an effective confirmation to Stas's determinations of 1882.

(To be continued).

METAL SEPARATIONS BY MEANS OF HYDROCHLORIC ACID GAS.*

By J. BIRD MOYER.

(Concluded from p. 65).

XV.—*Separation of Arsenic from Zinc.*

In some preliminary work zinc oxide was treated with acid gas at 200°. It completely changed to chloride, and was not volatile. Pure zinc sulphate was used to precipitate the arsenate; it was washed, dried, and ignited to 150°. The same difficulty appeared as was encountered under iron. Zinc arsenate melts down to a liquid mass as soon as the acid gas strikes it, which is extremely hard to evaporate without spattering. A small glass cover was placed over the boat, which tended to lessen the spattering, but did not entirely prevent it.

The zinc was estimated by taking the chloride up in a little hydrochloric acid and running it down with pure mercuric oxide. It was then ignited and weighed as zinc oxide. One good result was obtained, but generally the residues of zinc contained arsenic and the results were far from being concordant.

XVI.—*The Separation of Arsenic from Cobalt and Nickel.*

Cobalt and nickel were precipitated as arsenates in the usual manner, with a solution of pyroarsenate.

Cobalt nitrate, a Merck preparation, was carefully purified; considerable manganese was found and eliminated. This gave the pink salt $Co_3As_2O_8+8H_2O$, which was ignited to the blue anhydrous compound.

Cobalt arsenate is very readily attacked by the acid gas in the cold, yielding a pink chloride. A slight heat, not much above 120°, changed it to the blue chloride and drove out the arsenic. At first it was quickly weighed as chloride, then it was taken up in a little hydrochloric acid and evaporated down with mercuric oxide. On ignition, black Co_3O_4 was obtained and weighed.

The arsenic was eliminated as usual.

	Experiment I. Grm.	Experiment II. Grm.
$Co_3As_2O_8$ taken	0·1509	0·2029
$CoCl_2$ obtained	0·1309	—
$CoCl_2$ required	0·1293	—
Co_3O_4 obtained	0·0738	0·0969
Co_3O_4 required	0·0731	0·0983
Difference	+0·0007	−0·0014
As_2O_5 obtained	0·0770	—
As_2O_5 required	0·0764	—
Difference	+0·0006	—

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* "Jean Servais Stas. Oeuvres Complétes.' Edited by W. Spring. Bruxelles, 1894.

* From author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Ph.D., 1896. From the *Journ. Amer. Chem. Soc.*, xviii., December, 1896.

On testing the cobalt residue by the Marsh test, no trace of arsenic was found. No cobalt was found in the sublimate. Some of the first experiments gave cobalt too low; it was thought that they had been heated too high, but testing showed no volatilised cobalt.

A temperature of 125° is sufficient to drive out all of the arsenic, and at this temperature there is no danger of volatilising the cobalt.

In working with nickel, the green arsenate was simply dried in the first experiment. It therefore had the composition $Ni_3As_2O_8+8H_2O$.

Hydrochloric acid gas attacked it in the cold. A slight heat drives out the arsenic and moisture and leaves a salmon-coloured chloride. The nickel chloride was changed to oxide by evaporating it with nitric acid and igniting.

	Experiment I. Grm.
$Ni_3As_2O_8+8H_2O$ taken	0·1502
NiO obtained..	0·0554
NiO required..	0·0561
Difference	−0·0007

In Experiments II. and III. the salt was made anhydrous by ignition.

	Experiment II. Grm.	Experiment III. Grm.
$Ni_3As_2O_8$ taken	0·1166	0·1040
NiO obtained..	0·0577	0·0523
NiO required	0·0575	0·0513
Difference	+0·0002	+0·0010
As_2O_5 obtained	—	0·0515
As_2O_5 required	—	0·0526
Difference	—	−0·0011

The Marsh test showed no arsenic with the nickel.

XVII.—*Behaviour of Minerals in Hydrochloric Acid Gas.*

Niccolite.—One half grm. of the mineral was finely powdered and subjected to the action of acid gas for a day, at a temperature of 200° C. It was only very slightly affected.

A second portion was dissolved in nitric acid and evaporated down in a porcelain dish. It was then transferred to a boat and evaporated to dryness. To remove all the acid it was heated in an oven to 110° for half an hour. The dry substance was acted upon by the acid gas in the cold for five hours. It changed completely to chloride. A temperature of 150° for an hour removed all the moisture and arsenic.

The nickel chloride was evaporated down with nitric acid, ignited, and weighed as NiO. The arsenic was estimated as usual.

	Per cent.
Nickel found	43·79
Nickel calculated	43·60
Difference	0·19
Arsenic found	56·66
Arsenic calculated	56·40
Difference	0·26

Undoubtedly there is still a wide field open in regard to the behaviour of hydrochloric acid gas upon mineral species. Smith and Hibbs (*loc. cit.*) showed that mimetite lost its arsenic quantitatively, when heated in a stream of acid gas. In this laboratory others are being investigated with favourable indications. The direct employment of hydrochloric acid gas upon a powdered mineral would simplify many a tedious gravimetric process, leaving the separated elements in a desirable condition for further treatment.

In the case of a mineral such as niccolite, where it must first be decomposed with nitric acid and then transferred to a boat, the advantage is not so great, This, however, can be modified, so that the time factor is reduced and the advantage of the method still retained. Instead of using a boat, which has no advantage unless the non-volatile chlorides are to be weighed directly, a hard glass bulb can be substituted. The mineral is placed in the bulb, dissolved in nitric acid, and evaporated down by the aid of a current of air drawn through the bulb.

The residual oxides are then separated in a stream of hydrochloric acid gas as usual.

THE DETERMINATION OF ATOMIC MASSES OF SILVER, MERCURY, AND CADMIUM, BY THE ELECTROLYTIC METHOD.*

By WILLETT LEPLEY HARDIN.

(Continued from p. 63).

PART II. (*continued*).

THIRD SERIES.

Experiments on Mercuric Cyanide.

A SERIES of observations was made on several organic salts of mercury with a view of selecting a compound suitable for atomic mass determinations. Mercuric acetate and other similar salts were found to be unstable in the air and unsuited for accurate analyses. Mercuric cyanide, on the other hand, was found to be perfectly stable and to form well-defined crystals.

Preparation of Hydrocyanic Acid.

Five hundred grms. of potassium ferrocyanide were placed in a two litre retort connected with a condenser. A cooled mixture of 300 grms. of pure sulphuric acid and 700 c.c. of distilled water was then poured into the retort, and the mixture carefully heated until the hydrocyanic acid was distilled over into the receiver. The product obtained was re-distilled and used immediately in the preparation of mercuric cyanide.

Preparation of Mercuric Cyanide.

Fifty grms. of mercuric oxide, prepared as already described in the experiments on mercuric oxide, were dissolved in pure warm hydrocyanic acid. The solution was then filtered and evaporated to crystallisation. The transparent crystals of mercuric cyanide which separated were dissolved in pure water and re-crystallised. The product obtained by the second crystallisation was quickly rinsed with cold water and dried for six hours in an air bath at a temperature of 50°. The crystals were then ground to a finely divided powder in an agate mortar and re-dried for twenty-four hours in an air bath at a temperature of 55°. The dry white powder was then placed in a weighing tube and kept in a desiccator.

Mode of Procedure.

The mode of procedure with mercuric cyanide was somewhat different from that of the preceding experiments, in that no potassium cyanide was used in preparing the solution for electrolysis. A weighed portion of the material was dissolved in pure water in a platinum dish. When the crystals had completely dissolved, the dish was filled to within a quarter of an inch of the top with water, after which one drop of pure sulphuric acid was added. The solution was then electrolysed, and the resulting metal weighed. The strength of the current and the time of action were the same as for mercuric chloride. In the last four experiments, where rather large quantities of mercury were deposited, the strong current was allowed to act from two to six hours longer.

The results of ten experiments on mercuric cyanide, reduced to a vacuum standard on the basis of—

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* Contribution from the John Harrison Laboratory of Chemistry No. 13. From the author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Ph.D.—From the *Journal of the American Chemical Society*, xviii., p. 990.

4·0 = density of mercuric cyanide,
13·59 = ,, metallic mercury,
21·4 = ,, platinum dish,
8·5 = ,, weights,

and computed for the formula $Hg(CN)_2$, assuming 12·01 and 14·04 to be the atomic masses of carbon and nitrogen, respectively, are as follows:—

	Weight of $Hg(CN)_2$. Grms.	Weight of Hg. Grm.	Atomic mass of mercury.
1	0·55776	0·44252	200·063
2	0·63290	0·50215	200·092
3	0·70652	0·56053	200·038
4	0·80241	0·63663	200·075
5	0·65706	0·52130	200·057
6	0·81678	0·64805	200·103
7	1·07628	0·85392	200·077
8	1·22615	0·97282	200·071
9	1·66225	1·31880	200·057
10	2·11170	1·67541	200·077

Mean .. .. = 200·071
Maximum .. = 200·103
Minimum .. = 200·038

Difference .. = 0·065
Probable error = 0·005

From the total quantity of material used and metal obtained the atomic mass of mercury is 200·070.

FOURTH SERIES.

According to Faraday's law the quantities of different metals deposited from their solutions by the same current are proportional to their equivalent weights. In this series of experiments an attempt was made to determine the ratio of the atomic mass of mercury to that of silver by passing the same current through the solutions of the two metals and weighing the two resulting deposits. If the proper conditions could be obtained, this would certainly be the simplest and most direct method for comparing the equivalent weights of different metals. But so many difficulties were met that the method on the whole was not satisfactory.

In the "Revision of the Atomic Weight of Gold" (*Amer. Chem. Journ.*, xii., 182), Mallet made use of this method, and in a series of careful preliminary experiments determined the conditions most favourable to its application. From a number of experiments made by passing the same current through two different solutions of copper sulphate, using pure electrotype copper for both anode and cathode in each solution, Mallet found:—

First.—Other conditions being the same, the difference in the quantities of metal deposited from solutions of unequal concentrations was very slight and somewhat variable, but the tendency was toward a slightly larger quantity from the more concentrated solution.

Second.—With equal quantities of metal in the two solutions, and unequal quantities of free acid, the difference in the results obtained were almost insignificant and somewhat variable in direction, the tendency being toward a slightly larger quantity from the less acid solution.

Third.—Other conditions being the same, a difference in the temperature of the two solutions invariably caused a slightly larger deposit from the cooler solution.

Fourth.—Other conditions being the same, a difference in the size of the copper plates, and hence a difference in the "current density," caused a slightly greater deposit on the smaller plate.

Fifth.—A difference in the distance between the two plates did not produce a constant difference of result, but the tendency was toward a slightly larger deposit on the cathode plate farther separated from its anode.

From the foregoing experiments it is evident that the conditions most favourable to this method are, that the two solutions should be equally concentrated, of the same temperature, and should contain equal amounts of free acid, or when the double cyanides are used, equal quantities of free potassium cyanide. And, moreover, that the two cathodes and also the two anodes should be of the same size, and that the distance between the anode and cathode should be the same in both solutions. These conditions were closely observed throughout this work.

Arrangement of Apparatus.

The deposits in this series of experiments were made in two platinum dishes of equal capacity and equal internal area. The anode in each case consisted of a coil of rather large platinum wire, the two coils being of the same shape and size. The dishes were insulated from each other by means of two glass stands. The platinum coils were completely immersed in the solutions, and the portion of the wire near the surface of the liquid was covered with paraffin to prevent surface contact. The current, after passing through the two solutions, was allowed to pass through a hydrogen voltameter in order that its strength might be observed at any time.

In the second arrangement of apparatus the platinum dishes were made the anodes, and two pieces of platinum foil of the same shape and size were used for the cathodes. The results, however, from this second arrangement were not as satisfactory as from the first.

Mode of Procedure.

A solution of the double cyanide of silver and potassium was placed in one of the platinum dishes, and a solution of the double cyanide of mercury and potassium in the other. The quantities of silver and mercury present in their solutions were approximately proportional to their equivalent weights. Each solution contained a slight excess of potassium cyanide. The dishes were placed in their positions, and the anodes immersed some time before the current was allowed to act. When the temperature of the two solutions was the same as that of the room the connection was made, and the same current allowed to pass through the two solutions. The quantity of metal deposited was never allowed to exceed one-half of the metal present in the solution at first. Before interrupting the current, the solutions were syphoned from the two platinum dishes at the same time with two syphons of the same bore. The deposits were then washed several times with boiling water, carefully dried, and their weights determined. Experiments were made with currents of different strength, and with solutions of various degrees of concentration. The results obtained were far from being satisfactory. The strength of current which seemed best adapted to the work was that which deposited about one-tenth of a grm. of silver per hour.

From a large number of experiments, only seven results were obtained which seem of any value in determining the atomic mass of mercury. And it must be added that many others were rejected, not because they were known to be vitiated in any way, but because the results obtained for the atomic mass of mercury differed from those obtained from other methods. It is possible that, in a large number of experiments the condition would be more favourable in some than in others, but whether the close agreement of the results selected was due to this or to the balancing of errors could not be determined.

Seven results computed on the basis of 107·92 for the atomic mass of silver are as follows. (See next column).

Computing from the total quantities of mercury and silver obtained we have 199·971 for the atomic mass of mercury.

Although the cause of the large variation in the rejected observations could not be definitely determined, several sources of error suggest themselves.

First, small quantities of hydrogen were undoubtedly set free in the process of electrolysis, and unless these quantities were always equal in the two solutions, which is not probable, an error would be introduced.

Second, in some solutions an error might easily be

	Weight of Hg. Grm.	Weight of Ag. Grm.	Atomic mass of mercury.
1	0·06126	0·06610	200·036
2	0·06190	0·06680	200·007
3	0·07814	0·08432	200·021
4	0·10361	0·11181	200·011
5	0·15201	0·16402	200·061
6	0·26806	0·28940	199·924
7	0·82808	0·89388	199·929

Mean .. .. = 199·996
Maximum .. = 200·061
Minimum .. = 199·924

Difference .. = 0·137

introduced by a change in the atomicity of mercury, but in a solution of the double cyanide of mercury and potassium this change is hardiy probable.

Third, the occlusion of hydrogen by the two metallic deposits would also be a possible source of error; but only small errors could be introduced in this way.

To account for the difference of several units in the results, the source of error first mentioned seems by far the most probable.

Summary.

In the discussion of the results obtained in the different series of observations on the compounds of silver, the probable sources of error and likewise the advantages of the method were pointed out. The same discussion applies equally well to the observations on mercury.

It is evident that the first three series of observations on mercury are entitled to more weight than the last series. Just why the results on mercuric bromide should be lower than those on mercuric chloride is not clear. Both compounds are certainly well adapted to atomic mass determinations, inasmuch as they can be purified by both crystallisation and sublimation. The most probable impurity in mercuric bromine would be mercuric chloride, but that would tend to increase rather than lower the results. The series of observations on mercuric cyanide have, perhaps, one advantage over the others, in that no potassium cyanide was used. The results obtained in this series are still higher than those obtained from mercuric chloride, and almost two-tenths of a unit higher than those obtained from mercuric bromide. However, as the same care was exercised in the purification of the material for each of the three series, and as there was no apparent error in either case, equal weight must be given to each of the three series in determining the most probable value of the atomic mass of mercury. And, as the mean of the last series is almost identical with the mean of the first three, equal weight can be given to this series without introducing any error.

Computing the general mean from the separate observations we have :—

	Atomic mass of mercury.
First series	200·006
Second ,, ...	199·883
Third ,, ...	200·071
Fourth ,, ...	199·996

General mean = 199·989

From the total quantities of material used and metal obtained, the general mean is :—

	Atomic mass of mercury.
First series	199·996
Second ,, ...	199·885
Third ,, ...	200·070
Fourth ,, ...	199·971

General mean = 199·981

Combining this with the first general mean we have :—

	Atomic mass of mercury.
First general mean	= 199·989
Second ,, ,, ...	= 199·911

Most probable mean of all the results = 199·985 or 200 for the atomic mass of mercury.

(To be continued).

ALUMINUM ANALYSIS.*

By JAMES OTIS HANDY.

(Concluded from p. 68).

Hydrated Alumina.

HYDRATED alumina is analysed for water, silica, and sodium carbonate.

Water.—Ignite 1 grm. in a closely covered crucible, at first gently and then intensely for fifteen minutes over the strongest blast. The loss on ignition includes water and the carbon dioxide of the sodium carbonate. Calculate the carbon dioxide from the sodium oxide found and deduct it from the loss on ignition.

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

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

Calcined Alumina.

Water and soda are determined as in hydrated alumina.

Silica.—Fuse 1 grm. of the finely ground alumina with 10 grms. of potassium bisulphate. If this does not make a clear fusion add 2 grms. of bisulphate and heat up again. Dissolve the fusion when cool in water and filter. Burn off the insoluble residue. Fuse it with 1 grm. of sodium carbonate and cool in fifteen c.c. of water in a four-and-a-half-inch evaporating dish. Add twenty-five c.c. of 25 per cent sulphuric acid. When all soluble matter has dissolved, remove the crucible and evaporate down until sulphuric acid fumes escape. Cool, dilute with water, boil, filter, ignite, and weigh silica plus crucible, treat with sulphuric and hydrofluoric acids, and weigh again. Loss equals silica.

Analysis of Bauxite.

(Method adopted, May, 1895.)

No unusual apparatus or reagents are required.

One and five-tenths grms. of very finely ground bauxite (previously dried at 100° C. and bottled), is taken for analysis. Weigh into a five-inch porcelain evaporating dish and dissolve in fifty c.c. of acid mixture. This mixture is the same as that used for aluminum analysis. Boil the solution down until fumes escape and keep the residue fuming strongly for about fifteen minutes. Cool, add 100 c.c. of water, stir and then boil for ten minutes. Filter, wash well with water, receiving the filtrate in a beaker of about 300 c.c. capacity. The filtrate and washings

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* From the *Journal of the American Chemical Society*, Sept., 1896.

should amount to about 175 c.c. Burn off the insoluble residue (which consists chiefly of silica, with a little titanic acid, oxide of iron, and alumina) and weigh it in the crucible, add three drops of 25 per cent sulphuric acid and about five c.c. of hydrofluoric acid and evaporate slowly to dryness. Ignite very strongly and weigh. The loss in weight equals silica. Add to the residue in the crucible 1 grm. of potassium bisulphate and fuse quickly and thoroughly over a Bunsen burner, cool and place the crucible in the beaker containing the main sulphuric acid solution. The small residue from this fusion will be silica, and is to be added to the silica already found. Having obtained the sulphate solution containing all the alumina, ferric oxide, and titanic oxide, make it up to 550 c.c. and mix. Then fifty c.c. will equal three-tenths grm. bauxite. Take fifty c.c. and dilute to 300 c.c. Add two c.c. of concentrated hydrochloric acid and ammonia in slight excess, boil for five minutes, let the precipitate settle, filter, and wash very thoroughly with hot water. Test the filtrate for further alumina by boiling. Burn off the filter paper and ignite the precipitate very strongly after crushing all the lumps of alumina. Weigh alumina, ferric oxide, and titanic oxide.

Titanic Acid.—Take 100 c.c. of the original sulphate solution (six-tenths grm.), add ammonia until a slight permanent precipitate is formed, then add sulphuric acid from a pipette or burette until this precipitate just re-dissolves. Finally add 1 c.c. more of 25 per cent. sulphuric acid and dilute to 400 c.c. If the bauxite is high in iron (which will be indicated by the distinct yellow colour of this solution) sulphur dioxide gas must be run into it until it is decolourised and smells strongly of sulphur dioxide, but if the solution is nearly colourless, indicating a low percentage of iron, only sulphur dioxide water need be used for the reduction. Boil well for one hour, adding water saturated with sulphur dioxide occasionally. Filter off the titanic oxide through double filters, and wash well with hot water. If the precipitate is yellow, indicating the presence of iron, it can be fused with 1 grm. of potassium bisulphate, the fusion dissolved in water, and the iron determined in this solution by reducing with zinc and titrating with permangate. This is not often necessary.

Oxide of Iron.—Take 50 c.c. of the sulphate solution, add 10 c.c. of dilute sulphuric acid, and 1 grm. of granulated zinc, and set the beaker in a warm place. When reduced, filter and titrate the iron with standard potassium permanganate. More zinc is used for bauxites high in iron.

Method for Iron Determination, using a larger Quantity of Bauxite. (Applicable to Purest Ores).

Place a half grm. of the finely powdered ore in a large platinum crucible, and add 3 c.c. of 25 per cent. sulphuric acid and 5 c.c. of hydrochloric acid, and evaporate very slowly to fumes; drive off the excess of sulphuric acid by heat, boil out the residue with water, and add 10 c.c. of dilute sulphuric acid. Remove the crucible and reduce with zinc, as above, and titrate.

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

ON THE ACTION OF WAGNER'S REAGENT UPON CAFFEINE, AND A NEW METHOD FOR THE ESTIMATION OF CAFFEINE.*

By M. GOMBERG.

The use of iodine in potassium iodide as a general qualitative reagent for alkaloids dates as far back as 1839 (Bouchardat, *Comp. Rend.*, ix., 475). It was, however, R. Wagner (*Dingl. Poly. Journ.*, clxi., 40; *Ztschr. Anal. Chem.*, i., 102) who first employed it for the quantitative estimation of vegetable bases, and this solution has since been known as Wagner's reagent. He based his conclusion upon trials with solution of quinine and cinchonine, showing that under approximately similar conditions they always require the same amount of iodine for complete precipitation. Hence empirical factors could be established which would enable one to use a standard solution of iodine for the titration of all such alkaloids as form insoluble superiodides. The method, however, was not frequently employed, for the reason that there was no experimental proof as to the constancy of composition of the precipitates. Moreover, it was noticed that some of the precipitates give up a portion of their iodine to water, *i.e.*, they are not completely insoluble. Hence concordant results could not be obtained. Later, Schweissinger (*Arch. d. Pharm.*, lxiv., 615, 1885) applied this method to the estimation of strychnine and brucine. His results have led him to the conclusion that while the method is very satisfactory for strychnine, it is far from being so for brucine. Recently Kippenberger (*Ztschr. Anal. Chem.*, xxxiv., 317; xxxv., 10), in his research upon the isolation and separation of alkaloids for toxicological purposes, has reviewed the subject of the action of Wagner's reagent upon alkaloids, and gives considerable prominence to this as one of the best methods for the estimation of the vegetable bases. His method of procedure was practically the same as that first proposed by Wagner. The alkaloid is dissolved in acidulated water, and to the solution a tenth or twentieth normal solution of iodine in potassium iodide is gradually added until all the alkaloid is precipitated and the supernatant liquid shows a slight excess of iodine. Instead of filtering and washing the precipitate, as was done by Wagner and Schweissinger, Kippenberger allows the precipitate to settle, and either decants or filters off an aliquot portion of the mother-liquid for the estimation of iodine not taken up by the alkaloid. The estimation of iodine is always done by means of a standard solution of sodium thiosulphate.

It has been usually assumed, for reasons not entirely clear, that the composition of the precipitates is $Alk.HI.I_2$, *i.e.*, diiodides of the hydriodides of the alkaloids are formed. Of the three atoms of iodine only two can be estimated directly by titration with sodium thiosulphate. The hydriodic acid is supposed to come from the potassium iodide, while the two "superiodine" atoms are furnished by the free iodine dissolved in the potassium iodide. The quantity of an alkaloid precipitated by a known volume of Wagner's reagent is calculated on this assumption, 2I : molecular weight of alkaloid : : amount of iodine taken up : x = amount of alkaloid. Schweissinger found that the method of calculation agrees entirely with the theoretical figures for strychnine. Kippenberger has called into question the correctness of this mode of calculation. He, too, assumes that the composition of the precipitates is to be represented by the formula $Alk.HI.I_2$, but he claims that all three atoms of iodine are supplied by the free iodine, and none by the potassium iodide. Therefore the calculation of the amount of alkaloid precipitated is to be done, according to Kippenberger, by the use of the proportion, 3I : molecular weight of alkaloid : : amount of iodine taken up : x = amount of alkaloid.

The hydriodic acid, it is supposed by Kippenberger, results from the interaction of iodine and water,

$$2I + 2H_2O = 2HI + H_2O_2,$$

a reaction which is facilitated or induced by the avidity of the alkaloids to form insoluble periodides of the hydriodides. His reasons for assuming that such a peculiar reaction takes place under the simple conditions of precipitation are too lengthy to be given here. All his arguments rest upon the assumption that all alkaloids form

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* From the *Journal of the American Chemical Society*, xviii., No. 4.

periodides of uniform composition, Alk.HI.I_2, and that the same alkaloid gives always the same periodide. Now, there is no reason, *à priori*, why this should be the case. Jörgenson's (*Journ. Prakt. Chem.*, 1870-78, [2], ii., 433, &c.) extended researches show that different alkaloids, when treated under apparently the same conditions, give periodides of entirely different compositions. Thus, morphine gives with Wagner's reagent Alk.HI.I_3 (Jörgenson, 1870, *Journ. Prakt. Chem.*, [2], ii., 438); codeine furnishes with excess of Wagner's reagent Alk.HI.I_4; and caffeine, as will be shown, gives Alk.HI.I_4, &c. It is safe to say that not until we ascertain exactly the composition of the different periodides as produced under the conditions of titrations, will the use of Wagner's reagent for quantitative purposes be placed upon a sound basis.

I have dwelt at such length upon this subject, because the method for the estimation of caffeine presently to be described, is based upon experimental evidence which is entirely contradictory to Kippenberger's conclusions. Whatever the cause may be with other alkaloids, his theory as to the production of hydriodic acid from iodine and water does not hold good in the case of caffeine.

Wagner, in describing his method, gives a list of alkaloids which are completely precipitated by iodine solution, and also mentions that "caffeine, theobromine, piperine, and urea are not precipitated at all" (*loc. cit.*, 41). His statement, so far at least as caffeine is concerned, has stood since then uncontradicted. It has found its way not only into standard treatises and text-books,[*] but even into periodical literature of recent date. As late as 1894, Kunze (*Ztschr. Anal. Chem.*, xxxiii., 23), in reviewing the chemistry of caffeine and theobromine, calls attention to this peculiarity of the two alkaloids. The non-precipitation of caffeine by Wagner's reagent has come to be recognised as a distinguishing feature of this alkaloid from almost all other vegetable bases.

And yet this is entirely contrary to actual facts. Instead of forming an exception, caffeine conforms to all the requirements[†] necessary in the application of this test. It is well known that most of the alkaloids as such are insoluble, or only very slightly soluble in water; they require the presence of some acid for their complete solution. In other words, alkaloids in the form of their salts are soluble in water. Whenever Wagner's reagent is applied for the precipitation of an alkaloid, it is always applied to a solution of some salt of it, preferably acidulated with sulphuric or hydrochloric acid. Therefore, even when strictly neutral salts of alkaloids are employed, there is still the possibility of the formation of hydriodic acid, or rather of the hydriodides of the alkaloid, as, for instance, Alk.HCl+KI=Alk.HI+KCl. The hydriodide thus produced is at once precipitated as a periodide. Now, it so happens that caffeine is tolerably soluble in water, and it has become customary to work with solutions of caffeine as a free alkaloid, and not in the form of its salts. The question as to whether solutions of free alkaloids are precipitated with Wagner's reagent has not, to my knowledge, been studied. My preliminary experiments in that direction show that at least some alkaloids (morphine, atropine, strychnine, &c.), are precipitated. I have not examined yet whether these periodides are identical in composition with those produced from the salts of the alkaloids. But so far as caffeine is concerned, it is true that a neutral solution of it gives no precipitate when treated with a solution of iodine in potassium iodide. When, however, the addition of Wagner's reagent is either followed or preceded by the addition of some dilute acid, there is at once thrown down a dark-reddish precipitate, remaining amorphous even on long standing.[*] The composition of this periodide is, as will be shown, $C_8H_{10}N_4O_2$.HI.I_4. It was obtained for analysis in many different ways—by using either caffeine or iodine in excess, and by employing different acids. The periodide produced is, however, always of the same composition. The precipitates were allowed to settle, filtered by means of a pump, washed with water to remove the excess of potassium iodide, dried on porous plates, and finally in a *vacuum* over sulphuric acid.

(To be continued).

SOME ANALYTICAL METHODS INVOLVING THE USE OF HYDROGEN DIOXIDE.[†]

By B. B. ROSS.

THE use of hydrogen peroxide as a laboratory reagent, although originally restricted to a few operations of minor importance, has within recent years met with a much wider extension, and its numerous applications in both qualitative and quantitative analysis render it at present almost indispensable in every well-equipped analytical laboratory.

Among the more interesting applications of this substance in quantitative estimations are those which are based on the reaction which takes place when an excess of hydrogen dioxide is brought in contact with an acid solution of chromic acid, and Baumann (*Zeitschr. Anal. Chem.*, xxxi., 436) several years since described quite fully a number of analytical processes growing out of the reaction referred to.

In the process for the estimation of chromic acid in soluble chromates as outlined by Baumann, the substance under examination is first brought into a state of solution, and the not too concentrated liquid is transferred to a generating flask of special construction.

Ten c.c. of dilute sulphuric acid are next added, after which from 5 to 10 c.c. of commercial hydrogen peroxide are run in from a small closed vessel connected with the generating flask, while the oxygen which is evolved, after the vigorous shaking of the contents of the flask, is collected over water in an azotometer.

The following equations given by Baumann illustrate the chemical changes connected with the above-described reaction:—

$$K_2Cr_2O_7+H_2O_2+H_2SO_4=K_2SO_4+2H_2O+Cr_2O_7;$$
$$Cr_2O_7+3H_2SO_4+4H_2O_2=Cr_2(SO_4)_3+7H_2O+O_8.$$

From these equations it will be seen that for 2 molecules of chromic acid, or 1 molecule of potassium dichromate, there are evolved 8 atoms of oxygen, giving an equivalent of 445·3 c.c. of oxygen (measured at 0° C. and 760 m.m. pressure) for each grm. of chromic acid which may be present.

The writer, soon after the appearance of the original article by Baumann, made a number of experimental tests of this method, with a view to applying it to some other analytical processes, and still more recently has conducted a series of tests for the purpose of determining the adaptability of Baumann's method to the indirect volumetric estimation of iron.

In the dichromate method for the volumetric determination of iron, as commonly employed, the end-point

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[*] Prescott, "Organic Analysis," p. 80; Allen, "Comm. Organic Analysis," iii., (2), 481; Fluckiger, "Reactions" (Nagelvoort's Translation), p. 26; not affected by Wagner's reagent in either neutral or acid solutions; Dragendorff, 1888. Ermittelung von Giften says that caffeine gives a dirty-brown precipitate. From the text it is not improbable he used iodine in hydriodic acid.

[†] This test is perhaps most frequently made in a neutral solution, representing, as customary state free caffeine and *normal salts* of other alkaloids.

[*] Almost the same can be said of theobromine, making allowance for the difference of solubility of the alkaloid in water. A saturated solution of it (containing one part of theobromine to 1600 of water) gives no precipitate with Wagner's reagent, but on the addition of a drop of acid there separates in a short time a crystalline periodide. Contrary to usual statements, I find that theobromine in acid solutions gives a heavy precipitate with Wagner's reagent, of a peculiar dirty-blue colour.

[†] Read at the Buffalo Meeting, August 22, 1896. From the *Journal o the American Chemical Society*, xviii., p. 918.

of the oxidation process is ascertained by the reaction with potassium ferricyanide.

As the end of this reaction is almost invariably difficult to determine, particularly if zinc has been employed as a reducing agent, the dichromate process has met with but limited application.

In order to apply the principle of the chromic acid method of Baumann to the estimation of iron, an excess of dichromate solution was employed in all of the tests and experimental determinations, the amount of the excess of chromic acid being determined by the volume of oxygen evolved upon treatment with hydrogen dioxide.

The mode of procedure adopted was as follows:—

A dichromate solution was prepared by dissolving 4·913 grms. of C. P. crystallised potassium dichromate in water and diluting to a bulk of 1 litre.

The iron solution employed in standardising the dichromate and permanganate solutions was obtained by dissolving iron wire in dilute sulphuric acid, the solution being reduced with metallic zinc, as usual, previous to titration.

The dichromate solution was also titrated against a freshly-prepared solution of ammonium ferrous sulphate, the strength of which had been determined by titration with permanganate solution, which had also been carefully standardised by means of iron wire.

In order to ascertain the strength of the dichromate solution by the hydrogen dioxide method, about 15 c.c. of the dichromate solution is run into the generating flask above referred to, and there is also added an amount of ferric sulphate solution (free from ferrous sulphate) equivalent to about 0·06 to 0·10 grm. of iron. The object of employing the ferric sulphate in this standardisation is to supply approximately the same conditions as obtain in the process for the actual determination of iron.

The amount of oxygen given off from chromic acid in the presence of ferric sulphate is slightly less than that evolved when ferric sulphate is absent, but the amount of ferric iron present may vary considerably without affecting the volume of oxygen liberated.

To the contents of the generating vessel about 10 c.c. of dilute sulphuric acid are now added, and the flask is then connected by means of a rubber tube with a Schulze's azotometer, which has been filled with water to the zero point.

From 5 to 10 c.c. of hydrogen dioxide are next run in from a small closed vessel connected with the generating flask, and the mixed liquid is then shaken, at first gently, and afterwards vigorously. The tube leading from the flask to the azotometer should be provided with a stopcock, which should be closed before and opened immediately after each shaking.

The last trace of the oxygen liberated will not be disengaged until after the lapse of about five minutes, but it is not necessary to continue the shaking during the whole of this period. After equalising the height of the water in the two tubes of the azotometer, the volume of oxygen is noted, and is easily corrected for temperature and pressure by reference to proper tables.

In order to test the strength of the dichromate solution by means of iron wire, a given weight of the wire is dissolved in dilute sulphuric acid, the solution reduced with zinc, as usual, and rapidly transferred to the generating flask (filtering, if necessary).

An excess of dichromate solution is now run in, hydrogen dioxide is added, and the oxygen is set free and collected as before described.

If a large excess of dichromate has been used in the preliminary test, duplicate tests should be made with employment of a small excess, say from 2 to 3 c.c. of the dichromate.

The strength of the solution can then be readily calculated by difference, and, if necessary, the results can be checked by still further tests.

In the determination of iron in ores by this process, the solutions of ferric iron are reduced by zinc, as in the common permanganate method, and the remainder of the process is conducted just as described for the standardisation of the dichromate by means of iron wire.

In addition to numerous tests of solutions of pure iron, several estimations of iron in iron ores were made by this process, the results obtained being compared with those secured by the permanganate method.

The following are the results of the tests of the iron ores referred to:—

	Permanganate method. Mean of several determinations.	Dichromate method.
Iron ore No. 1 ..	40·92	40·59
		41·25
		55·35
Iron ore No. 2 ..	54·71	55·43
		55·50

In the determination of iron in ores by this process, it is best, as in the case of the tests with iron wire, to employ only a small excess of the dichromate solution, after making a preliminary determination, as the results are much more accurate with a small than with a large excess of chromic acid.

While a sufficient number of determinations have not been made to ascertain the probable value of this method as an independent process for the estimation of iron, nevertheless some of the results secured would seem to warrant the conclusion that it might prove of utility as a check method, it being easy of execution and not at all time-consuming.

The following equation represents the changes which take place when the dichromate is brought in contact with the iron solution after reduction:—

$$6FeSO_4+K_2Cr_2O_7+7H_2SO_4= \\ =3Fe_2(SO_4)_3+K_2SO_4+Cr_2(SO_4)_3+7H_2O.$$

The writer has also attempted to apply the principle of the chromic acid method above described to the estimation of invert sugar, or rather to the determination of the amount of cuprous oxide thrown down from Fehling's solution in the process commonly employed for estimating reducing sugars.

The following equation represents the changes which take place when cuprous oxide is brought in contact with potassium dichromate in the presence of dilute sulphuric acid:—

$$3Cu_2O+K_2Cr_2O_7+10H_2SO_4= \\ =6CuSO_4+K_2SO_4+Cr_2(SO_4)_3+10H_2O.$$

The cuprous oxide thrown down from the sugar solution under examination is brought upon an asbestos filter connected with a filter-pump, and thoroughly and rapidly washed with hot water. The filter and contents are next transferred to the generating flask of the apparatus before described, and after the addition of dilute sulphuric acid an excess of dichromate is run in.

Very thorough and long-continued agitation of the contents of the flask is necessary in order to effect the complete oxidation and solution of the cuprous oxide, and the hydrogen peroxide must not be added until the solution is complete.

The oxygen liberated on the addition of the hydrogen dioxide is collected, and the volume noted as before described. The equivalent amounts of chromic acid, cuprous oxide, and invert sugar can be easily calculated from the data thus secured.

This method, while apparently satisfactory from a theoretical standpoint, has so far failed to give sufficiently uniform results, one of the chief objections to the process being the difficulty attendant upon the solution of the cuprous oxide.

With improvements in the details of manipulation of the process, however, it is quite possible that more satisfactory results could be obtained.

NOTICES OF BOOKS.

The University Tutorial Series. The Tutorial Chemistry. Part I.—Non-metals. By G. H. Baily, D.Sc., Ph.D. Heidelberg, Lecturer on Chemistry in the Victoria University. Edited by William Briggs, M.A., F.C.S., F.R.A.S., Principal of University Correspondence College. London: W. B. Clive, University Correspondence College Press. Warehouse, 13, Booksellers Row, Strand, W.C. Pp. 226.

We must confess our partial inability to explain the nature or characteristics of "tutorial chemistry." We know that certain Universities, such as, *e.g.*, Oxford and Cambridge, call themselves "tutorial," whilst others, such as Munich and Heidelberg, rank as investigational, and one at least, that of London, is purely examinational. But how any given Science, or modification of a Science, can be called tutorial we doubt. From our inspection of the volume before us we should think that tutorial chemistry must approximate closely to examinational chemistry, or to the preparatory work required for passing examinations. If the Correspondence College facilitates the process of "passing," and thus helps to shake public faith in the Chinese system of higher education now dominant in Britain, it will have done a valuable and needful work.

The author and editor very justly contend that it is unwise in the earlier stages to overburden the student with chemical theory. They are also, in our opinion, right in referring the study of the principles of light, heat, and electricity to works on physics.

The leading truths and laws of chemistry are here expounded in a most masterly manner; made, in fact, accessible to very moderate capacities, if only perseveringly and honestly applied to the task.

There is no attempt to introduce novel matter or to initiate the student into research, either of which aim would have been distinctly outside the plan of the work, if not outside the entire scope, of the University Correspondence College. Within that scope, if we rightly apprehend it, a better manual could scarcely be written.

The Australian Medical Directory and Handbook; including a Short Account of the Climatic and Sea-side Health Resorts in Australia, Tasmania, and New Zealand. Edited and Compiled by Ludwig Bruck, Fourth Edition, corrected up to September, 1896. (Copyright). Sydney: L. Bruck, Medical Publisher. London: Baillière, Tindall, and Cox. 1896.

The scope of this useful work is somewhat wider than it would appear from the title. It comprehends also Fiji and the British portion of New Guinea. We are glad to find that the author calmly ignores all the non-qualified practitioners, who are now so numerous.

There is an abstract of the Medical Acts of Australia, Tasmania, New Zealand, and Fiji. There is a list of the medical and allied scientific societies in Australasia. Some of them are of high standing, and have done good work. Such are, *e.g.*, the Royal and the Linnean Societies of New South Wales, the former of which bodies has a medical and a microscopical section. The Intercolonial Medical Congress of Australasia is an itinerant body after the pattern of the British Association.

The scale of fees legally recoverable by medical men are certainly not exorbitant, and, in comparison with the wages of mechanics, servants, &c., may be called paltry. In the local Medical Directory for each Colony, the altitudes to the various towns above sea-level are given, and a rough view of the racial character of the population. We are sorry to see to what an extent the "heathen Chinee" predominates in some localities. An interesting feature is the chapter on health-resorts. Here we find given the average rainfall, the extreme and average temperatures, and the kind of constitution for which they are most adapted.

At some of the littoral towns sea-bathing is mentioned as one of the local attractions or beneficent features. The abundance or scarcity of sharks in the sea—a point of great importance—is not mentioned. At some places a range for bathing is fenced in with iron chains.

City and Guilds of London Institute for the Advancement of Technical Education. Examinations Department. Report of the Work of the Department for the Session 1895-96. Exhibition Road, London, S.W. 1896.

The activity of the Examination Department is greater and wider than we might expect from its unhappy name. It includes the arrangement of courses of instruction in technical subjects, the consideration of the qualifications of teachers.

A distinction seems to have been made between the certificate granted to students who have attended a course of lessons at a recognised school and that given to candidates who produce no evidence of such training. The results are said to have been very satisfactory.

The total number of subjects is 62, but in five of these no examinations have actually been held. Of the greatest percentage of failures, viz., 76, 1 per cent was in lithography, and the smallest, 00·0, were in the alkali and soap manufacture, in the lace manufacture, and in ship carpentry.

At Aylesbury there was one candidate for examination, who passed.

La Unifikazion da las Medidas. Par K. Newman. Valparaiso: Karlos Kabazon. 1897.

Chili is a perfect focus of reforms, especially orthographic. Senhor K. Newman's publications remind us of our old friend the *Fonetic Nuz.* The present object of the author is to advocate the metric system "pure and simple." He urges its adoption by all nations in its original polysyllabic nomenclature, in preference to the more convenient form devised in Holland.

The names proposed by the French revolutionary commission may be unobjectionable for wholesale transactions, but for the retail business of daily life they have proved themselves impracticable.

We should recommend K. Newman, when advocating any reform, to do so in a language "understanded of the people," and not bring it in a novel and fantastic orthography.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on Feb. 1st, Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—Mr. Alfred Louis Cohen, Mrs. Delaforce, Sir Charles A. Elliott, K.C.S.I., LL.D., Mr. John Lawson Johnson, Dr. A. Liebmann, Mr. T. George Longstaff, Mr. Howard Marsh, F.R.C.S., the Rev. E. G. C. Parr, M.A., Mr. Charles Rose, and Mr. Edward P. Thompson. The special thanks of the Members were returned to Sir Frederick Abel, Bart., K.C.B., for a donation of £50, and to Mr. J. Wolfe Barry, C.B., for a donation of £25 to the fund for the promotion of Experimental Research at Low Temperatures.

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.

Epsom Salts.—A correspondent asks whether Epsom salts are best reduced to the state of a dry powder by hot cylinders or in an oven, and then rolling in a mill.

MEETINGS FOR THE WEEK.

Monday, 15th.—Society of Arts, 8. (Cantor Lectures). "Industrial Uses of Cellulose," by C. F. Cross, F.C.S.

—— Society of Chemical Industry, 8. Adjourned Discussion on Mr. W. J. Dibdin's Paper on "The Character of the London Water Supply."

Tuesday, 16th.—Royal Institution, 3. "Animal Electricity," by Prof. A. D. Waller, F.R.S.

—— Society of Arts, 8. "The Progress of Canada during the past Sixty Years of Her Majesty's Reign," by Joseph G. Colmer, C.M.G.

Wednesday, 17th.—Society of Arts, 8. "Light Railways," by Everard R. Calthrop.

Thursday, 18th.—Royal Institution, 3. "The Problems of Arctic Geology," by J. W. Gregory, D.Sc., F.R.S.

—— Chemical, 8. "The Oxidation of Sulphurous Acid by Potassium Permanganate," by T. S. Dymond and F. Hughes. "Sodamide and some of its Substitution Derivatives," and "Rubidamide," by A. W. Titherley, M.Sc., Ph.D.

—— Society of Arts, 8. "The Mechanical Production of Cold," by Prof. James A. Ewing, M.A., F.R.S.

Friday, 19th.—Royal Institution, 9. "The Approaching Return of the Great Swarm of November Meteors," by G. Johnstone Stoney, M.A., F.R.S.

Saturday, 20th.—Royal Institution, 3. "The Growth of the Mediterranean Route to the East," by Walter Frewen Lord.

TO CORRESPONDENTS.

R. G. B.—We do not think any notice of the mentioned patents has yet appeared.

C. Stanley.—The responsibility of advising in such a case is more than we care to take.

A. S. Chase.—Consult "Explosives and Their Powers," by Col. J. P. Cundill," and "A Handbook of Modern Explosives," by M. Eissler.

CIVIL SERVICE COMMISSION.

FORTHCOMING EXAMINATION.

Second Assistant to the Lecturer on Electricity at the ARTILLERY COLLEGE (20–25), 24th February. Technical training and qualifications necessary.

The date specified is the latest at which applications can be received. They must be made on forms to be obtained, with particulars, from the Secretary, Civil Service Commission, London, S.W.

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Laboratory Attendant required in the State Medicine Laboratory. Wages, 15s.—Apply to the Secretary, King's College, Strand, W.C.

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THE CHEMICAL NEWS.

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HOW SOON SHALL THE STUDENT BEGIN THE STUDY OF QUALITATIVE ANALYSIS?

By ALFRED C. BEEBE.

In the following paper I shall attempt to show at what stage of laboratory work the student can most advantageously be introduced to the study of qualitative analysis.

To the teachers who begin the laboratory course with qualitative analysis I have nothing to say. But to the teachers who require the student to devote all, or a large part, of the first months in the laboratory to the study of the preparation and properties of the non-metallic elements, I wish to present some arguments for replacing that department of the subject by the study of qualitative analysis.

I have three objections to requiring the student *beginning* laboratory work to perform experiments relating to the non-metallic elements. First, the experiments are more or less dangerous. Second, the student nearly always fails to connect the different experiments with each other. Third, the work does not awaken and hold the student's interest as well as qualitative analysis does. Of course, the student must have a good knowledge of the properties and preparation of the non-metallic elements, but it seems to me this is best gained from lectures, illustrated by the proper experiments given by the teacher before the entire class. I wish to say that I think this part of the subject is often made so unnecessarily complex that the student's ideas of it are very confused and hazy. Let the first ideas of chemistry, both in the lecture room and the laboratory, be as simple as the subject will permit. The details are easy enough to learn afterwards if they be necessary.

Let me consider at greater length the three objections made above to the study in the laboratory of the non-metallic elements by the beginner.

First: Danger. A university professor said to me recently, "I always dread hydrogen day; I am nervous every minute the students are working with this dangerous gas, for I feel as if a serious explosion might occur at any time when students have as little experience as the beginner possesses." This state of mind is, I believe, not uncommon among teachers who require their students to experiment with hydrogen soon after beginning the laboratory work. I feel sure that almost every teacher knows of several serious explosions with hydrogen, and of many more that might have been serious except for good luck. Considering these facts it seems to me unwise to expose the student to this unnecessary danger, for no amount of chemical knowledge can repay a pupil for the loss of his eyesight. The danger is, however, much lessened by some months' experience in the laboratory, and then explosive gases may be given to the pupils should the teacher think fit to do so. The preparation of oxygen is attended with more or less danger, and I know of several serious accidents from this cause. Phosphorus is not a substance to trust a beginner with, and yet I know some widely-used text-books which give this dangerous substance to the pupil soon after his entrance to the laboratory. One text-book even goes so far as to give work with the iodide of nitrogen!

The handling of acids, the use of chlorine, bromine, &c., make trouble enough without adding work on explosive gases like hydrogen, or work with dangerous substances like phosphorus.

Qualitative analysis, on the other hand, has no experiments that are even moderately dangerous. Of course, dangerous experiments may be included in the branch of the subject, but they are unnecessary, while for the non-metallic elements they form an essential part of the course.

Second: Unconnectedness. Although the experiments on the non-metallic elements are connected it is very difficult, in my experience, to make the student see that connection. For instance, after oxygen is experimented with no further work on that subject is required, and the teacher must be continually asking review questions if the subject is to remain fresh in the student's mind. After several weeks' experimenting has been done, the amount of back work becomes too large for the teacher to review, and as the experiments do not require repetition, those on one element seem to have almost no connection with those on other elements. I have taken some trouble to look into this matter, and have heard so many students complain about it, that I consider it an important point. Qualitative analysis, on the other hand, requires that experiments once learned be remembered, for the future work uses them repeatedly, since each day's work in a good text-book on this subject is closely related to what has gone before and what is to follow. This fact and the repetition necessary while analysing unknown substances oblige the student to remember his work, and he goes out of the laboratory with a scheme for analysis containing facts as valuable as those relating to the non-metallic elements, fixed with reasonable firmness in his mind, instead of a confused mass of material such as the work on the non-metallic elements too often leaves. Even reasonable repetition will not fix seemingly unconnected facts, while connected phenomena almost fix themselves in the mind.

Third: Interest. In no part of the work in the chemical laboratory is so much interest shown as in the analysis of unknown solutions and substances. This one fact would, to me, be sufficient argument for the use of qualitative analysis for the student's first laboratory work. It were a waste of words for me to say that we should endeavour to awaken and sustain the student's interest in a subject as much as possible, for every teacher knows how smoothly and advantageously things run when a genuine interest is taken in any sort of work or study. From my experience, as student and teacher, I feel perfectly confident that qualitative analysis is much more fitted to do this than the study of the non-metallic elements. The student feels he is a real chemist as soon as he analyses his first "unknown solution." Be that solution ever so simple he realises that he has acquired a new power, and in most cases he becomes anxious to increase it. This feeling of independence is helped if no results to experiments are given in his text-book, for he thereby becomes an original investigator, and not merely a student who is required to perform certain experiments which shall agree with his text-book. This attitude sharpens the observing and reasoning faculties immensely. The interest shown in qualitative analysis is oftentimes amazing. For example, I have often seen the majority of a university class work from four to six hours *extra* a week simply from interest in this branch of the subject. I know of one teacher whose student became so interested in qualitative analysis, that in self-defence he had to refuse to remain in the laboratory more than two hours after the regular hour for closing had come. This last happened in a public high school, with a class of boys and girls averaging sixteen years old, where we surely ought to find average work. Some of this interest may be due to the teachers, but from the fact that it is not an uncommon experience, I am inclined to think that much of it is due to the fascination of qualitative analysis. I have never seen any such results from the study of the non-metallic elements.

Summing up the advantages of the study of qualitative analysis for the beginner, when compared with the study of the non-metallic elements, I think I may say that the former is less dangerous, more connected, and holds the student's interest much better.

Savanna, Ill.

VISCOSE AND VISCOID.*

By CLAYTON BEADLE.

(Concluded from p. 75).

Production of Viscoid.

For Use in Turning, &c.—Viscoid is prepared by coagulating the viscose in the same way as described above for the production of veneers or sheets, but the moulds are circular instead of rectangular. As might well be supposed, the difficulties of coagulating the viscose increase with the diameter of the cylinder. Great care has to be taken in the early stages to prevent the material from cracking. Immediately after coagulation takes place there is a considerable shrinkage, and unless the coagulation proceeds uniformly throughout the mass there is danger of it cracking. The time of coagulation increases with the diameter. The moulds in which the material is coagulated are specially constructed, and made of a material which is unaffected by the viscose, and the interior surface has to be such that the coagulum does not adhere to it, otherwise it is sure to crack on shrinking. After setting, the solid cylinders of coagulum are removed from their moulds. At this stage they are elastic and pliable, somewhat like rubber, but have to be handled with great care. They consist of about 15 per cent of cellulose, 7 per cent of chemical by-products, and 78 per cent of water of hydration.

Washing.—They are next placed in water for the removal of the by-products. We have done much work to determine the best conditions, and the cheapest and most effective method for getting rid of the by-products.

When the cylinders of coagulum are placed vertically in tanks provided with false perforated bottoms and immersed in water, the by-products are found to diffuse out and creep down the sides of the coagulum and to accumulate in the space below the false bottom. This action is so perfect that often, when the water is undisturbed, the top portion contains only a trace of by-products and the lower portion is heavily charged with them. The removal of by-products is accelerated by the use of hot water. We find that the time required for the removal of the by-products varies as the square of the diameter of the coagulum. During washing the coagulum undergoes a further shrinkage, so that when the washing is complete the coagulum contains about 20 per cent of cellulose.

Drying.—The washed coagulum is next removed from the tanks and dehydrated or dried. The dehydration of the coagulum has presented us with some very interesting problems, which we have to a large extent solved. When the washed material is exposed to the air, it gradually contracts and loses weight, and this goes on until it is finally deprived of moisture, and nothing is left but the dry viscoid. We found it difficult to ensure that the material should retain its proper shape on drying. With "rack" or air drying at from 90° to 110° F., a solid cylinder remains flat at the ends, provided that the length is four times that of the diameter. If it is less than this it has a tendency to become concave on the ends, and it becomes more concave up to a certain point as the length diminishes in proportion to the diameter. The sides of a solid cylinder have a tendency sometimes to become convex in proportion as the ends become concave. Unless drying is uniform, a cylinder of 1½ inches diameter, and less, will bend less towards the driest side. With larger cylinders this is not so noticeable. When cylinders are placed upon a rack that is not perforated, the top end contracts and dries the most rapidly, so that the cylinder becomes tapered towards the top. When the rack is perforated so as to allow of the free passage of air, the cylinder is sometimes found to be smallest at the bottom. Sometimes the cylinders are irregular in diameter or warped in final drying. During the process of drying the coagulum is in a semi-plastic state, and when the drying is uneven is under considerable stress. The viscoid is caused to flow in the direction to relieve the stress, so that, when finally dried and rigid, it is found to have assumed its original shape. It generally, however, leaves some marks of its temporary distortion. The time of drying, so far as our determinations have gone, varies as the square of its diameter.

When hot air is used the rate of drying cannot be increased beyond a certain degree without serious injury to the solid. The solid, by constant exposure to hot air, becomes skin-dried, whilst the interior remains comparatively moist. The outer dried skin offers a great resistance to the passage of further moisture, and so the drying is very much retarded. If, under these conditions, the moisture is able to escape from the interior, the exterior—being dry and consequently rigid—offers great resistance to the contraction of the interior, and the consequence is that fracture often takes place. If the drying be not quite so rapid as to produce fracture, the interior is under tremendous stress, and, when the cylinder is cut in section, cleavage often takes place in the direction of the length of the cylinder. When, however, the drying is conducted much slower, the moisture—which is always tending to pass from the wetter to the drier portions—finds a way of escape, and is removed from the surface by the atmosphere. We have been able to overcome these difficulties, and the product obtained is almost free from structure. The washed or unwashed coagulum has a natural inclination to contract when surrounded by a hot medium, even when the same has no drying capacity whatever. The rate of contraction increases with the temperature; thus, a coagulum containing 10 per cent of cellulose will rapidly contract to about half its bulk on immersion in boiling water. When heated in this way there is no indication of case hardening. There is a limit, however, to this contraction. We tried the effect of saturated steam at different pressures upon cylinders of washed coagulum, which contained about 15 per cent of cellulose. The pressure was varied from 3 to 8 atmospheres; the time of exposure was one hour in each case. The average contraction was about 25 per cent. The experiments go to show that there is little or no difference between the 3 atmospheres or 8 atmospheres on the amount of contraction. As the diameter increases the rate of contraction diminishes. The next set of trials were made to determine what effect time had upon the shrinkage in an atmosphere of saturated steam at 4 atmospheres. Taking the original weight as 100, after one hour's treatment, the weight became 82·9.

After two hours, the weight became 74·5
,, three ,, ,, ,, 65·7
,, four ,, ,, ,, 63·0.

The above was on a piece of washed coagulum, containing about 15 per cent of cellulose. We next took some unwashed coagulum, containing about 11 per cent of cellulose, and suspended it in an atmosphere of saturated steam at 4 atmospheres. It lost 44·8 per cent during the first hour, 14·7 during the second hour; therefore it had contracted during the two hours' treatment to 40·5 per cent of its original weight. A receptacle was placed immediately beneath the coagulum to catch the by-products, which were found to be recovered without dilution. With blocks of double the diameter of the above, *i. e.*, 75 m.m., the weight after two hours' treatment was 56·6 per cent of the original. The effect of saturated steam is to produce a rapid contraction of the coagulum, if it contains from 10 to 15 per cent of cellulose,

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* *Journal of the Franklin Institute*, January, 1897.

and this contraction is rapid until a concentration of about 20 per cent of cellulose is reached. By a prolonged treatment in saturated steam the coagulum gradually contracts until it contains about 25 per cent of cellulose, beyond which point it does not alter.

Ivory coloured Viscoid.

Ordinary viscose has about the colour and consistency of molasses, and yields a viscoid which has the general appearance of horn. We set to work to produce viscoid in imitation of ivory, and whilst doing this we discovered a new combination of viscose, which gave rise to a creamy white solution. This was found to last longer in the liquid form than the ordinary viscose. On drying down it yielded a product which is a very fair substitute for ivory. It has a specific gravity of 1·8 to 1·85. We had several sets of billiard balls turned from this, and they were found to play very well indeed. The angle, however, at which the balls left each other after striking was somewhat less than that of ivory balls. With the plain viscoid balls, which have a sp. gr. of 1·5, the angle is greater than that of ivory, and we believe it possible to mix these two compositions in such a way that both the specific gravity and the angle at which they leave each other after striking resemble that of ivory. This "ivory" viscoid has been used for various articles, such as acorns for blind-cords, knife-handles, brush-backs, &c.

Viscoid for Electrical Work.—The plain viscoid was carefully tested to determine its insulating properties. It is about equal to vulcanised fibre for insulating purposes. It appears that if great care is taken to thoroughly remove the last traces of by-products, and to well season the viscoid, the insulating properties can be made much superior to vulcanised fibre. Cellulose, when completely deprived of moisture, is almost a perfect insulator, and its insulation diminishes as the hygroscopic moisture increases. Viscoid will probably replace vulcanised fibre to a large extent for electrical work, but at present it is very much inferior to vulcanite. It is likely that we shall find some means of improving it, so that it may be made to replace that substance.

Black Viscoid.—We next set to work to prepare an ebony-black viscoid, and after about six months' work we have obtained a uniform black viscoid, which in some respects appears to be superior to the plain substance. The ebony viscoid will probably have a greater range of utility than any of the other products we have obtained. A jet-black is preferable to white or any colour for machine-tool handles, &c.

Blue Viscoid.—We have obtained a somewhat more expensive product, very much resembling *lapis lazuli.* This is very nice for turning and carving, and takes a very high polish, and looks very well when made into fancy articles, such as umbrella and walking-stick handles.

Various Colours.—We have now got viscoid in a large variety of colours and shades, and have also succeeded in producing grained and mottled effects, which have a very pretty appearance when turned and polished. We see no reason why viscoid should not be used in place of celluloid for many purposes. Some samples have been kept two or three years, and they do not discolour. Keeping the viscoid for a long time appears rather to improve it than otherwise.

Paper Sizing.

Mr. Little mentioned this application of viscose in his paper (*Journal of the Franklin Institute*, cxxxviii., No. 824). Viscose is now being extensively used in paper-mills for this purpose. It does not size the paper in the sense that rosin does, although when viscose is used a large proportion of the rosin can be dispensed with. It is added to the beater, and a chemical substance is afterwards added which precipitates the cellulose among the fibres as a flocculent mass. The effect that it has upon the paper is, of course, dependent upon the amount used. It strengthens the paper from 30 to 100 per cent, and the paper produced with viscose, besides being much stronger, is also harder, has a better "feel" and rattle, and admits of a much better surface when calendered. It also assists in the retention of clay, and prevents the loss of short fibres which, as a rule, pass through the wire cloth of the machine. It therefore gives a larger output to the machine. It is chiefly used in the manufacture of "wrappings" and bag papers, but it is coming into use also for news and other papers. Where additional strength is not required, it enables the paper-maker to use a lower-class and weaker fibrous material, without prejudicing either the strength or quality of his paper. By this means it decreases the cost of production. The precipitation of the cellulose requires a great deal of skill. Unless care is taken to ensure the right conditions, and to add the precipitating agents in the right proportions, the cellulose is precipitated as a non-adhesive mass, which gives neither strength nor hardness to the paper. It is necessary to know exactly the conditions of working in each mill before good results can be ensured, but when once these are known and understood there is no difficulty in obtaining uniform results.

The Nature of Hygroscopic Moisture in Cellulose.

The behaviour of viscoid on drying in the mass opened up some very interesting problems. It appeared to throw light upon the hygroscopic moisture of celluloses. I had previously observed (*Nature*, xlix., No. 457) that the cotton fibre, when deprived of moisture (either by drying in an air-bath at 105° C., or in a desiccator over sulphuric acid) and exposed to the air, rose in temperature rapidly for about eight minutes. It reached a temperature of about 4½° F. above that of the atmosphere, where it remained nearly stationary for a few minutes. It then fell gradually, and after about seventy minutes' exposure it again reached the temperature of the surrounding atmosphere. I endeavoured to find what connection this had with the rate at which bone-dry cotton fibre assumed its hygroscopic moisture. I found that cotton fibre took about seventy minutes, and, by weighing the cotton at different intervals, and comparing the rate of gain in weight with the rate of increase in temperature, I was led to the conclusion that the two were closely connected. The same experiments were repeated with anhydrous viscoid which had been ground to a powder before drying. The viscoid first of all suddenly fell below the temperature of the atmosphere. It fell much slower than the cotton fibre, and even at the end of 160 minutes' exposure it was still about 3° above the atmospheric temperature. At this point it had only recovered about 90 per cent of its hygroscopic moisture, and it only came to a constant weight after about 210 minutes' exposure. By grinding viscoid to a much finer powder than was used for the above, and repeating the experiments, a much more regular curve was obtained, and the hygroscopic moisture was very much diminished; but the time required for the material to fall to the temperature of the atmosphere was not lessened. I took some cotton-wool which I ground to a fine powder, and I found that, although it took about sixty minutes to recover its hygroscopic moisture, it contained only about 4 per cent instead of 7 per cent moisture. All these experiments were repeated with similar results. From this it is evident that the hygroscopic moisture of a cellulose, whether amorphous or in the fibrous condition, is dependent not only upon the character of the cellulose itself, but also upon the extent to which the cellulose is disintegrated. This is contrary to accepted views on the subject. It is only when particles of viscoid are below a certain size that the hygroscopic moisture is materially diminished. It appears that the cellulose that composes the cell-walls of the ultimate fibre is under certain stress when deprived of moisture, in the same way that lumps of viscoid are when they are dried, and that the amount of stress determines the amount of moisture that it will take up to relieve the stress. Cellulose expands when hydrated, and it appears that the hygroscopic moisture is really water of hydration of the cellulose, and that it tends to hydrate in proportion to the stress that exists in the anhydrous cellulose. This accounts for the fact that the smaller particles of viscoid contain less hygroscopic moisture than the larger; also, which is more marked, disintegrated cotton fibre contains much less hygroscopic moisture than when the fibre is left intact. I have prepared small particles of viscoid, which, when bone-dry, would fly to pieces on being scratched, like "Prince Rupert Drops;" but the same particles, on being placed in a damp atmosphere, swell somewhat and recover their strength.

Particles can, on the other hand, be prepared in such a way that they do not exhibit brittleness, and they expand to a much less degree on being placed in a moist atmosphere. The results all tend to the same conclusion, in my mind, as to the nature of hygroscopic moisture in cellulose.

THIRD ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED DURING 1895.*

By F. W. CLARKE.

(Continued from p. 76).

Cobalt.—The atomic weight of cobalt has been redetermined by Thiele ("Die Atomgewichts bestimmung des Kobalts," a doctoral dissertation, Basel, 1895). First, carefully purified oxide of cobalt, CoO, was reduced in hydrogen. The weight and results are as follows:—

Residual Co.	Loss of O.	Atomic weight of Co.
0·90068	0·24429	58·843
0·79159	0·21445	58·912
1·31558	0·35716	58·788
	Mean	58·848

Reduced to vacuum standards this becomes—

Co = 58·826,

when O = 15·96.

In a second method metallic cobalt was dissolved in hydrochloric acid, and the solution evaporated to dryness with special precautions against dust. The chloride thus obtained was then dried at 150° in a stream of pure gaseous hydrochloric acid, so that basic salts could not be formed. From the weight of cobalt and of cobalt chloride the ratio Co : Cl_2 is determined. The chlorine was afterwards re-estimated as silver chloride, giving the ratio Co : 2AgCl. The weights are subjoined:—

Co taken.	Cl taken up.	AgCl.
0·7010	0·8453	—
0·3138	0·3793	—
0·2949	0·3562	1·4340
0·4691	0·5657	2·2812
0·5818	0·7026	2·8303
0·5763	0·6947	—
0·5096	0·6142	2·4813

Hence, with Cl=35·37, and Ag=107·66, Co=

Co : Cl_2.	Co : 2AgCl.
58·66	—
58·52	—
58·57	58·828
58·66	58·825
58·52	58·803
58·68	—
58·69	58·750
Mean 58·64	Mean 58·801

The second column is subject to a small correction for dissolved silver chloride, which reduces the mean to Co=58·770. Reduced to a vacuum this becomes 58·765, and the value from the Co : Cl_2 ratio becomes 58·61. Thiele regards Co=58·765 as the most probable value to be derived from his experiments. This becomes—

With O=16 Co=58·912

,, O=15·88 Co=58·470

In my report for 1894 I gave Winkler's work on cobalt and nickel, which involved their ratios to iodine. In a supplementary paper Winkler (*Ztschr. Anorg. Chem.*, viii., 291) gives some similar experiments with iron, intended to show that errors due to metallic occlusion of hydrogen are absent from his determinations. He succeeds in proving that such errors, if they exist, must be very small. Thiele also considered their possibility, and guarded against them in the preparation of his cobalt.

Zinc.—Atomic weights re-determined by Richards and Rogers (*Ztschr. Anorg. Chem.*, x., 1; calculations made with O=16, Ag=107·93, and Br=79·955), who used the bromide method. Zinc bromide, carefully purified, was treated gravimetrically with standard silver solution. The weights and results are subjoined:—

First, $ZnBr_2$: 2AgBr.

$ZnBr_2$.	AgBr.	Atomic weight of *Zn*.
1·69616	2·82805	65·469
1·98198	3·30450	65·470
1·70920	2·84549	65·487
2·35079	3·91941	65·470
2·66078	4·43751	65·400
	Mean.. ..	65·459

Second, same ratio.

$ZnBr_2$.	AgBr.	Atomic weight of *Zn*.
2·33882	3·90067	65·400
1·97142	3·28742	65·434
2·14985	3·58539	65·402
2·00966	3·35074	65·463
	Mean.. ..	65·425

Third, $ZnBr_2$: Ag_2.

$ZnBr_2$.	Ag.	Atomic weight of *Zn*.
2·33882	2·24063	65·409
1·97142	1·88837	65·444
2·14985	2·05971	65·396
2·00966	1·92476	65·472
	Mean.. ..	65·430

Two additional series of data are given by Richards alone, as follows:—

First, $ZnBr_2$: Ag_2.

$ZnBr_2$.	Ag.	Atomic weight of *Zn*.
6·23833	5·9766	65·403
5·26449	5·0436	65·404
9·36283	8·9702	65·392
	Mean.. ..	65·402

Second, $ZnBr_2$: 2AgBr.

$ZnBr_2$.	AgBr.	Atomic weight of *Zn*.
2·65847	4·43358	65·410
2·30939	3·85149	65·404
5·26449	8·77992	65·404
	Mean.. ..	65·406

The final mean adopted by Richards is 65·404. With O=15·88 this becomes—

Zn = 64·913.

Cadmium.—Mr. Bucher's paper,* as its title indicates,

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* Read at the Cleveland Meeting, December 31, 1895. From the *Journal of the American Chemical Society*, xviii., No. 3.

* "An Examination of some Methods Employed in Determining the Atomic Weight of Cadmium," by John E. Bucher. Johns Hopkins University doctoral dissertation. Baltimore (Friedenwald), 1895.

is a study of methods rather than a final determination of atomic weight; but the results recorded in it compare well with those reached by others. His starting-point is metallic cadmium, purified by nine distillations *in vacuo*, and from this material, with pure reagents, his various preparations were made. Vacuum weights are given, and the antecedent values used in calculation are O, 16; S, 32·059; C, 12·003; Cl, 35·45; Br, 79·95; and Ag, 107·93.

First, cadmium oxalate, dried for fifty hours at 150°, was decomposed by heat, and so reduced to oxide. The variations are mainly attributed to imperfect dehydration of the oxalate. Weights and results are as follows:—

Oxalate.	Oxide.	Atomic weight of Cd.
1·97674	1·26474	111·74
1·94912	1·24682	111·83
1·97686	1·25886	111·85
1·87099	1·19675	111·81
1·37550	0·87994	111·86
1·33313	0·85308	111·96
1·94450	1·24452	112·02
2·01846	1·29210	112·09
	Mean.. ..	111·89

Second, cadmium oxalate was transformed to sulphide by heating in a stream of hydrogen sulphide. The data are:—

Oxalate.	Sulphide.	Atomic weight of Cd.
2·56319	1·84716	112·25
2·18364	1·57341	112·19
2·11643	1·52462	112·03
3·13105	2·25582	112·12
	Mean.. ..	112·15

Third, cadmium chloride, dried at 300° in a stream of dry, gaseous hydrochloric acid, was precipitated by silver nitrate, and the silver chloride was collected with all necessary precautions. The weights and results are subjoined:—

$CdCl_2$.	AgCl.	Atomic weight of Cd.
3·09183	4·83856	112·34
2·26100	3·53854	112·33
1·35729	2·12431	112·32
2·05582	3·21727	112·34
1·89774	2·97041	112·31
3·50367	5·48473	112·28
2·70292	4·23087	112·30
4·24276	6·63598	112·44
3·40200	5·32314	112·37
4·60659	7·20386	112·47
2·40832	3·76715	112·42
2·19144	3·42724	112·46
2·84628	4·45477	112·32
2·56748	4·01651	112·41
2·31003	3·61370	112·41
1·25008	1·95652	112·32
1·96015	3·06541	112·47
2·29787	3·59391	112·45
1·94227	3·03811	112·42
1·10976	1·73547	112·47
1·63080	2·55016	112·48
	Mean.. ..	112·39

Fourth, cadmium bromide was analysed in much the same way as the chloride. The weights and results are as follows:—

$CdBr_2$.	AgBr.	Atomic weight of Cd.
4·39941	6·07204	112 35
3·18030	4·38831	112·42
3·60336	4·97150	112·45
4·04240	5·58062	112·29
3·60505	4·97519	112·38
	Mean.. ..	112·38

Fifth, cadmium sulphate was formed by synthesis from metallic cadmium. 1·15781 grms. cadmium gave 2·14776 cadmium sulphate. Hence Cd=112·35. As any impurity in the sulphate would tend to lower the atomic weight found, this is probably a minimum value.

Sixth, metallic cadmium was converted into oxide by solution in nitric acid and ignition of the nitrate. The ignition was performed in double crucibles, both porcelain in Experiments 1 and 2, the inner one of platinum in the rest of the series. Weights and results as follows:—

Cd.	CdO.	Atomic weight of Cd.
1·26142	1·44144	112·12
0·99785	1·40135	112·04
	Mean.. ..	112·08
1·11321	1·27247	111·84
1·02412	1·17054	111·91
2·80966	3·21152	111·87
	Mean.. ..	111·87

In this case additional experiments were made to discover the sources of error, leading to corrections which bring the results near to those found in the chloride and bromide series. Each of the methods is quite fully discussed, and the sources of error are noted. With O=16, 112·39 seems to be a close approximation to the true atomic weight of cadmium.

Molybdenum.— Seubert and Pollard (*Ztschr. Anorg. Chem.*, viii., 434; calculations on the basis of O=15·96), by two distinct methods, have re-determined the atomic weight of this element. First, molybdenum trioxide was dissolved, in weighed quantities, in a standard solution of caustic soda. The excess of soda was then measured by titration with standard sulphuric acid and lime water. In another set of experiments the volumetric value of the caustic soda had been estimated with standard hydrochloric acid, while the last compound had also been determined gravimetrically in terms of silver chloride. Hence the data, all considered together, give from their true end terms, the ratio $MoO_3 : 2AgCl$, although in a very indirect manner; and for this indirection the authors give good reasons. The weights and results, considering only the end terms, are as follows:—

MoO_3.	AgCl.	Atomic weight of Mo.
3·6002	7·1709	95·734
3·5925	7·1569	95·708
3·7311	7·4304	95·757
3·8668	7·7011	95·749
3·9361	7·8407	95·720
3·8986	7·7649	95·740
3·9630	7·8941	95·723
3·9554	7·8806	95·694
3·9147	7·7999	95·686
3·8543	7·6767	95·740
3·9367	7·8437	95·688
	Mean.. ..	95·722

Reduced to vacuum standards this becomes Mo=95·729. With O=16, Mo=95·969; and with O=15·88, Mo=95·249.

Another series of determinations, in confirmation of the first, was made by the old method of reducing molybdenum trioxide in hydrogen. The weights and results are subjoined:—

MoO_3.	Mo.	Atomic weight of Mo.
1·8033	1·2021	95·736
1·7345	1·1564	95·777
3·9413	2·6275	95·756
1·5241	1·0160	95·741
4·0533	2·7027	95·813
	Mean.. ..	95·765

Reduced to vacuum, Mo=95·735, a value very close to the other. When O=16, the atomic weight of molybdenum is very near the even number 96.

(To be continued).

ON THE ACTION OF WAGNER'S REAGENT UPON CAFFEINE, AND A NEW METHOD FOR THE ESTIMATION OF CAFFEINE.*

By M. GOMBERG.

(Continued from p. 81).

I. This sample was obtained by slowly adding a solution of iodine in potassium iodide to a solution of caffeine acidulated with sulphuric acid. The iodine was added until the supernatant liquid was decidedly red. The whole was allowed to stand three hours, filtered, washed, and dried as described above. The total iodine was estimated in the usual way, *i.e.*, by suspending a weighed sample in water, adding sulphurous acid solution, then silver nitrate and nitric acid; filtered, washed, and dried. The "exterior" iodine, *i.e.*, the iodine not as hydriodic acid, was estimated by direct titration with standard sodium thiosulphate.

0·2002 grm. gave for total iodine 0·2785 grm. AgI.
0·2358 ,, ,, exterior ,, 0·1433 ,, I.

II. This sample was obtained by adding to an acidulated solution of caffeine enough iodine to precipitate about one-half of the caffeine present.

0·2563 grm. gave for total iodine 0·3591 grm. AgI.
0·1659 ,, ,, exterior ,, 0·0997 ,, I.

III. A neutral solution of caffeine was mixed with an excess of Wagner's reagent, and to the mixture dilute sulphuric acid was gradually added so long as a precipitate was produced.

0·4039 grm. gave for total iodine 0·5668 grm. AgI.
0·1424 ,, ,, exterior ,, 0·0866 ,, I.

IV. Filtrates from I. and III, on long standing, gave a deposit of dark blue needle-like crystals, which were collected, washed, and dried as before.

0·7884 grm. gave for total iodine 1·1064 grm. AgI.
0·4450 ,, ,, exterior ,, 0·2685 ,, I.

V. This was obtained by re-crystallising the amorphous precipitate from methyl alcohol.

0·2890 grm. gave for exterior iodine 0·1756 grm. I.

VI. Obtained by re-crystallising the amorphous periodide from hot ethyl acetate.

0·4807 grm. gave for total iodine 0·6709 grm. AgI.
0·2777 ,, ,, exterior ,, 0·1622 ,, I.

	Calculated for $C_8H_{10}N_4O_2.HI.I_4$. Per cent.	Found.					
		I.	II.	III.	IV.	V.	VI.
Total iodine..	76·44	75·12	75·66	75·84	75·83	—	75·40
Exterior iodine	61·15	60·79	60·11	60·81	60·34	60·76	60·22

When some of the periodide is treated with a solution of sulphur dioxide, and then extracted with chloroform, it furnishes unchanged caffeine.

The composition of this periodide of caffeine appears to be different from that described by Tilden (*Journ. Chem. Soc.*, xviii., 99, 1865), which he obtained by exposing to sunlight an alcoholic solution of caffeine containing some hydriodic acid. The slow oxidation of the hydriodic acid furnished the iodine, and the compound thus obtained has the composition, according to Tilden, $2(C_8H_{10}N_4O_2HI{\cdot}I_2){\cdot}3H_2O$. It is a lower periodide than the one which is obtained when iodine dissolved in potassium iodide is directly added to caffeine, as the latter has the composition $C_8H_{10}N_4O_2.HI.I_4$. Tilden also mentions that by the addition of alcoholic iodine to a solution of caffeine in weak sulphuric or hydriodic acid, he obtained a deposition of black granules, which upon analysis furnished about 75 per cent of total iodine. He says that it probably consists of a compound containing nine atoms of iodine. But there is hardly any doubt that he had the tetraiodide of caffeine hydriodide.

Properties.—When dry the periodide is a violet-blue amorphous powder melting at 213° C. When moist it rapidly loses iodine on exposure to air. It is permanent when dry, and suffers but slight loss when heated to 100° C. Two grms. heated for four hours at that temperature lost only 0·027 grm. = 1·33 per cent. It loses but very little of its iodine when suspended in water, giving up enough iodine to saturate the liquid. The presence of potassium iodide in the water favours the liberation of iodine, but even then it is but slight. The periodide dissolves readily in alcohol, especially when heated, with considerable decomposition into the free base and iodine. It is more soluble in methyl alcohol and suffers less decomposition in that solvent. It can be obtained from methyl alcohol, on spontaneous evaporation of the solvent, in the form of beautiful crystals, with a metallic dark bluish lustre. When examined under the microscope the crystals appear to consist of six-sided prisms. Ether, whether cold or warm, decomposes it but slightly. The periodide is insoluble in chloroform, carbon disulphide, and benzene. It is soluble without decomposition in hot ethyl acetate, from which it separates on cooling as a dark granular crystalline deposit, which melts at 215° C.

Limits of Precipitation.—Like most alkaloids, caffeine is precipitated by Wagner's reagent even from very dilute solutions of the base. Although not characteristic, it is yet as delicate a test for caffeine as we have. The limits of precipitation, under the influence of different acids, will appear from the accompanying table. The tests apply to 1 c.c. of the solution mentioned, acidulated with two or three drops of the acid, and to this two drops of Wagner's reagent (twentieth normal) was added.

(To be continued).

Dilution.	Sulphuric acid. 5 per cent.	Hydrochloric acid. 5 per cent.	Nitric acid. 5 per cent.	Acetic acid. 5 and 50 per cent.	Oxalic acid. 5 per cent.	Tartaric acid. 10 per cent.	Citric acid. 10 per cent.
1 : 250	Very heavy.	Very heavy.	Very heavy.	None.	Heavy.	Slight.	Faint.
1 : 1000	Very heavy.	Very heavy.	Very heavy.	—	Heavy.	Very slight.	None.
1 : 1500	Heavy.	Heavy.	Heavy.	—	Slight.	None.	—
1 : 3000	Fair.	Fair.	Fair.	—	Faint.	—	—
1 : 5000	Very slight.	Slight.	Slight.	—	—	—	—
1 : 8000	Very slight.	Slight.	Slight.	—	—	—	—
1 : 10000	None.	Very slight.	Very slight.	—	—	—	—

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* From the *Journal of the American Chemical Society*, xviii., No. 4.

THE ACTION OF BORON ON IRON AND STEEL, AND ERRORS IN IRON ANALYSIS ACCOUNTED FOR BY THE PRESENCE OF THAT ELEMENT.

By H. N. WARREN, Principal, Liverpool Research Laboratory.

SOME five or six years ago a somewhat lengthy description was published in the CHEMICAL NEWS with respect to the action of boron upon metallic iron, which researches at that time led to the discovery of the now well-known compound boroneisen.

Quite recently some rather remarkable notes have appeared in scientific literature of the preparation of that compound by the aid of electrical furnaces; it is therefore the author's intention, after a long and varied experience with the element, to deny most emphatically that anything like such a temperature as the electric arc is required in order to form a boro-ferric compound. Even ordinary ferric borate, obtained by precipitating ferric chloride by means of a soluble borate, may, after drying, be readily reduced, at a red heat, to an amorphous—and at the same time pyrophoric—boride; or may be obtained of a silvery whiteness, fusible at a white heat and containing from 6 per cent boron, by melting the above-mentioned compound under a layer of borax, the compound being of sufficient hardness to cut glass and even scratch flint, the horon being set free in the elementary condition by means of electro dissolution. This, however, is by no means the only way of impregnating iron with boron; on the other hand, it is extremely difficult to prevent the formation of a boride, when a mixture of iron oxide and carbon is exposed to a temperature sufficient to melt the cast-iron thus produced, provided a fusible borate is used as a flux. Again, borax being such a desirable fluxing agent for metallurgic reductions, this compound is generally made use of in smelting small quantities of iron ores, for the purpose of further examination of the iron thus obtained. This reaction is, however, perfectly useless, provided a fluxable borate has been employed, as one hundred samples thus reduced by the author all contained more or less boron, averaging up to 2 per cent, while at the same time the iron in most cases appears solely as white cast, the carbon existing in the combined form; also, as a verification test, samples of cast-iron were exposed to different temperatures in common with fusible borates, the analyses of all these samples showing a deficiency on the total averaging from ½ to 2 per cent.

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VOLUMETRIC DETERMINATION OF MOLYBDENUM AND VANADIUM.*

By CARL FRIEDHEIM.

IN concert with H. Euler I have elaborated a volumetric method for determining molybdenum. It consists in decomposing the molybdate or molybdenum teroxide in Bunsen's apparatus with potassium iodide and hydrochloric acid, absorbing the liberated iodine in potassium iodide, and titrating with sodium thiosulphate in the usual manner.

F. A. Gooch and Charlotte Fairbanks (*Zeit. Anorg. Chem.*) have submitted this process to a re-examination, with the result that satisfactory values can be obtained only under conditions which they have ascertained and communicated.

Strictly speaking, it might be sufficient to point out that (as it appears from the figures given in my former communication), in my method the errors fluctuate between −0·09 and +0·36 (and not as Gooch and Fairbank state, between +0·05 and 1·13 per cent), whilst the authors just named obtain errors of from −0·14 to +0·45, in order to prove that, according to the proposed modification, the results obtained are not better, but worse. But as my method admits of more general application, and on this account any additional difficulty must be avoided such as would be involved in the new proposals, I must examine more closely some of the declarations of Gooch and Fairbanks.

The hydriodic acid liberated on treating molybdenum teroxide with potassium iodide and hydriodic acid is naturally—in as far as it is not oxidised by the molybdenum teroxide—decomposed by the oxygen of the atmosphere, which naturally must signify an increased elimination of iodine. This I pointed out expressly in my former communication, in which it is stated:—"We have found that this process of determination can be carried out—with the due observation of certain precautions—much more rapidly and quite as accurately in Bunsen's apparatus, and therefore by distilling the substance with potassium iodide and hydrochloric acid."

But if we heat the mixture of the above substances rapidly, too much iodine is liberated in the receiver; but if we work in such a manner that the reduction of the substance is effected before hydriodic acid escapes, we obtain the theoretical quantity of iodine.

Hence the following *modus operandi* results for the execution of the method:—0·2 to 0·3 grm. of the molybdate are mixed in the decomposition flask of Bunsen apparatus with 0·5 to 0·75 grm. of potassium iodide, and so much hydrochloric acid of sp. gr. 1·12 that the liquid may fill two-thirds of the flask. After connection with the escape tube and its introduction into the receiver, the contents of the flask are very slowly heated so as to reach ebullition, when the escape tube is filled as far as possible with iodine vapour and is just on the point of reflux. When the iodine is completely expelled, *i.e.*, when no more violet fumes are visible, and the solution takes a light-green colour, the distillation is at once broken off, and the iodine absorbed by potassium iodide in the receiver is titrated with sodium thiosulphate.

When Gooch and Fairbanks repeat these directions with the words "that the flask is two-thirds filled," and continue "the solution is not raised to ebullition until the flask is entirely filled with the heavy vapours of iodine, and is continued until iodine is no longer visible, and the liquid has taken a light-green colour," they have evidently quite overlooked that I laid particular emphasis on the exclusion of air; that is, on the non-contact of air and hydriodic acid.

(To be continued).

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* *Berichte d. Chem. Gesell.*

THE DETERMINATION OF ATOMIC MASSES OF SILVER, MERCURY, AND CADMIUM, BY THE ELECTROLYTIC METHOD.*

By WILLETT LEPLEY HARDIN.

(Continued from p. 79).

PART III.

Determination of the Atomic Mass of Cadmium.

NINE experimenters have determined the atomic mass of cadmium by many different methods, but the large variations in the results given by different chemists leave the true value of this constant still uncertain.

Stromeyer (Berzelius' "Lehrbuch," 5th Edition, iii., 1219) gave no details of his method of operation, but

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* Contribution from the John Harrison Laboratory of Chemistry No. 13. From the author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Ph.D.—From the *Journal of the American Chemical Society*, xviii., p. 990.

found that 100 parts of cadmium combined with 14,352 parts of oxygen. On the basis of O = 16, this ratio gives 111·483 for the atomic mass of cadmium. This result is much lower than those obtained by other experimenters, and is perhaps only of historical interest.

In a series of nine experiments, Von Hauer (*Journ. Prakt. Chem.*, lxxii., 350) determined the ratio of cadmium sulphate to cadmium sulphide. The sulphate used was purified by repeated re-crystallisations, and was finally dried at a temperature of 200°. After weighing the sulphate was always dried a second time and re-weighed. The two weighings never differed as much as one m.grm. The sulphide obtained was in each case tested for sulphate The reduction of the sulphate to sulphide was accomplished by heating the sulphate in a current of dry hydrogen sulphide under pressure. The mean of nine observations computed on the basis of O = 16 and S = 32·06 gives 111·93 for the atomic mass of cadmium. Considering the large quantity of material used each time, and the precautions taken to insure accuracy, there seems to be little objection to the method.

Dumas (*Ann. Chim. Phys.*, [3], lv., 158) determined the ratio of cadmium chloride to metallic silver by titrating a solution containing a weighed quantity of cadmium chloride with a silver nitrate solution of known strength. The cadmium chloride was prepared by dissolving metallic cadmium in boiling hydrochloric acid. The solution was evaporated to dryness, and the chloride fused for six hours in a current of hydrochloric acid gas. The mean of six determinations gives 112·24 for the atomic mass of cadmium (O = 16).

Maximum result, Cd = 112·759
Minimum ,, Cd = 111·756

Difference = 1·003

This large variation in the results obtained indicates the presence of impurities in the material used. In the first three experiments the cadmium was not purified; the mean of these three is Cd = 112·476. The metal used in the last three experiments was considered by Dumas to be absolutely pure; the mean of the last three results is Cd = 112·007. From the degree of purity of the cadmium chloride used in the different experiments, Dumas was inclined te reject the higher results, and concluded that the true atomic mass of cadmium was about 112.

Lensen (*Journ. Prakt. Chem.*, lxxix., 281) prepared pure cadmium oxalate by precipitating a solution of cadmium chloride, purified by repeated crystallisation, with pure oxalic acid. The precipitate was washed and carefully dried at a temperature of 150°. The mean of three results obtained by converting a weighed portion of the oxalate to oxide gives 112·06 for the atomic mass of cadmium (O = 16), The small quantity of material used in the different experiments is somewhat objectionable.

Huntington (*Proc. Amer. Acad.*, xvii., 28) under the direction of Cooke, determined the ratio of cadmium bromide to silver bromide, and also the ratio of cadmium bromide to metallic silver. The bromide used was prepared by dissolving cadmium carbonate, which had been carefully purified, in pure hydrobromic acid. The product obtained was dried at a temperature of 200°, and finally sublimed in a porcelain tube in a current of dry carbon dioxide. In the first series of experiments the silver bromide corresponding to the cadmium bromide used was weighed. The mean of eight determinations computed from the total quantity of material used and silver bromide obtained, on the basis of Ag = 107·93 and Br = 79·95, is Cd = 112 24. In the second series of experiments the quantity of metallic silver required to precipitate a known quantity of cadmium bromide was determined. The mean of eight determinations computed as in the first series gives 112·245 for the atomic mass of cadmium. The separate determinations in both series agree very closely.

Partridge (*Amer. Journ. Sci.*, [3], xl., 377) made three series of determinations. The first depended upon the conversion of cadmium oxalate into oxide, the second, on the reduction of the sulphate to sulphide, and the third, on the conversion of the oxalate into sulphide. The cadmium used in these experiments was purified by distilling twice *in vacuo*. Ten observations on the conversion of the oxalate into oxide, computed on the basis of O = 16 and C = 12, give 111·801 as a mean for the atomic mass of cadmium. Re-calculated by Clarke (*Amer. Chem. Journ.*, xiii., 34), on the basis of O = 16 and C = 12·005, the atomic mass of cadmium becomes 111·818. The mean of ten results obtained by reducing the sulphate to sulphide, computed on the basis of O = 16 and S = 32, gives 111·797 for the atomic mass of cadmium. Re-calculated by Clarke on the basis of O = 16 and S = 32·074, the atomic mass of cadmium is 111·711. In the third series the oxalate of cadmium was converted into sulphide by heating in a current of dry hydrogen sulphide. The mean of ten determinations, computed on the basis of O = 16 and S = 32, gives 111·805 for the atomic mass of cadmium. Re-calculated by Clarke on the basis of O = 16 and S = 32·074, the mean becomes 111·589. Partridge gives 111·8 for the atomic mass of cadmium, as a mean of the three series. If the higher values for carbon and sulphur be introduced this value becomes somewhat lower.

Jones (*Amer. Chem. Journ.*, xiv., 261) determined the atomic mass of cadmium by two different methods. The first was based on the conversion of the metal into oxide, and the second on the conversion of the oxalate into oxide. The cadmium used was distilled six times *in vacuo*. The last distillate was tested spectroscopically, and found to be free from impurities. In the first series of experiments a weighed portion of the pure metal was dissolved in pure nitric acid in a porcelain crucible. The solution was evaporated to dryness, and the resulting cadmium nitrate ignited to oxide. The final decomposition was accomplished by means of a blast lamp. Reducing gases were carefully excluded from the crucible during the process of ignition. The weighings were all made against a tared crucible. The mean of ten observations, computed on a basis of O = 16, gives 112·07 for the atomic mass of cadmium. The different determinations agree very closely. In the second series of experiments cadmium oxalate, prepared by precipitating pure cadmium nitrate with pure oxalic acid, was converted into oxide. The material was carefully ignited until the oxalate was decomposed; it was then treated with nitric acid, and again ignited in a manner similar to that described in the first series. The mean of five determinations computed on the basis of O = 16 and C = 12·003, is Cd = 111·032. From all the observations Jones concludes that 112·07 represents very closely the atomic mass of cadmium (O = 16).

Lorimer and Smith (*Ztschr. Anorg. Chem.*, i., 364) determined the ratio of the atomic mass of cadmium to that of oxygen by dissolving pure cadmium oxide in potassium cyanide and electrolysing the solution. To obtain pure material, the commercial cadmium was dissolved in nitric acid, and the solution evaporated to crystallisation. The crystals of cadmium nitrate were removed from the liquid, dissolved in pure water, and re-crystallised. The product obtained by the second re-crystallisation was dissolved in a little water and treated with a slight excess of potassium cyanide in a platinum dish. From this solution the metallic cadmium was thrown out by means of the electric current. The nitrate obtained by dissolving the electrolytic cadmium in pure nitric acid was tested spectroscopically and found to be free from impurities. The pure cadmium nitrate was digested with ammonium hydroxide and ammonium carbonate, and the resulting cadmium carbonate ignited to oxide in a platinum crucible. The method of operation was very simple, a weighed portion of the oxide was dissolved in pure potassium cyanide, the solution electrolysed, and the resulting metallic cadmium weighed. The mean of nine observations computed on the basis of $O=16$ gives 112·055 for the atomic mass of cadmium.

Bucher (Thesis, Johns Hopkins University, 1894) made six series of experiments. The cadmium used was purified by nine distillations *in vacuo*. The weighings were all reduced to a vacuum standard, and computed on the basis of $O=16$, $S=32·059$, $C=12·003$, $Cl=35·45$, $Br=79·95$, and $Ag=107·93$.

In the first series cadmium oxalate, dried for fifty hours at 150°, was ignited to oxide. The mean of eight observations gives 111·89 for the atomic mass of cadmium.

In the second series, cadmium oxalate was converted into sulphide by heating in a current of dry hydrogen sulphide. Ths mean of four determinations is $Cd=112·15$.

In the third series a weighed quantity of cadmium chloride, dried at a temperature of 300° in hydrochloric acid gas, was precipitated with silver nitrate, and the resulting silver chloride weighed. The mean of twenty-one determinations is $Cd=112·39$. The separate observations in this series agree very closely.

The fourth series was similar to the third, except that cadmium bromide was used instead of the chloride. The mean of five determinations is $Cd=112·38$, a result almost identical with that obtained from the chloride.

In the fifth series a weighed portion of metallic cadmium was converted into sulphate, which was dried at 400° and weighed. The excess of sulphuric acid which remained with the sulphate was estimated and its weight deducted. The only result given is $Cd=112·35$.

In the last series metallic cadmium was converted into oxide by dissolving in nitric acid and igniting the resulting cadmium nitrate. The mean of two determinations made by igniting the material in a porcelain crucible gives 112·08 for the atomic mass of cadmium. Three similar determinations made with a platinum crucible gave as a mean $Cd=111·87$. From a series of experiments on cadmium oxide, Bucher concluded that a correction should be applied to the last and also the first series. By making this correction, the results in these two series would be very close to those obtained from the chloride and bromide.

From all the preceding determinations Clarke gives 111·93 as the most probable value for the atomic mass of cadmium. The large variation in the results of different experimenters has not been fully explained. Some chemists think that the larger values are due to a higher degree of purity in the metallic cadmium used, and hence regard these values as being more nearly correct. But it must be remembered that the reverse is true in the experiments of Dumas. From material which had not been purified, Dumas obtained results ranging from 112·32 to 112·76 for the atomic mass of cadmium, while from material which he considered absolutely pure, the results were from 111·76 to 112·13.

Preparation of Pure Cadmium.

The metallic cadmium used in these experiments was purified by distillation in a current of hydrogen which had been passed through solutions of caustic potash, lead nitrate, potassium permanganate, and sulphuric acid. A hard glass combustion tube was heated to redness, and the walls of the tube indented at two points with a three-cornered file. This divided the tube into three parts. Commercial cadmium was placed in one end of the tube, and connection made with the hydrogen generator. After complete removal of the air, the tube was carefully heated in a combustion furnace until one-half of the metal had distilled over into the middle portion of the tube. The metal was cooled in a current of hydrogen. The tube was then broken and the metal removed. The portions in the first and last sections of the tube were rejected. The middle portion was placed in a second combustion tube, similar to the first, and the distillation repeated. After three distillations the metal was examined spectroscopically and found to be free from impurities.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Special General Meeting, February 12th, 1897.

The Chair was taken by Captain Abney, who, as retiring President, referred to some of the changes which had occurred in the Society during the past year.

The Annual Subscription had been raised, but a satisfactory number of new Fellows had been enrolled. The Society had lost two by death. A good deal of work had been done in the direction suggested by the discoveries of Röntgen.

The Treasurer, Dr. Atkinson, then presented his Report and Balance-sheet for the year 1896. There was evidence of improvement in the financial position, but there was still a deficiency to be met. Profits from sales of publications had been small; it was desirable to reduce the price of the volumes of collected papers of Joule and Wheatstone, and to call the attention of physicists to these valuable records of classical work.

Mr. Walker suggested that physical laboratories, especially those in London, should be visited by Fellows of the Society, with a view to comparing notes as to the construction of apparatus; professors of colleges and other institutions should be invited to appoint visiting days for this purpose.

Votes of thanks were passed to the retiring President, Council, and Officers, and also to the Council of the Chemical Society for the use of their rooms at Burlington House.

In replying, Capt. Abney said that the coming year would probably bring about further improvements in the system of abstracting and indexing, by co-operation with other societies at home and abroad. He then read the list of Council and Officers for the year 1897-8:—

President—Shelford Bidwell, M.A., LL.B., F.R.S.

Vice-Presidents, who have filled the Office of President—Dr. Gladstone, Prof. G. C. Foster, Prof. Adams, The Lord Kelvin, Prof. Clifton, Prof. Reinold, Prof. Ayrton, Prof. Fitzgerald, Prof. Rücker, Capt. Abney.

Vice-Presidents—Maj.-Gen. E. R. Festing, L. Fletcher, Prof. Perry, G. Johnstone Stoney.

Secretaries—T. H. Blakesley, H. M. Elder.

Foreign Secretary (new office)—Prof. S. P. Thompson.

Treasurer—Dr. Atkinson.

Librarian—C. Vernon Boys.

Other Members of Council—Walter Bailey, L. Clark, A. H. Fison, Prof. Fleming, R. J. Glazebrook, Prof. A. Gray, G. Griffith, Prof. Minchin, Prof. Ramsay, J. Walker.

The newly-elected President, Mr. Shelford Bidwell, then took the Chair, and an Ordinary Meeting was held.

Mr. Blakesley read a paper by Mr. H. H. Hoffert, "*On the Use of very small Mirrors with Paraffin Lamp and Scale.*"

For the mirrors of reflecting instruments the author prefers small rectangular strips of microscope cover-glass, chosen thin and plane. These are first silvered, and then cut to shape by a splinter of diamond embedded in wax. They are about 8 m.m. long by 1·5 m.m. broad, and are suspended so that their longest sides are vertical. Rectangular mirrors suspended in this way are lighter, and have less inertia than round mirrors of equal aperture. A paraffin-lamp flame placed edgewise to the mirror gives sufficient illumination. The image of the flame is focussed on the mirror by a lens midway between them; it is a right vertical line, and thus conforms to the shape of the mirror. A scale is fixed upon a screen between the lens and lamp; and the screen has a circular aperture just below the centre of the scale, provided with a vertical cross-wire. The relative position of screen and lens is adjusted so that an image of the wire is formed upon the scale after reflection at the mirror.

Mr. **Boys** said he had frequently used small mirrors constructed as described by the author, and he could not see what was new in the method, except that a paraffin lamp had been found sufficiently bright for the purpose. It is desirable to diminish inertia by choosing extremely thin glass. Microscope cover-glasses are generally supplied in squares or discs very fairly equal in size; if they are dealt out on a table, like a pack of cards, their relative thicknesses can be judged by the note produced as they fall. Flatness can be estimated nearly enough by balancing them one by one upon the knuckle, nearly level with the eye, and observing the reflection of an illuminated straight edge, such as a window-bar. All rejected glasses should be broken. The good ones can be further examined by a telescope and artificial star. A common writing diamond is best for cutting the thin plates. Special care must be taken not to distort the mirror in fixing to the suspended system. If liquid shellac is used in the attachment distortion will certainly occur,—at any rate, if it is applied throughout the whole length of the mirror. The best way is to make the attachment at a mere point, near the top of the mirror, using a speck of shellac as viscous as possible, and heating, if necessary, by radiation, not by conduction. Mr. Boys thought that a reflecting prism near the mirror might be used in certain cases where a paraffin lamp with its inevitable vertical flame was required for horizontal projections. For general purposes Mr. Boys prefers some such arrangement as the following:—If the source of light is a point, a lens is employed, forming an image of the source upon the mirror. (If the source of light is a surface, this lens is evidently superfluous). The cross-wire is stretched near to the lens on the side towards the mirror. It is now necessary to focus the cross-wire upon the scale, and this is best done by a plano-convex fixed lens as near as possible to the mirror, with its plane face towards the mirror. The light passes twice through the lens. As it may be necessary to change the plano-convex lens from time to time, according to the distance of the scale, Mr. Boys attaches it with a little vaseline to a strip of plate glass in front of the instrument. One advantage of such an optical system is that it allows the instrument to be set up in the same position with respect to the scale at all times.

Dr. **Thompson** pointed out that Mr. Hoffert had obtained his results using only *one* lens, by properly choosing the position of the cross-wire.

A vote of thanks was given to the author, and the meeting adjourned until February 26th.

NOTICES OF BOOKS.

Water and its Purification; a Handbook for the Use of Local Authorities, Sanitary Officers, and others interested in Water Supply. By **Samuel Rideal**, D.Sc., Fellow of University College, London, F.I.C.; Examiner in Chemistry to Royal College of Physicians; Public Analyst for the Lewisham District Board of Works; Water Examiner to the Guildford Rural District Council; Author of "Disinfection and Disinfectants." With numerous Illustrations and Tables. London: Crosby Lockwood and Son, Stationers' Hall Court. Pp. 292. 1897.

Writings discussing municipal water supply resolve themselves into two grand categories. The one deals with the outgoing waters, their purification or disinfection, and their utilisation. The other class, of which the volume before us is an excellent specimen, discusses the incoming waters, their suitability for domestic and industrial purposes, and their improvement whenever practicable.

In the remarks on natural waters Dr. Rideal shows that an appeal to the physical characters of a water is not trustworthy, and may even be dangerously deceptive. He rightly urges that even traces of the poisonous metals render a water inadmissible for household consumption. Lead, the most insidious and dangerous of metallic impurities, is, unfortunately, often introduced by lead service-pipes. Some waters, however, have the dangerous property of rapidiy attacking lead. This is especially the case with peaty waters. Cisterns for water-supply are rightly and emphatically condemned.

It is an unfortunate circumstance that the upland areas, uncultivated and unpeopled, are not sufficient to afford drainage grounds for the supply of adjacent cities. The instance of Manchester is most instructive. A few years ago its supply from a series of reservoirs constructed in Longdendale (not Longerdale), the drainage off the millstone grit, and the uncultivated moor-lands, was viewed as sufficient not merely for the present but the future. But recently it has been found insufficient, and an additional supply has been obtained from Thirlmere in Cumberland. Contrary to our fears the engineering operations near this lake have not interfered with the beauty of the scenery.

Dr. Rideal rightly holds that it is the duty of the State to apportion the upland water-sources to the needs of the population.

Mention is made of the Holmfirth catastrophe, and of the still more appalling disaster at Sheffield.

The London County Council proposes to derive the future supply of the metropolis from Wales, taking the head waters of the Usk, Wye, and Towey, and conveying them by two aqueducts of respectively 150 and 175 miles in length. The great objection to this scheme would be the necessity of guarding the aqueducts and bridges from possible mischief on the part of bodies whom—as we are not a political organ—we cannot here point out. The suggestion that the purer mountain water might be "exclusively used for drinking purposes," and employing ordinary waters for washing, trade, and sanitary purposes, would certainly lessen the demand on the upland areas, but would at the same time burden the consumer with the expense of a duplicate system of mains and service pipes.

On page 101 we find the standards of the Thames Conservancy. This body demands that discharges into the river must be:—

1. Free from offensive odour.
2. Free from suspended matter.
3. Neither acid or alkaline to test papers.

This requirement Dr. Rideal acutely pronounces impossible, since natural waters are almost invariably acid to one test on account of free carbonic acid, and alkaline to another owing to carbonates. The author suggests that limits of permissibility should be given.

4. Not more than 60 grs. per gallon of total solids.
5. Not more than 2 grs. per gallon of organic carbon, and 0·75 grs. per gallon of organic and ammoniacal nitrogen.
6. Not less than one cubic inch of free oxygen per gallon.

Concerning the action of soft waters upon leads we find two conflicting statements. On page 117 we read "that its (the water of Loch Katrine) only fault is that it acts rapidly upon lead, of which we shall speak further." But on page 137, after speaking of the soft water of the Varty (Dublin), the author writes: "The equally soft water of Lock Katrine has little or no action upon this metal."

On page 97 Dr. Rideal points out the danger of allowing pigs to wade in streams, and consequently to introduce into them parasites.

The self-purification of rivers is exemplified in Dr. P. Frankland's paper on the river Dee (p. 105).

On the question of constant *v.* intermittent water service the author takes the right view, condemning the latter procedure, which has justly gone out of use in most places except London.

In speaking of filters, which the author does at great length and with thorough fairness and accuracy, he shows that all domestic filters, except the Pasteur-Chamberland, are of very doubtful efficacy, if not positively harmful. The Berkenfeld filter requires to be boiled either once or twice every twenty-four hours.

Referring to the mains and service pipes for the distribution of water in cities, our author recommends that the pipes should be laid not less than four feet below the surface, and should pass within about three feet of the kitchen grate before branching off to different parts of the establishment.

It is unfortunate that no one has the power to enforce these standards as against "Jerry."

In our opinion Dr. Rideal has made in this book a valuable contribution to our sanitary literature.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 3, January 18, 1897.

Researches on Helium.—M. Berthelot.—The author has succeeded in combining helium, both with the elements of the hydrogen carbides, and with those of carbon disulphide, with the intervention of mercury and the influence of the electric effluve, all precisely under the same conditions in which he has realised the combination of argon. In both cases these syntheses have been checked by analysis; that is to say, by the regeneration of the element in a free state.

Remarks on the Specific Heats of Elementary Gases, and on their Atomic Constitution.—M. Berthelot.—The author calls attention to the following values of specific heat at constant volumes, referred to an identical volume of the elements, such as that occupied by 2 grms. of hydrogen:—

Gas with a monatomic mol.	3·0
Diatomic gas	4·8 (not split up at present, and 6·6 split up above 1500°).
Tetratomic gases	11·4

It will be remarked that the ratio of these values, measured near the ordinary temperature (between 0° and 300°), is not remote from that of 1 : 2 : 4; that is to say, that the specific heats of the simple gases at a constant volume are approximately proportional to the number of atoms contained in the molecule. Besides the four groups of gaseous elements just distinguished, there are others, such as contain triatomic elements, *e.g.*, ozone, comparable to hyponitric gas; and certain hexatomic elements, sulphur and selenium. But their specific heat is hitherto unknown. We know how for the simplified notions deduced from a first study of the elementary gases anciently known, *e.g.*, hydrogen, oxygen, and nitrogen, there are being substituted more profound notions on the physico-chemical constitution of the elements.

Classification of the Chemical Elements.—Lecoq de Boisbaudran.—This paper will be inserted at some length.

Certain Salts and Derivatives of Dinitro-orthocresol.—P. Cazeneuve.

Law of the Transparency of Gases for X Rays.—L. Benoist.—In the earliest experiments on the X rays it was remarked that the opacity of different bodies for the rays increased in general with their density, and it was thought that a simple relation such as direct proportionality might exist between these two characters. With gaseous bodies the case is different. With sulphurous acid, methyl chloride, and air the absorption produced is proportional to the density of the gas employed. This is the relation which Lenard has already obtained for the kathodic rays before Röntgen's discovery. As the specific absorbent power of gases resulting from the foregoing measurements gives the value 0·14, aluminium gives the value 0·09; the deviation is not great, whence aluminium would almost satisfy a general law of proportionality between the absorbent power and the density. On the contrary, silver gave 0·84—a number six times too great.

Speed of the Reduction of Chromic Acid by Phosphorous Acid.—G. Viard.—This paper requires the formulæ and the table here introduced.

Action of Hydrogen Sulphide and Selenide upon Phosphonyl Chloride.—A. Besson.—If we dissolve dry hydrogen sulphide at 0° in $POCl_3$ and leave it in a closed vessel, in a few hours the liquid becomes milky, and after twenty-four hours there collects at the lower part of the vessel a light bulky amorphous precipitate, whilst the supernatant liquid becomes limpid. If the experiment is prolonged, there is a slow formation of crystalline needles. Both the amorphous precipitate and the crystalline needles have the same composition, $P_2O_2S_3$; that is, an oxy-sulphide. Dry hydrogen selenide has no perceptible action upon $POCl_3$ in the cold, but at 100° it reacts slowly, forming phosphonyl selenide.

Action of Ethyloxalyl Chloride upon Pseudocumène and Mesitylene.—E. Bouveault.—These two papers are not suitable for abridgment.

Decrease of the Nitrogenous Matter in the Wheats of the Department "Du Nord."—M. Balland.—The nitrogenous matter, which in 1848 varied between 10·23 and 13·02 per cent, is now between 8·96 and 10·62 per cent.

The Reproduction of Colour by Photographic Methods.—Sir Henry Trueman Wood is announced to read a paper at the Society of Arts on this subject on the 24th inst. Captain Abney, C.B., F.R.S., will preside. Illustrations will be shown of several of the recently invented processes for the photographic reproduction of colour.

On Chromium and Manganese Phosphides.—A. Granger.—The analysis of these phosphides is delicate, on account of the difficulty ot separating phosphoric acid from chromium and manganese oxides. The author reduced the substances to a fine powder, treated them with melting potassa, raising the temperature gradually to dull redness, and keeping the mass in tranquil fusion for 1½ hours. The mass, when cold, is dissolved in boiling water, acidified with nitric acid in the case of chrome, or with hydrochloric acid in the case of manganese. The chromic solution is then treated with ammonium molybdate to precipitate phosphoric acid. In the filtrate the chlorate is reduced to the state of a salt of chrome which is precipitated in the state of sesquioxide, carrying molybdenum down with it. The precipitate, dissolved and re-precipitated, yields an oxide sufficiently free from foreign salts. The manganic solution, evaporated to dryness with hydrochloric acid in excess, is neutralised with ammonia, and ammonium sulphide is added. We evaporate to dryness, and add a further quantity of the latter reagent; re-dissolved in water, and filtered, the precipitate contains all the manganese, and in the filtrate the phosphoric acid is determined as usual.

MEETINGS FOR THE WEEK.

MONDAY, 22nd.—Society of Arts, 8. (Cantor Lectures). "Industrial Uses of Cellulose," by C. F. Cross, F.C.S.

TUESDAY, 23rd.—Royal Institution, 3. "Animal Electricity," by Prof. A. D. Waller, F.R.S.

WEDNESDAY, 24th.—Society of Arts, 8. "Reproduction of Colour by Photographic Methods," by Sir Henry Trueman Wood.

THURSDAY, 25th.—Royal Institution, 3. "The Problems of Arctic Geology," by J. W. Gregory, D.Sc., F.R.S.

—— Society of Arts, 8. "The Mechanical Production of Cold," by Prof. James A. Ewing, M.A., F.R.S.

FRIDAY, 26th.—Royal Institution, 9. "Palestine Exploration," by Lieut.-Col. C. R. Conder, R.E.

—— Physical, 5. "Photography of Ripples," by J. H. Vincent.

SATURDAY, 27th.—Royal Institution, 3. "The Growth of the Mediterranean Route to the East," by Walter Frewen Lord.

TO CORRESPONDENTS.

A. G. A.—You had better write to the Secretaries of the various societies to which you wish to belong. They will send full particulars of qualifications required.

Analytical and Manufacturing Chemist wanted. One with a good knowledge of the Manufacture of Small Chemicals preferred.—Please apply, in strict confidence, giving full information as to age, experience, and salary required, to "Manufacturer," CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Chemist wanted, Chemical Works in London. —His duties would be principally in the Lsboratory, but it would be essential that applicants should have had practical experience as Works Manager.—Reply, stating age, past experience, and salary required, to C.C.C., care of Clarke, Son, and Platt, 85, Gracechurch St., London.

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THE CHEMICAL NEWS.

VOL. LXXV., No. 1944.

ON THE
REMOVAL OF OXIDE FROM MELTED COPPER AND COPPER ALLOYS.

By SERGIUS KERN, M.E., St. Petersburg.

THE following is perhaps not new to many metallurgists, but the *modus operandi* of the application of phosphorus for cleaning copper alloys, just before casting them into ingots or mouldings, must be new to many.

In order to reduce the oxides and to obtain dense and solid castings, for several years the Obouchoff Works here have successfully used our plan, which is as follows:—

In order to safely throw the phosphorus into the pots of melted copper, just before drawing them out of the furnace, the phosphorus is submitted to the following treatment: — Phosphorus is cut into pieces, weighing about 3 ounces each, and placed in a concentrated solution of copper sulphate, where it is kept for further use. From time to time fresh copper sulphate is added, and pieces of phosphorus also, after taking out for foundry uses pieces of phosphorus already covered with precipitated copper.

In this manner it is easy to handle phosphorus, which also when thrown into pots does not take fire at once, but safely reaches the melted metal to act in the desired manner.

About two pieces are usually sufficient for 1 cwt. of metal in the pot.

The addition of phosphorus in the mentioned manner to copper plays the part of ferromanganese to steel.

February 13, 1897.

HYPOIODOUS ACID AND HYPOIODITES.*

By R. L. TAYLOR, F.C.S.

THE author confirms and extends the observations of Schönbein, using, as he did, *an aqueous solution of iodine*. When a little alkali is added there is practically no iodate formed, from 90 to 95 per cent of the iodine undergoing the reaction represented by the equation—

$$2KOH + I_2 = KI + KOI + H_2O.$$

This is proved by the bleaching action upon a standard solution of indigo, and also by Schwicker's method of decomposing the hypoiodite by a bicarbonate or by carbonic acid.

The solution bleaches indigo much more rapidly than chlorine or hypochlorites, but does not bleach litmus. It gives a precipitate with cobalt nitrate which blackens on standing, and an immediate brown precipitate with manganous salts and lead salts. Stronger solutions are obtained by using iodine water containing a little suspended iodine. All the solutions are decomposed completely by boiling for three or four minutes. The author concludes that the reaction represented above, as Walker and Ray have also recently stated, is a balanced one. He has repeated Lunge and Schoch's experiments, who obtained, by the action of iodine upon lime in presence of comparatively little water, a bleaching liquid which stood being boiled for hours without being decomposed. He concludes that their observations were practically only correct so far as they agreed with those of Schönbein. The author has also investigated the action of precipitated mercuric oxide upon iodine water, and find that hypoiodous acid is formed. The filtered (colourless) solution possesses only the feeblest possible bleaching properties, but the addition of a little alkali transforms it at once into as strong a bleaching solution as Schönbein's, and which it now exactly resembles. By the methods mentioned above it is found that from 40 to 45 per cent, out of a possible 50 per cent, of the iodine used exists in the solution as hypoiodous acid. By using iodine water and a little suspended iodine, a stronger solution is obtained, which very soon decomposes, turning brown, owing to the liberation of iodine. The hypoiodous acid probably decomposes as follows:—

$$3HOI = 2HI + HIO_3.$$

and the hydriodic acid and iodic acid immediately decompose each other, with liberation of iodine. The author suggests a possible explanation of the feeble bleaching power of the free acid in the instability of the hydriodic acid which will be left, compared with the alkaline iodides.

A solution containing hypoiodous acid also appears to be formed by the action of various silver salts upon iodine water, the best results being obtained with silver nitrate and silver carbonate. These liquids bleach much more rapidly than the one described above, probably because of the silver which is present; but they are much less rapid in their bleaching action than the alkaline hypoiodites. In other respects they resemble Schönbein's solutions, being, however, much less stable, this again being probably due to the presence of silver in the solution. The liquid obtained by adding a few drops of nitrate of silver to aqueous iodine loses 90 per cent of its bleaching power in five minutes.

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* Summary of a Paper read at the Manchester Literary and Philosophical Society, February 9th, 1897.

OPENING UP OF SILICATES.

By P. JANNASCH.

FOR this purpose the author uses pure lead silicate, and finds it satisfactory. He proceeded from Bong's proposal to use lead oxide for this purpose, supported upon the favourable experiments which he made in concert with J. Locke in determining the water in topaz. Jannasch proposes to mix the silicate (freed from organic matter, if necessary by ignition) with from ten to twelve parts of lead carbonate, and heat it in a platinum crucible, 52 to 53 m.m. in height, and 45 m.m. wide at top, for from fifteen to twenty minutes at first, with a flame of about an inch in height. It is then heated to fusion, but the crucible must not be red-hot for more than one-third of its height. The fusion is continued for ten to fifteen minutes. Care must be taken that the flame does not smoke in order to avoid any reductive action. The crucible is taken directly from the flame and plunged into cold distilled water. The melt is removed from the crucible by gentle tapping and squeezing, and decomposed with nitric acid, and finally evaporated repeatedly to dust-dryness with concentrated nitric acid, and the residue is taken up with 10 c.c. of concentrated nitric acid, diluted with 75 to 100 c.c. of water, heated on the water-bath for fifteen minutes, filtered and washed.

The filtrate is mixed with abundance of hydrochloric acid; after settling the lead chloride is sucked off and washed with hydrochloric acid (1 vol. concentrated acid + 1 vol. water). The filtrate is evaporated down (to expel nitric acid) with 30 c.c. hydrochloric acid (1 : 4) and as much water. The residue of the lead chloride is filtered off and quickly washed with cold water. The traces of lead left in the filtrate are precipitated with sulphuretted hydrogen. The hydrogen sulphide is then entirely removed from the filtrate.—*Zeit. Anorg. Chemie.*

A SENSITIVE SIMPLE REACTION FOR NITROUS ACID.

By Prof. Dr. E. RIEGLER.

We introduce into a small test-tube about 2 or 3 centigrms. of crystallised naphthionic acid, and from 5 to 6 c.c. of the liquid to be examined for nitrous acid, shake up well, add 2 or 3 drops of concentrated hydrochloric acid, shake up thoroughly for a minute, and allow from 20 to 30 drops of ammonia to flow slowly into the test-tube whilst held in a slanting position; when there appears at the surface of contact of the liquids a rose-coloured ring, even if only traces of nitrous acid are present. If we shake up the entire liquid it becomes rose-coloured or deep red, according to the quantity of the nitrous acid.

As very dilute solutions of naphthionic acid have a violet-blue fluorescence, it is advantageous to examine the colour by transmitted light.

The reaction consists herein, that the naphthionic acid is converted by the nitrous acid into diazo-naphthalin sulphonic acid, which forms with another mol. of naphthionic acid, and with ammonia a colouring matter which determines the rose colouration.

In rain and drinking waters the nitrous acid can be very finely shown by means of this reaction. The detection of nitrites in saliva is extremely instructive. To this end we dilute the saliva with five times its volume of pure distilled water, filter, and treat 5 or 6 c.c. of the filtrate as above directed.

Traces of nitrous acid may in like manner be detectable in urine.—*Zeit. Analyt. Chemie.*

WORKING UP URANIUM RESIDUES.

By A. GOWALOWSKI.

In this paper I formerly described a method for working up uraninm phosphate residues. Supported upon Laugier's observations I used ammonium carbonate for dissolving hydrated uranium phosphate, but I have now abandoned this method in favour of sodium carbonate (ammonia soda), which is both cheaper and has a greater solvent power. By introducing the uranic precipitate into a strong solution of ammonia soda, I dissolve the uranium phosphate, filter, and add rather more ferric chloride than is necessary to take up all the phosphoric acid, and filter again, when iron phosphate and ferric hydrate remain, which are washed with water. I treat the entire filtrate in small portions with magnesia mixture as long as there appears a turbidity of ammonio-magnesium phosphate, whereby any residues of phosphoric acid are separated. From the solution precipitate uranium oxide with sodium carbonate; filter after standing for twenty-four hours, and dissolve either at once in acetic acid or acidify previously with hydrochloric acid, boil to expel carbonic acid, precipitate with ammonia, collect the ammonia-uranic oxide on the filter, wash, and dissolve in acetic acid or in nitric or hydrochloric acid.—*Zeit. Analyt. Chemie.*

Isomerism of Structure and of Rotatory Power.—Ph. A. Guye and J. Guechgorine.—It results from these researches that we know at present three series of propylic isomers and three series of butylic isomers among the derivatives of active amylic alcohol. If we take account of the decreasing character of the rotatory powers in each of these series, we conclude that in all these series the propylic group behaves as heavier than the isopropyl group, and that the isobutyl group behaves as heavier than normal butyl, which in turn acts as heavier than secondary butyl.—*Comptes Rendus*, cxxiv., No. 5.

ON THE ACTION OF WAGNER'S REAGENT UPON CAFFEINE, AND A NEW METHOD FOR THE ESTIMATION OF CAFFEINE.*

By M. GOMBERG.

(Concluded from p. 90).

Estimation of Caffeine.

All the methods for the estimation of caffeine depend upon the extraction of the alkaloid by an immiscible solvent from either a dry residue or from its solution in water. But Spencer (*Journ. Anal. Chem.*, iv., 390, 1890) has recently shown how difficult it is to remove the alkaloid from its solution in water. According to him, it is necessary to shake out the liquid at least seven times with chloroform, in order to remove caffeine quantitatively. It is usually stated that caffeine does not form any stable salts in a watery solution, and consequently it can be shaken out with immiscible solvents from either alkaline or acid solutions. But this is only relatively true, as will appear from the following illustrations. 1·0085 grms. of caffeine were dissolved in 60 c.c. of sulphuric acid (1 : 10), and this solution was repeatedly shaken out with chloroform, 25 c.c. at a time.

10 consecutive portions of chloroform gave a total of	0·3514	grm. caffeine.
3 additional portions of chloroform made a total of..	0·4859	,, ,,
3 more additional portions of chloroform made a total of ..	0·5034	,, ,,

The extreme delicacy of the test for caffeine by means of Wagner's reagent has suggested the possibility of applying this reagent for the quantitative estimation of the alkaloid. Its successful application necessitates, of course, a solution of the alkaloid free from other substances that are precipitated by, or absorb iodine,—a condition requisite in the estimation of any base by means of Wagner's reagent. This method gives very satisfactory results, as nearly theoretical as could be expected. I am indebted for the analytical data of the subjoined table to Mr. James W. Knox, holder of the Stearns' Fellowship in the School of Pharmacy. The method of procedure employed by us was practically the same as that used by Kippenberger. Definite volumes of acidulated solutions of caffeine were precipitated with a known volume of iodine in potassium iodide. After complete precipitation an aliquot portion of the supernatant liquid was obtained, either by decantation or filtration, and the excess of iodine was estimated by titrating against a tenth normal solution of sodium thiosulphate. The precipitation is best performed in a tall test-tube on foot, and the solution for titration is removed directly by immersing the end of the burette into the liquid and applying suction at the upper end. When it is desirable to filter off an aliquot portion, a filter of glass-wool and asbestos gives very satisfactory results.

We have tested the method on solutions of caffeine acidulated with sulphuric acid, the solutions being of different strengths, namely, containing 0·25 per cent of caffeine, 0·50 per cent, 0·75 per cent, and 1·00 per cent respectively. We have varied in different series of experiments the amounts of Wagner's reagent, employing just the theoretical quantities, a small and large excess above that, as well as quantities below those required by the theory. Columns I., II., III., and IV., give the results obtained by allowing the solutions to stand for an hour before decanting an aliquot portion for titration; column V. shows the results obtained when the liquid for titration was filtered off within five minutes after the addition of Wagner's reagent. The results are calculated on the basis that the periodide has the composition

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* From the *Journal of the American Chemical Society*, xviii., No. 4.

$C_8H_{10}N_4O_2.HI.I_4$. The amount of alkaloid is calculated from the amount of iodine used up, by the formula—

$$4I : C_8H_{10}N_4O_2 :: 506 : 194;$$

i.e., one part of iodine represents 0·3834 part of caffeine. Or, 1 c.c. tenth normal iodine = 0·00485 grm. caffeine.

The results presented below show that the estimation of caffeine by this method is very exact. The best results are obtained when iodine is in considerable excess, as is evident from the figures obtained where one and one-third and twice the theoretical quantities of Wagner's reagent were used. All the results in the table were obtained on solutions of caffeine acidulated with sulphuric acid, the acidulation being tolerably strong, about 1 c.c. of the concentrated acid to 50 c.c. of the liquid. Experiments upon the influence of the acid indicate that a large excess of sulphuric acid interferes to some extent with the reaction. The amount of recovered caffeine falls as low as 95 per cent of the quantity taken, when 4 c.c. of the concentrated acid to 50 c.c. of the liquid are used. The results are also not very uniform and concordant. The fact that the precipitation of caffeine by Wagner's reagent is more delicate in presence of hydrochloric acid than any other acid would make it advisable to employ that acid in quantitative estimation of the base by iodine.

This method could easily be employed for the estimation of the alkaloid in caffeine-bearing drugs. Of course, it is necessary to have the final solution of the alkaloid in water as free as possible from other substances that may be precipitated by Wagner's reagent. The estimation of caffeine by this method is likely to give higher results than have hitherto been obtained. The following procedure is recommended:*—The drug is thoroughly digested with water for some time, by the aid of heat, cooled, and made up to a definite volume, and filtered. An aliquot portion of the filtrate is treated with lead acetate, the precipitate allowed to settle and filtered. The whole of the filtrate, or a given portion of it, is treated with hydrogen sulphide to remove the lead, and filtered. This filtrate, after boiling off the hydrogen sulphide, is divided into two equal portions, and each treated with a definite volume of the standard iodine solution,—the first portion without the addition of any mineral acid, the second with the addition of hydrochloric or sulphuric acid. After five to ten minutes' standing the excess of iodine is estimated in each of the two solutions, as described above. The first portion, containing no other but some acetic acid, serves to indicate whether the filtrate from the lead sulphide contains any other materials besides caffeine that are likely to be precipitated by Wagner's reagent,—for caffeine itself is not precipitated by it even in presence of tolerably strong acetic acid. If any absorption of iodine be found in the first portion, then that quantity is to be subtracted from the amount of iodine taken up by the second portion; the difference represents the iodine used up in the formation of the periodide of caffeine. The amount thus used up multiplied by 0·3834 gives the amount of caffeine in that particular portion of the liquid.

Wagner's reagent employed.	I. Solution containing 0·25 per cent of caffeine.			II. Solution containing 0·50 per cent of caffeine.			III. Solution containing 0·75 per cent of caffeine.			IV. Solution containing 1·00 per cent of caffeine.			V. Solution containing 0·50 per cent of caffeine.		
	Taken.	Found.	Per cent recovered.	Taken.	Found.	Per cent recovered.	Taken.	Found.	Per cent recovered.	Taken.	Found.	Per cent recovered.	Taken.	Found.	Per cent recovered.
Theoretical quantity + 2 c.c.	0·0600	0·0591 0·0589	98·33	0·1200	0·1175 0·1175	97·82	0·1500	0·1481 0·1471	98·40	0·1200	0·1182 0·1179	98·38	0·1200	0·1154 0·1165	96·78
1⅓ theoretical quantity ..	0·0750	0·0749 0·0749	99·88	0·1200	0·1191 0·1189	99·17	0·1500	0·1489 0·1485	99·13	0·1200	0·1191 0·1187	99·12	0·1200	0·1196 0·1197	99·75
Twice the theoretical quantity	0·0500	0·0502 0·0506	100·80	0·0800	0·0805 0·0789	99·63	0·1200	0·1184	98·67	0·1100	0·1091 0·1091	99·18	0·0800	0·0802 0·0791	99·63
One-half of the theoretical quantity	0·0750	0·0363 0·0363	48·40	0·1600	0·0794 0·0794	49·62	0·2250	0·1107	49·20	0·2000	0·1067 0·1067	53·35	0·1600	0·0791 0·0791	49·44

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending January 31st, 1897.

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

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

London, February 11th, 1897.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples

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* These directions are in part given by Spencer, 1890 (*Journ. Anal. Chem.*, iv., 390).

of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Jan. 1st to Jan. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month still shows a small deficiency, the average fall for the last thirty years is 2·16 inches, the actual fall in January was 1·85 inches, making a deficiency of 0·31 inch; it has been pretty fairly distributed through the month, the greatest fall being 0·58 inch on the 8th.

Our bacteriological examinations have been, and will in future be, conducted on a much larger scale; this month 105 samples were examined, with the following results:—

	Colonies per c.c.
Thames water, unfiltered	6409
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	75
Ditto ditto .. .. lowest	4
Ditto ditto .. (45 samples) mean	30
New River water, unfiltered	1420
New River water, from the Company's clear water well	37
River Lea water, unfiltered	1460
River Lea water from the East London Company's clear water well	20

With regard to the above results, it is our duty to say that one very exceptional result was also recorded during the month, viz., on the 14th, when one of the wells was found to contain, in our judgment, too great a number of microbes, having regard to the usual high quality of the filtered supply. A serious warning of the abnormal bacteriological condition of the water was immediately communicated to the Engineer of the Company, and the next sample of water, taken within 48 hours, had resumed its normal condition.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

THIRD ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS.
RESULTS PUBLISHED DURING 1895.*

By F. W. CLARKE.

(Continued from p. 90).

Tellurium.—The determinations of atomic weight by Staudenmeier (*Ztschr. Anorg. Chem.*, x., 189; calculations based upon O=16 and H=1·0032) all start out from telluric acid, $H_2TeO_4 \cdot 2H_2O$, which had been purified by repeated crystallisation. Two essentially different methods were adopted. First, telluric acid was dehydrated, and reduced to TeO_2 by heating. Secondly, telluric acid was reduced by heating in hydrogen to metallic tellurium, finely divided silver being mixed with the acid to retain the tellurium by preventing volatilisation. In four experiments, TeO_2 was reduced to Te in the same manner. The weights and results may be classified as follows for the convenience of comparison:—

TeO_2 : Te.

TeO_2.	Loss on reduction.	Atomic weight of Te.
0·9171	0·1839	127·6
1·9721	0·3951	127·7
2·4115	0·4835	127·6
1·0172	0·2041	127·5

Telluric Acid : TeO_2.

Telluric acid.	Loss.	Atomic weight of Te.
1·7218	0·5260	127·2
2·8402	0·8676	127·1
4·0998	1·2528	127·1
3·0916	0·9450	127·05
1·1138	0·3405	127·0
4·9843	1·5236	127·05
4·6716	1·4278	127·1

Telluric Acid : Te.

Telluric acid.	Loss.	Atomic weight of Te.
1·2299	0·5471	127·3
1·0175	0·4526	127·3
2·5946	1·1549	127·2

There is a good discussion in the paper as to the possible cause of error in these determinations, and also concerning the place of tellurium in the periodic system. Staudenmeier upholds the homogeneity of tellurium as an element, as against the supposition that it is a mixture.

Some years ago Brauner, in an elaborate paper upon tellurium, sought to show that the ordinary element was a mixture of true tellurium with a higher homologue of atomic weight 214. He now (*Journ. Chem. Soc.*, lxvii., 549) concludes that this is very improbable, and suggests that tellurium may contain a homologue of argon, of atomic weight 130. For this supposition no evidence is given apart from the abnormality of the atomic weight, which should fall below that of iodine.

Yttrium.—The atomic weight of this metal has been re-determined by Jones (*Am. Chem. Journ.*, xvii., 154; calculations based upon O = 16 and H = 1·0032), who started out with material purified by Rowland's process; that is, by precipitation with potassium ferrocyanide. First, oxide was converted into sulphate; and secondly, sulphate was transformed to oxide by calcination. The weights and results were as follows:—

First Method.

Y_2O_3.	$Y_2(SO_4)_3$.	Atomic weight of Y.
0·2415	0·4984	88·89
0·4112	0·8485	88·92
0·2238	0·4617	88·97
0·3334	0·6879	88·94
0·3408	0·7033	88·90
0·3418	0·7049	89·05
0·2810	0·5798	88·94
0·3718	0·7803	88·89
0·4379	0·9032	89·02
0·4798	0·9901	88·91
	Mean.. ..	88·94

Second Method.

$Y_2(SO_4)_3$.	Y_2O_3.	Atomic weight of Y.
0·5906	0·2862	88·91
0·4918	0·2383	88·89
0·5579	0·2705	89·03
0·6430	0·3117	88·99
0·6953	0·3369	88·89
1·4192	0·6880	88·99
0·8307	0·4027	88·99
0·7980	0·3869	89·02
0·8538	0·4139	88·99
1·1890	0·5763	88·96
	Mean.. ..	88·97

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* Read at the Cleveland Meeting, December 31, 1895. From the *Journal of the American Chemical Society*, xviii., No. 3.

These determinations are probably the best hitherto made, although they have been briefly criticised by Delafontaine (Chem. News, lxxi., 243), who prefers the lower value obtained by himself, Y=87·3. Delafontaine reaffirms the existence of phillipium, and regards gadolinium as identical with decipium. Jones (Chem. News, lxxi., 305), in a brief rejoinder, defends his own work, and urges that Delafontaine has failed to show wherein it is defective.

The Cerite Earths.—Papers upon this subject have been published by Schützenberger and by Brauner. In his first communication, Schützenberger (*Compt. Rend.*, cxx., 663) deals with cerium, which had been freed from lanthanum and "didymium" by fusion of the mixed nitrates with saltpetre. The yellowish white cerium oxide was converted into cerium sulphate, which was dried at 440°. In this salt, with special precautions, the sulphuric acid was estimated by precipitation with barium chloride. One hundred parts of cerium sulphate gave 123·30 of barium sulphate. Hence, Ce=139·45, according to Schützenberger's calculations. Re-computing with—

O=16, S=32·07, and Ba=137·43,
Ce=139·96.

In a second paper (*Compt. Rend.*, cxx., 962) Schützenberger describes the results obtained by the fractionation of cerium sulphate. Preparations were thus secured giving oxides of various colours, such as canary-yellow, yellowish rose, reddish, and brownish red. These, by the synthesis of the sulphates, the barium sulphate method, &c., gave varying values for cerium, ranging from 135·7 up to 143·3. Schützenberger concludes that the cerium sesquioxide from cerite contains small quantities of another earth of lower atomic weight. In a third paper (*Compt. Rend.*, cxx., 1143) he continues the investigation with the other cerite earths. For the didymiums he finds a range in atomic weight from 137·5 to 143·5 approximately.

Brauner's paper (Chem. News, lxxi., 283) is partly a reclamation of priority over Schützenberger, and partly a preliminary statement of new results. In his earlier work he found that cerium oxide was a mixture of two earths; one white, the other flesh colour with a tinge of orange, and atomic weights for the contained metal of 140·2 and 145·72 respectively. In his later researches Brauner fractionates his material by several methods. One constituent obtained from cerium oxide is a dark salmon-coloured earth, the oxide of a metal which he calls "metacerium." The other constituent he calls cerium. Pure cerium oxalate by Gibbs's permanganate method gave 29·506 and 29·503 per cent of cerium sesquioxide with 46·934 per cent of cerium dioxide, Hence, Ce=139·91, or, with a slight correction, Ce=140·01. This is not far from Schützenberger's value.

(To be continued).

THE DETERMINATION OF ATOMIC MASSES OF SILVER, MERCURY, AND CADMIUM, BY THE ELECTROLYTIC METHOD.*

By WILLETT LEPLEY HARDIN.

(Concluded from p. 93).

Part III. (*continued*).

First Series.

Experiments on Cadmium Chloride.

Dumas and Bucher have both determined the ratio of cadmium to chlorine in cadmium chloride. The results given for the atomic mass of cadmium by the latter experimenter are almost four-tenths of a unit higher than those given by the former.

Preparation of Cadmium Chloride.

Hydrochloric acid was purified by first passing chlorine through the commercial C. P. acid to remove any sulphur dioxide; the excess of chlorine was removed by a current of carbon dioxide. The acid was then distilled from calcium chloride and the hydrochloric acid gas collected in pure water. Pure metallic cadmium was then dissolved in the acid and the solution evaporated to crystallisation. The crystals of cadmium chloride were removed from the liquid and thoroughly dried. The material was then placed in a hard glass combustion-tube, similar to that used in the distillation of metallic cadmium, and carefully sublimed in a current of dry carbon dioxide. The first and last portions of the sublimate were rejected. The middle portion, which consisted of pearly leaflets, was placed in a weighing tube and kept in a desiccator. As only a small quantity of the material could be sublimed at a time, the different analyses were made from different sublimations.

Mode of Procedure.

A weighed portion of the cadmium chloride was dissolved in a little water in a platinum dish, a slight excess of potassium cyanide was added and, after diluting to 200 c.c. with pure water, the solution was electrolysed. Before interrupting the current, the liquid was syphoned from a dish in a manner already outlined in the experiments on silver. The metallic deposit was washed several times with boiling water and carefully dried. The strength of the current and time of action were as follows:—

Time of action.	Strength of current.
12 hours	$N.D_{100}=0·1$ ampère.
4 "	$N.D_{100}=0·15$ "
4 "	$N.D_{100}=0·30$ "

The cadmium was thrown down as a dense white deposit. Ten results on cadmium chloride reduced to a vacuum standard on the basis of—

3·3 = density of cadmium chloride,
8·55 = " metallic cadmium,
21·4 = " platinum dish,
8·5 = " weights,

and computed for the formula $CdCl_2$, assuming 35·45 to be the atomic mass of chlorine, are as follows:—

	Weight of $CdCl_2$. Grms.	Weight of Cd. Grm.	Atomic mass of cadmium.
1	0·43140	0·26422	112·054
2	0·49165	0·30112	112·052
3	0·71752	0·43942	112·028
4	0·72188	0·44208	112·021
5	0·77264	0·47319	112·036
6	0·81224	0·49742	112·023
7	0·90022	0·55135	112·041
8	1·02072	0·62505	112·002
9	1·26322	0·77365	112·041
10	1·52344	0·93314	112·078

Mean .. .. = 112·038
Maximum .. = 112·078
Minimum .. = 112·002

Difference .. = 0·076
Probable error = ±0·005

From the total quantity of material used and metal obtained, we have 112·040 for the atomic mass of cadmium.

Second Series.

Preparation of Cadmium Bromide.

The bromine used in this series was purified as outlined in the experiments on mercuric bromide. The

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* Contribution from the John Harrison Laboratory of Chemistry, No. 13. From the author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Ph.D.—From the *Journal of the American Chemical Society*, xviii., p. 990.

cadmium bromide was prepared by allowing bromine water to act on metallic cadmium for several days at the ordinary temperature. When the action was complete, the solution was filtered and evaporated to crystallisation. The crystals of cadmium bromide were removed from the liquid and thoroughly dried. The material was then placed in a hard glass combustion-tube and carefully sublimed in a current of dry carbon dioxide. The first and last portions of the sublimate were rejected. The middle portion was removed from the tube, placed in a weighing bottle and kept in a desiccator. The product obtained in this way consisted of a crystalline pearly leaflet which dissolved immediately in water without leaving a residue.

Mode of Procedure.

The method of operation was the same as for cadmium chloride. A weighed portion of the material was dissolved in a little water in a platinum dish. A slight excess of potassium cyanide was then added, and after diluting to 200 c.c. the solution was electrolysed and the resulting metal weighed. The strength of current and time of action were the same as for cadmium chloride.

Ten observations on cadmium bromide reduced to a vacuum standard on a basis of—

4·8 = density of cadmium bromide,
8·55 = ,, metallic cadmium,
21·4 = ,, platinum dish,
8·5 = ,, weights,

and computed for the formula $CdBr_2$, assuming 79·95 to be the atomic mass of bromine, are as follows:—

	Weight of $CdBr_2$. Grm.	Weight of Cd. Grm.	Atomic mass of cadmium.
1	0·57745	0·23790	112·031
2	0·76412	0·31484	112·052
3	0·91835	0·37842	112·067
4	1·01460	0·41808	112·068
5	1·15074	0·47414	112·053
6	1·24751	0·51392	112·019
7	1·25951	0·51905	122·087
8	1·51805	0·62556	112·076
9	1·63543	0·67378	112·034
10	2·15342	0·88722	112·041

Mean .. .. = 112·053
Maximum .. = 112·087
Minimum .. = 112·019

Difference .. = 0·068
Probable error = ±0·005

From the total quantity of material used and the metal obtained, Cd = 112·053.

THIRD SERIES.

In these experiments an attempt was made to determine the ratio of the atomic mass of cadmium to that of silver by allowing the same electric current to pass successively through solutions of the two metals and weighing the resulting deposits. The arrangement of apparatus and the details of the method were described under the mercury-silver series. The results were not as satisfactory as the corresponding results obtained for mercury. A large number of determinations were made with currents of different strength and solutions of different concentration, but the results were, in most cases, far below those obtained in the first two series. A current which deposited about twelve-hundredths of a grm. of silver per hour seemed to give the best results. From all the observations, five results were selected which differed only about one-tenth of a unit from those of the first two series. Results selected in this way are entitled to but little weight, and perhaps should not be used in determining the general mean of all the observations.

Computed on the basis of 107·92 for the atomic mass of silver, the only admissible results are as follows:—

	Weight of Ag. Grm.	Weight of Cd. Grm.	Atomic mass of Cadmium.
1	0·24335	0·12624	111·928
2	0·21262	0·11032	111·991
3	0·24515	0·12720	111·952
4	0·24331	0·12616	111·916
5	0·42520	0·22058	111·971

Mean .. .. = 111·952
Maximum .. = 111·991
Minimum .. = 111·916

Difference .. = 0·075

This method was discussed under mercury. The probable sources of error pointed out there apply equally well in the case of cadmium. Until the large variations can be accounted for and the difficulties overcome, the method must be regarded as unsatisfactory.

Summary.

Inasmuch as but one method of analysis has been used throughout this work, it is useless to discuss it here. The advantages and objections pointed out under silver apply also to cadmium.

In summing up the work on cadmium, equal weight must be given to the first two series. The last series must be considered alone, and all that need be said of it is, that the results obtained for the atomic mass of cadmium never exceeded 112. In the corresponding series on mercury, the variations were in both directions from 200.

The general mean of the first two series calculated from the separate observations is—

	Atomic mass of Cd.
First series..	= 112·038
Second series	= 112·053
General mean	= 112·0455

From the total quantity of material used and metal obtained we have—

	Atomic mass of Cd.
First series..	= 112·040
Second series	= 112·053
General mean	= 112·0465

Combining this with the first general mean we have 112·046 as the most probable result of all the work, for the atomic mass of cadmium. This result is lower than those obtained by Huntington and Bucher, but agrees very closely with the results obtained by von Hauer, Dumas, Lensen, Jones, and Lorimer and Smith.

I wish here to express my sense of gratitude to Professor Edgar F. Smith, at whose suggestion this work was undertaken and under whose personal supervision it was carried out.

Radio-photography of the Soft Parts of Man and of the Lower Animals.—MM. Remy and Contremoulin. We have the honour of presenting to the Academy a new result of our researches on the application of the X rays to anatomical studies. By the aid of chemical preparations on the bodies of men and frogs, we have been able to place the muscles, the ligaments, and the tendons in such a state that they have yielded radio-photographic images. The muscle projected shows a dark tint, but within the limits thus indicated we perceive dark traits which pertain to the muscular bundles. The muscle is thus masked by bundles of longitudinal striæ very distinctly limited. In the frog, prepared by the same means, the muscles are fully visible. In this animal we have obtained an image of the crystalline lens and of the coatings of the eye.—*Comptes Rendus*, cxxiv., No. 5.

ELECTRIC SHADOWS AND LUMINESCENCE.*

By Prof. SILVANUS P. THOMPSON, D.Sc., F.R.S., M.R.I.

THE early days of the year 1896 were marked by the announcement telegraphed from Vienna to the effect that Professor Röntgen, a man whose name, though little known outside the world of science, was well known and highly esteemed by those who were initiates in physics, had discovered the existence of rays of a new and extraordinary kind. Taking a Crookes tube, excited of course by a proper electric spark, and covering it up within a case of black cardboard, he found it to produce in the surrounding space some entirely unexpected effects. Black cardboard is impervious not only to ordinary light and to radiant heat, but also to all those other known kinds of invisible light beyond the violet end of the spectrum, known as actinic waves, which are such active agents in the production both of fluorescence and of photographic actions. Yet the invisible emanations of the Crookes tube, which passed freely through the opaque cardboard, were found by Röntgen to be capable of revealing their presence in two ways. In the first place he had seen them to project shadows upon a luminescent screen of paper coated with the highly fluorescent substance called platino-cyanide of barium, and in the second place he had been able to photograph these shadows by letting them fall upon an ordinary photographic plate. The discovery was singular. It revealed the existence of a remarkable and hitherto unexpected species of radiation. It added another to the many puzzling phenomena attendant upon the discharge of electricity *in vacuo.* It proved that something which in the ordinary sense in which those terms are used is neither light nor electricity was generated in the Crookes tube, and passed from it through substances opaque alike to both.

But that which took the imagination of the multitude by storm, and aroused an interest the intensity the like of which has not been known to be aroused by any other scientific discovery in our times, was not the fact that Professor Röntgen had seen luminescent shadows from a Crookes tube, or had obtained a photograph of those shadows; it was the entirely subsidiary and comparatively unimportant point that to these mysterious radiations flesh is more transparent than bone.

Let me begin by showing you as a first experiment that same fact which Röntgen announced of the production of luminescent shadows by these invisible rays. Before you there stands a Crookes tube, of the most modern kind,† for this particular purpose. We have here an induction coil‡ capable of giving 6-inch sparks, with which we can send electric discharges through the tube, illuminating it with its characteristic golden-green glow. I now cover over the tube and exclude all ordinary light, not with a box of black cardboard but with a black velvet cloth. And now in the darkness I am able to show you how on a sheet of paper covered with the highly fluorescent platino-cyanide of barium—the well-known substance which Röntgen himself was using — the shadows of objects placed between. See how this sheet shines in the light of the tube transmuting the invisible radiations into visible light. I hold my purse behind the screen—you see the shadow of the metal clasp, and of the metal contents (two coins and a ring), but you see not the shadow of the leather purse itself, for leather is transparent to these rays while metal is opaque. I hold my hand behind and you see—or at least those of you who are within a few yards of me—the shadow of my hand, or rather of the bones of my hand, surrounded by a fainter shadow of the almost transparent flesh.

Now the second fact that Röntgen announced was that these same rays which escape through the opaque covering and excite fluorescence are also capable of taking photographic impressions of the shadows. There is nothing whatever new about this part of the subject: it is the old photograph; there is no "new photography." Here is a common camera back, and here inside it is a photographic dry-plate—quite a common dry-plate, such as has been known for ten years. This plate is covered with a black card, so that it may not become fogged by the light of the room when I draw the slide. All I have to do is to lay it upon the table below the Crookes tube so as to cast the shadow upon it, and after due exposure develop the plate in the ordinary well-understood way. Now it may be interesting to see the proof of the fact that bone is less transparent than flesh. So, with your permission, I will ask my little daughter to have her hand photographed. (Experiment made).

At the time of Röntgen's announcement, the exposure required with the Crookes tubes that were then in existence was from twenty minutes to, I think, two or three hours. Very shortly improvements were made; and with these modern tubes one minute is quite sufficient for an exposure. Indeed, one minute is too much for many objects. I have not previously tried this particular tube, though I judge by its appearance that it is in good condition. As soon as the exposure of one minute is over we will have the plate taken into the dark room and developed in the ordinary way; and when it is developed we will have it brought back into this room and put into the lantern, that you may see what has been done.

Now, while we are taking photographs, I may as well take a second to illustrate another point. Röntgen investigated in the most careful and elaborate way the relative transparency of different materials for these mysterious rays. He noticed that wood, and many substances which are opaque to ordinary light, are transparent to these rays; whilst, on the contrary, several substances that are transparent to light, such as calc-spar and heavy glass, are very opaque toward them. Many experimenters have examined this question of relative transparency. I devoted a day or two to the study of gems, and found that imitation rubies made of red glass are much more opaque than real rubies, and that paste diamonds are much more opaque than real diamonds. Real diamonds and rubies are indeed very transparent, and scarcely cast any shadows on the luminescent screen, though I have found diamond to be more opaque than an equal thickness of black carbon. There are laid upon this piece of card two rubies, one being only a glass ruby. There is also a row of four small diamonds. I will leave you to find out whether they are false or real. And then there are three larger diamonds, one of which is uncut and is a genuine South African stone. I lay them down upon a photographic plate and expose them to the Röntgen rays so that we may test their relative transparency. (The two photographs thus taken were projected upon the screen at the close of the lecture.)

Amongst the things which Röntgen told us was the fact that different kinds of glass are unequally transparent; that lead-glass, for instance, is much more opaque than soda-glass, or potash-glass, or, indeed, any glass which does not contain a heavy metal like lead. He found that practically the transparency was governed by the density; that the heavy or the dense substances were the more opaque. There is now some reason to correct that statement, though in the main as a first approximation it is perfectly true. Professor Dewar has shown that you must take into account, not the density in gross, but the atomic weight. Taking any homologous series, for example, such as a number of sulphides, or oxides, or chlorides, that one which contains the atomically heavier metal will be the more opaque. Again, the bromide of sodium is more opaque than the chloride of the same metal, and the iodide is more opaque than the bromide. But as the correspondence between relative

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* A Lecture delivered at the Royal Institution of Great Britain Friday, May 8, 1896.

† A Crookes "focus" tube (Jackson pattern), constructed by Messrs. Newton and Co., of Fleet Street, London.

‡ An Apps coil capable of giving sparks 25 centimetres in length, but on this occasion excited with only 5 cells, giving sparks about 6 inches in length.

opacity and molecular or atomic weight breaks down when we try to pass from one series of compounds to a different series, there is some reason to carry the matter to a further degree of approximation. We must go beyond the suggestion of atomic weight. The nearest approach to a law that I have been able to get at yet, on comparing tables of statistics, is that the transparency is proportional to the specific heat. For homologous series this is, of course, the same as saying that the transparency is inversely proportion to the molecular weight.

Röntgen found all the heavy metals to be remarkably opaque, while light metals like sodium and aluminium, and even zinc, are remarkable for their transparency. Aluminium, which is opaque to every known kind of light, is transparent, even in sheets half an inch thick, to these rays. Lithium, the lightest of solid metals, and with an atomic weight 7 as against aluminium 27, is so transparent that I have not been able yet even to see its shadow. Of all liquids water is the most transparent, and it has the highest specific heat of all of them.

Röntgen further found these rays to be incapable either of refraction by lens or prism,* or of reflection by any polished mirror. Reflection there is in one sense, that of diffuse reflection, such as white paper exercises on common light. No lens can concentrate these rays; they are also apparently incapable of being polarised. One difficulty in experimenting on these strange properties is that air itself acts as a turbid medium, reflecting back diffusely, as a smoky cloud would do for ordinary light, a portion of the rays.

Finding that these radiations differed in so many ways from ordinary light, and while resembling and even surpassing ultra-violet rays in their strong actinic properties, yet differed entirely from them in respect of the properties of refraction, reflection, and polarisation, he named them "X rays." To judge by his own writing, he appeared to wish that they might prove to be longitudinal vibrations in the ether, the possibility of the existence of which has been a subject of speculation on the part of some of the most learned of mathematical physicists. Others have suggested that these X rays are transverse vibrations of a much higher frequency and shorter wave-length than any known kind of ultra-violet light. Others, again, see in them evidence that radiant matter (*i.e.*, kathodic streams of particles) can traverse the glass of a Crookes tube, and regard them as material in their nature. Lastly, it has been suggested that they may be neither waves nor streams of matter, but vortex motions in the ether.

To follow out the bearings of these speculations, as well as to trace the development of discovery, let us go back a little and consider what was the starting-point of Röntgen's research. He was using a Crookes tube. It is one of the difficulties of my task to-night that I have to speak in the presence of him who is the master of us all in this subject of electric discharges in the vacuum tube. But to understand the discoveries of Crookes let us first witness a few experimental illustrations of the phenomena of electric discharges in vacuum tubes. Many of them have been known for half a century. We all know of the researches made in England by Gassiot, and by Varley and others, and the tubes of Geissler of Bonn are a household word. But there is one set of researches which deserves to be known far better than it is, that made by Dr. W. H. Th. Meyer, of Frankfort, whose pamphlet† I hold in my hand. In it he depicts a number of tubes in various stages of exhaustion, including one in that highest stage of exhaustion which one is prone to think of modern origin.

In order to illustrate the successive phenomena which are produced when electric discharges are sent through a tube during progressively increasing exhaustion, there is here exhibited a set of identical tubes. Each is a simple straight tube, having sealed in at each end an electrode terminating in a short piece of aluminium wire. The electrode by which the electric current enters is known as the anode, that by which it leaves the tube as the kathode. The only difference between these eight tubes lies in the degree of rarefaction of the interior air. The first one contains air at the ordinary pressure. As its electrodes are about 12 inches apart I am unable with the Apps induction coil (excited to throw an 8-inch spark) to send a spark through it. From the second tube about four-fifths of the air has been abstracted, and here we obtain a forked brush-like spark between the electrodes. The third tube has been exhausted to about one-twentieth part, and shows as the discharge a single thin red linear spark like a flexible luminous thread. When, as in the fourth tube, the exhaustion is carried so far as to leave but one-fortieth, the red line is found to have widened out into a luminous band which extends from pole to pole, while a violet mantle makes its appearance at each end and spreads over both of the electrodes. On carrying the exhaustion to the stage shown by the fifth tube, where only about 1-500th of the original air is left behind, we note that the luminous column has broken up transversely into flickering striæ, that the violet mantle round the kathode has become more distinct, and is separated by a dark interval from the luminous red column, while a second and very narrow dark space appears to separate the violet mantle from the surface of the kathode. In the sixth tube the exhaustion has been carried to about 1-10,000th. The flickering striæ have changed shape and colour, being paler. The light at the anode has dwindled to a small bright patch. The violet glow surrounding the kathode has expanded to fill the whole of that end of the tube; the dark space has become more distinct, and within it the kathode now shows on its surface an inner mantle of dull red light. There is a slight tendency for the glass to show a greenish fluorescence near the kathode end. In the seventh tube the luminous column has subsided into a few greyish white nebulous patches, the dark space round the kathode has greatly expanded, and the glass of the tube has now begun to show a yellow-green fluorescence. The exhaustion has been pushed so that only about 1-50,000th or less of the original air is present. In the eighth and last tube only one or two millionths of the original air have been left, with the result that the tube now offers an enormously increased resistance to the passage of the discharge. All the internal flickering nebulosities have vanished; the tube looks as though there were no residual air within. But now the glass itself shines with a fine yellow-green fluorescence which is particularly bright in the region around the kathode. Were the exhaustion to be carried much further the spark from this induction coil would no longer pass, so high would the resistance become. All these successive stages up to the last can be shown in one and the same tube attached to a modern rapid air-pump. But for the proper production of the high vacua of the last stages, where electric shadows are alone produced, nothing short of a mercurial pump, either in the form invented by Sprengel or in that used by Geissler (or one of the recent modifications) will suffice.

The phenomenon of fluorescence of the glass, which manifests itself when the exhaustion has become sufficiently high, was known in a general way as far back as 1869 or 1870. The tube next to be shown is a modern reproduction of a tube used at that time by Hittorf, of Münster. It differs from the tubes last shown by having a bend in it. Hittorf observed that when such a tube is exhausted sufficiently highly to give at the kathode the characteristic greenish yellow fluorescence, this greenish

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* Perrin, in Paris, and Winkelmann, in Jena, have independently found what they believe to be evidence of refraction through an aluminium prism. Both observers detected a slight deviation, but in a direction toward the refracting angle, showing aluminium to have for these rays a refractive index, slightly less with respect to air than unity.

† "Beobachtüngen über das geschichtete electrische Licht, sowie über den merkwürdigen Einfluss des Magneten auf dasselbe;" von Dr. W. H. Theodor Meyer. Berlin, 1858.

yellow fluorescence refused to go round the bend. It might appear at one end or the other, according to the direction in which the discharge was being sent, but would not go round the bend. The effect was as if the discharge went in straight lines from the bit of wire that served as kathode to the walls of the tube. Indeed shadow effects were observed by him, and by Wright, of Yale, and afterwards independently by Crookes, who greatly extended our knowledge of the facts. We may take this fact, that the fluorescence caused by the kathode will not go round a corner, as the starting-point of the memorable researches of Crookes on radiant matter a score of years ago.

Before you are several tubes which illustrate the researches made by Crookes. The first is a simple glass bulb into which are sealed the two electrodes,—the anode, by which the current enters, terminating in a bit of stout aluminium wire; the other, by which the current leaves, called the kathode, terminating in a small flat aluminium disk. The glass bulb was itself highly exhausted—how highly we shall presently see. From the flat front surface of the kathode, when sparks are sent through the bulb, a sort of back-discharge takes place in a direction normal to the surface. This discharge, which only occurs at a very high degree of exhaustion, possesses several properties which distinguish it from all other kinds of discharge. It is propagated in straight lines, causes a brilliant luminescence wherever it strikes against the glass walls of the tubes, casting shadows of intervening objects, it heats the surface on which it impinges, and strikes them with a distinct mechanical force. Singular to relate, it is also capable of being deflected by a magnet as though it were a flexible conductor carrying the current. Struck by the singularity of these kathode rays or kathode discharges, which formed the subject of several beautiful researches, Crookes advanced the hypothesis that they consisted of flights of negatively electrified particles or "radiant matter." The particles he sometimes spoke of as molecules, sometimes as dissociated atoms, or, as we should now say, ions. He studied the wanderings of these flying particles by inserting within the bulb at different points auxiliary electrodes. He found the interior of the bulb to be positively electrified in all parts except within the dark space which surrounds the kathode, that is to say, except within the range of the actual kathode discharge. The kathode discharge itself was found to be possessed, to an extent exceeding any other known agency, of the power of exciting fluorescence and phosphorescence in minerals and gems. The kathode rays were themselves discernible as they crossed the interior of the tube. In such a bulb the kathode rays would form a blue streak impinging straight upon the anode. The kathode used in the next Crookes tube is of a concave shape. Crookes found that, since the kathode rays left the surface normally, the result of curving the kathode was to focus the rays toward the centre of curvature. By so focussing the rays upon a bit of platinum foil, it was found possible to fuse and even melt the metal.

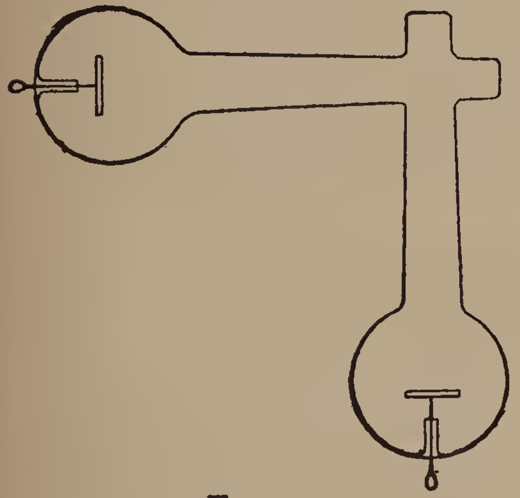

Fig. 1.

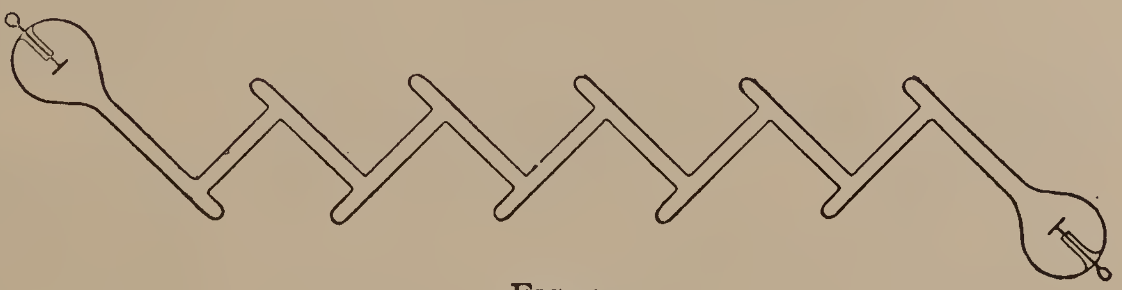

Fig. 2.

Unlike the discharges obtained at lower stages of rarefaction, the direction of these kathode rays was found to be independent of the position of the anode. He found kathode rays to be produced even when no internal electrodes were inserted, and when, instead, external patches of tinfoil were attached to the glass. Their mechanical action he studied by causing them to impinge upon the vanes of a pivoted fly, which was thereby set into rotation. In a later experiment he caused the fly of a "molecule mill" to be set into rotation, not by the impact of the kathodic discharge, but by the kinetic energy of the particles returning back toward the anode after they had impinged against the walls of the tube and lost their negative electric charges. A mere *resumê* of Crookes's work in those years beginning about 1869 or 1870, and extending not only for ten years actively, but going on at intervals until a year or two ago, would of itself fill a whole course of lectures. Into the controversy which has arisen between Crookes and the English physicists on the one hand, and the German physicists on the other, there is no need to enter. Suffice it to say that while the German physicists mostly reject Crookes's hypothesis of radiant matter, and regard all these various phenomena as the result of mere wave-motions within the tube, the British physicists, including Lord Kelvin and Sir George Stokes, accept Crookes's view of the material nature of the kathode rays. Who, indeed, that has seen the molecule mill at work can doubt that, whether vibrations are present or not (and doubtless there are vibrations present), there are actually streams of moving particles as an essential feature of the kathodic discharge? For the moment the victory undoubtedly rests with the views of Crookes.

But of all these phenomena the one which concerns us most is that of the production of electrical shadows. Erecting in the path of the kathode rays an obstacle cut out in sheet metal,—a cross of thin aluminium is the favourite object,—a shadow of it is observed to be cast upon the wall of the tube behind it; the glass phosphorescing brilliantly except where shielded from the impact of the kathode rays, so that the shadow comes out dark against a luminous background. Common soda-glass gives this greenish golden tint, while lead-glass exhibits a blue phosphorescence. Not glass alone, but diamonds, rubies, emeralds, calc-spar, and other earthy materials, such as alumina, and notably yttria, produce the most brilliant effects under the kathode discharge, some of them only fluorescing transiently, others with a persistent phosphorescence. As a sample is shown a tube in which a sea-shell, slightly calcined to remove organic matter, is made to emit a brilliant luminescence under the impact of rays from a kathode placed above it. The shell itself casts a shadow against the lower part of the tube. Some of the shadow effects are very mysterious, and have recently claimed much of my attention. The size of the kathodic shadows is affected by the electrical state of the object. Electrifying it positively makes its shadow shrink to smaller dimensions. Electrifying it negatively causes a singular enlargement of the shadow. There seems to be no difference between the shadow of a metallic body and that of a non-metallic body of the same size. All bodies cast shadows, however thin. Even a film of glass 1·10,000th of an inch thick—so thin that it showed iridescence like a soap-bubble—was found by Crookes to cast its shadow.

Another point noticed by Crookes was that if the exhaustion is carried very far, and the tube is stimulated by a sufficiently strong electromotive force, the phosphorescence may occur at points not in the line of discharge, but round a corner. Not that the kathode rays turn the corner, however. Apparently some of the more quickly moving, or perhaps more highly charged particles,—atoms, molecules, or ions, those, in fact, described by Crookes as "loose and erratic,"—would manage to get round the corners and produce effects of a more or less directly kathodic kind in places where they could not have penetrated by any motion in a straight line.

Here (Fig. 1) is a tube—a variation on one of Hittorf's. having two branches that cross one another at right angles. There are two small disks of aluminium in the bulbous ends to serve as electrodes. When either of these is made the kathode, the whole limb in which it is situated fluoresces brilliantly of a golden-green tint, particularly at the distant end. But the other limb remains dark, save for a little nebulous blue patch, near the anode, due to residual gas. Another tube (Fig. 2) is made as a zigzag, and here again only the end branch shines. On reversing the current the luminescence shifts to the other end. But when the tube is more highly exhausted, the phosphorescence is observed not only in the end branch where the kathode is, but also slightly at the end wall of each branch of the zigzag. Apparently the residual gas will act partly as its own kathode, and throw off something which causes the glass beyond to phosphoresce.

(To be continued).

NOTICES OF BOOKS.

Chemistry for Engineers and Manufacturers. A Practical Text-book. By Bertram Blount, F.I.C., F.C.S., Assoc. Inst. C.E., and A. G. Bloxam, F.I.C., F.C.S. With Illustrations. Vol. II., *Chemistry of Manufacturing Processes.* London: Charles Griffin and Co. (Ltd.). 1896. 8vo., pp. 484.

This volume is devoted to notices of the sulphuric acid manufacture; of alkali and its by-products; of destructive distillation, including the gas-manufacture; of artificial manures, petroleum, lime, and cement; of the clay industries, and glass, sugar, and starch; of brewing and distilling; oils, resins, and varnishes, soaps and candles, textiles and bleaching colouring-matters, dyeing and printing; of paper and pasteboard, pigments and paints, leather glue and size, explosives and matches; and of the minor chemical manufactures.

The reader will be surprised at finding all these arts and manufactures—some of capital importance—treated in the compass of 437 pages; but the authors explain in their Preface that they seek to expound those dominant principles which, they allege, "are too often hidden beneath masses of mere detail, and are consequently apt to be overlooked by the specialist in any one branch, to his detriment, in that he frequently fails to apply to his own work principles which are matters of common knowledge elsewhere."

It is to be regretted that no instances are given of this overlooking which so frequently happens. According to our own observation the specialist eagerly, and even anxiously, looks about for principles which may throw light upon his own department.

The bibliography seems to us somewhat deficient; not a few important works on different departments have been overlooked.

We regret to find that the authors have omitted the opportunity to deal a blow in passing at the recent stultification of the Methylated Spirit Act. If the Excise wished to render methylated spirit absolutely undrinkable, they might have demanded the addition to the spirit of a few drops of Dippel's animal oil, which is successfully used in Germany, and which does not interfere with industrial uses.

The addition of dyes and mordants to sugar—an increasing evil—should be carefully looked into.

Mention is made of a fraudulent custom in the pigment-trade, pale chrome-yellows being called and sold as pure when let down with lead sulphate. Hard waters for the use of the dyer and tissue-printer are rightly objected to; if a hard water is required for any special process, it is better to add a salt of lime to a pure-water supply.

The manufacture of artificial silk is considered as hitherto not a commercial success.

In the matter of the vinegar manufacture, it may be asked why sugar at its present prices is not used in preference to malt, save for domestic manufacture? No mention is made here of date vinegar, which is coming into use.

This work will be found useful to manufacturers who, without being chemical specialists, wish to have a general insight into chemical manufactures.

A Practical Treatise on Animal and Vegetable Fats and Oils, both Fixed and Volatile; their Physical and Chemical Properties and Uses, the Manner of Extracting and Refining them, and Practical Rules for Testing them — as the Manufacture of Artificial Butter, of Lubricants, &c. With Lists of American Patents relating to the Extraction, Rendering, Refining, Decomposing, and Bleaching of Fats and Oils. By William T. Brannt, Editor of the "Techno-chemical Receipt-Book," "Petroleum," &c. Second Edition, Revised and in great part Re-written. Illustrated with 302 Engravings. In Two Volumes. Vol. I., pp. 528; Vol. II., pp. 728. Philadelphia: H. C. Baird and Co. London: Sampson Low, Marston, and Co. (Ltd.). 1896.

We have here an encyclopædia of the animal and vegetable fats and oils from a botanical, chemical, industrial, and commercial point of view. The analysis of oils, whether for identification or for the detection of frauds, presents great difficulties. Numerous processes, physical and chemical, have been applied, not without success. But the properties of oils are apt to be modified by age, by climate, by the soils of their native countries, so that, especially in forensic cases, it becomes very difficult for the expert to give an apodictic decision as to the genuine or fraudulent character of any sample in question. We have here a most elaborate table of the colour reaction, with a mixture of sulphuric and nitric acids, with potash and soda lye, with zinc chloride, with hydrochloric acid and sugar. Next come the well-known elaidin test, the thermal test of Maumené, and Fehling test, depending on the heat liberated on mixing fatty oils with sulphuric acid at density 1·840; Tomlinson's cohesion figures, which require the outlay of much time before trustworthy results can be reached.

Among quantitative methods there rank the determination of the ester number, of the acid number, the acid number + the ester number being the Köttstorfer saponification number; the determination of the fatty acids insoluble in water (Hehner's number); determination of the volatile fatty acids (Reichert's number); the iodine absorption (Hübl's number). The determination of oxy-fatty acids gives the acetyl number of Benedikt-Ulzer.

In determining the purity of an oil, the author examines firstly the argonoleptic and generally the physical properties. He then applies the qualitative chemical methods, and, lastly, the quantitative procedures, among which Hübl's iodine number is most generally determined.

A table shows the approximate relative commercial value, and hence gives a key to the oils likely to be used for fraudulent purposes.

No small trouble is occasioned in commerce by the circumstance that the seeds of the three species of *Brassica*, which yield respectively colza, rape, and rubsen oils, cannot be decisively distinguished from each other, either by measurement or by the aid of the microscope.

The presence of any oil of this group—the products of the *Cruciferæ*—may be detected by boiling the oil with white-lead plaster (*Emplastrum plumbi*). The oil is turned brown or black by the formation of lead sulphide.

Sesame oil or gingelly oil is used as a table oil, and is esteemed fully equal to the best olive oils. It is a curious fact that, though the seed is chiefly grown in India, yet the oils pressed in Europe are considered superior to those pressed at home.

Olive oil, in consequence of its high price, is especially open to fraud. Its electric conductivity is much lower than that of any other vegetable oil. Accordingly Palmieri has devised an apparatus—the *diazometer*—which utilises this peculiarity. This instrument, however, is expensive, and not easy of manipulation. Moreover, leaving sophistication out of the question, olive oils are subject to spontaneous alterations which render the test untrustworthy.

The spectroscopic examination of olive oil is likewise not trustworthy. The absorption bands observed in olive oil are not due to the oil itself, but to chlorophyll, and do not occur at all in bleached oils.

M. Brullé, Director of the Agricultural Station at Nice, has devised two methods of testing the purity of olive oils, showing the kind and quantity of other oils used for their sophistication.

These two tests we shall give *in extenso* on a future occasion. We must remember that dishonest merchants and manufacturers now consult experts who are themselves unscrupulous, or who are carefully kept in ignorance of the purposes for which their advice is required.

We shall return to this most valuable work at the earliest opportunity.

CORRESPONDENCE.

HOW SOON SHALL THE STUDENT BEGIN THE STUDY OF QUALITATIVE ANALYSIS?

To the Editor of the Chemical News.

SIR,—Mr. Beebe's article in your last issue is an interesting one, and will I hope bring some comment. I should think, however, that few teachers would agree with him, for surely qualitative analysis is an application of the science and not the science itself. The great difficulty is to induce pupils to *think*, and though one may be careful to point out that qualitative analysis is really a chemical Euclid, I have found but few pupils who will work through their analyses according to the syllogistic method of the great geometer. The attention given to schemes of analysis, and the importance given to the testing of powders until recently by the Science and Art Department have done much to take away the educational value of chemistry as a school subject.

As regards danger in making the common gases, these will have to be made some time, and if it is pointed out to a pupil why there is danger, and how to guard against it, no mishap is likely to occur, even should that "dangerous gas" hydrogen be the subject of the lesson.—I am, &c.,

C. J. WOODWARD.

Municipal Technical Schools,
Birmingham, Feb. 20th, 1897.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 4, January 25, 1897.

A medal was presented to M. Faye on the occasion of the 50th anniversary of his nomination as a Member of the Academy of Sciences. M. Faye made a suitable reply.

Fluorescence of Vitrified Matters under the Action of Röntgen's Rays. — M. Ragiquet. — The following phenomena have, I believe, not been hitherto signalised. The substances mentioned below become luminous under the influence of the X rays, in the following decreasing order:—Baked enamels; crown glass; flint-glass; ordinary glass, and especially the kind known as crystal; sheet-glass from the works of Saint-Gobain; porcelain enamelled faience; enamel powder before baking; and even cut diamond. We know, also, that most of these substances are fluorescent in the violet and the ultra-violet rays. It is therefore possible to form with these substances fluorescent screens which enable us to repeat radioscopic experiments with this advantage, that the vitrified substances just mentioned may be worked optically. The images obtained are more definite, though less brilliant, than are those with crystals cemented upon card hitherto employed. We utilise also successfully these substances for shortening the exposure in radiographic experiments, and we have not to fear the granular spots produced by the crystals above mentioned. Does this fluorescence of glass not explain the disputed fact that persons affected with cataract see the X rays? In fact, if we place ourselves in the field of emission of a Crookes tube, furnished with thick spectacles with convex glasses, we experience the sensation of a light like that of phosphorus. This sensation is the result of the fluorescence of the glass, which forms before the eyes a luminous mist easily recognised by persons surrounding the patient. Besides the scientific applications there are an entire series of very beautiful experiments, which I am about classifying with a view to early publication.

Action of Carbon Dioxide and Monoxide upon Aluminium. — MM. Guntz and Masson. — This paper will be inserted in full.

Spectra of the Non-metals in Fused Salts — Silicon. — A. de Gramont. — This paper will be inserted in full.

On Chromium and Manganese Phosphides. — A. Granger.—Already inserted.

Influence of Temperature on Rotatory Power.— Ph. A. Guye and Mlle. E. Aston.—In all we know at least fifty active liquids whose rotatory power decreases with the elevation of temperature in the entire interval of the experiments.

On Two Isomeric Triethylene-diphenyl Hydrazines, *α* and *β*.—In presence of hyposulphites the action of aldehyd or phenylhydrazine yields the isomer *α* almost pure. In neutral solutions aldehyd acting upon phenylhydrazine phosphate produces chiefly the isomer *β*.

On a High Homologue of Urea. — Oechsner de Koninck.—It seems very admissible that in proportion as the oxidising power of the system is weakened, the number of the atoms of carbon of the quaternary compounds eliminated by the kidneys increases progressively.

Contribution to the Study of the Action of Zinc upon Red Wines.—L. A. Lovat.—Zinc denaturates red wines and renders them poisonous. Hence the use of this metal should be severely forbidden in the cock for casks, vats, &c.—*Comptes Rendus*, cxxiv., No. 5.

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.

Waterproofing Canvas.—I should like to know a good receipt for chemically rendering canvas, &c., waterproof, ours being a very old and almost obsolete method.—Weekly Reader.

MEETINGS FOR THE WEEK.

Monday, March 1st.—Society of Arts, 8. (Cantor Lectures). "Industrial Uses of Cellulose," by C. F. Cross, F.C.S.

— Society of Chemical Industry, 8. "Relation of Colour to Quality in Malt," by J. W. Lovibond. "Hehner's Bromine Tests for Oils," by J. H. B. Jenkins. "Analysis of Superphosphates," by J. H. Coste.

Tuesday, 2nd.—Royal Institution, 3. "Animal Electricity," by Prof. A. D. Waller, F.R.S.

— Society of Arts, 8. "Gesso," by Matthew Webb.

Wednesday, 3rd.—Society of Arts, 8. "English Orchards," by Geo. Gordon.

— Society of Public Analysts, 8. "The Composition of Milk and Milk Products," by H. Droop Richmond. "Estimation of Milk Sugar in Milk" and "Detection of Mixtures of Diluted Condensed or Sterilised Milk with Fresh Milk," by H. Droop Richmond and L. K. Boseley. "Constitution of Milk," by H. Droop Richmond. "Copper in Peas," by R. Bodmer and C. G. Moor, M.A. "Coffee Palace Coffee Infusions," by E. G. Clayton.

Thursday, 4th.—Royal Institution, 3. "Greek History and Extant Monuments," by Prof. Percy Gardner, F.S.A.

— Society of Arts, 8. "The Mechanical Production of Cold," by Prof. James A. Ewing, M.A., F.R.S.

— Chemical, 8. Ballot for Election of Fellows. "Some Hydrocarbons from American Petroleum — I. Normal and Iso-Pentane," by Sydney Young, F.R.S., and G. L. Thomas, B.Sc. "The Vapour Pressures, Specific Volumes, and Critical Constants of Normal Pentane, with a Note on the Critical Point," by Sydney Young, F.R.S. "On the Freezing-point Curves of Alloys containing Zinc," by C. T. Heycock, F.R.S., and F. H. Neville. "The Oxides of Cobalt and the Cobaltites," by A. H. McConnell and E. S. Hanes.

Friday, 5th.—Royal Institution, 9. "Some Curiosities of Vision," by Shelford Bidwell, F.R.S.

Saturday, 6th.—Royal Institution, 3. "Electricity and Electrical Vibrations," by Right Hon. Lord Rayleigh, M.A., F,R.S.

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THE CHEMICAL NEWS.

VOL. LXXV., No. 1945.

THE AGE OF COPPER IN CHALDEA.

By M. BERTHELOT.

THE discoveries made some years ago by M. de Sarzee, at Tello in Chaldea, have brought to our knowledge monuments of a high antiquity, extending back to the origin of civilisation, 5000 or 6000 years ago. They have furnished weapons, ornaments, and tools which throw a new light on the origin of the industry of metals. Such are the objects deposited at the Louvre, which our colleague, M. Heuzey, has kindly referred to my examination. We find here the first and most ancient monuments belonging to the age of copper.

1. I have analysed a colossal lance or blade showing various designs and inscriptions, with the name of a king of Kish which goes back to an epoch anterior to Our-Nina, *i.e.*, about 4000 years before our era. This lance has not been devoted to practical service, but has a hieratic character, having been consecrated to some deity. It is formed of a red metal, being strongly attacked in some parts and changed into a greenish paste.

The filings of the metal consist of copper approximately pure, and I have found in it no tin, zinc, arsenic, or antimony in any appreciable amount.

The oxidised portion consists of hydrated copper oxychloride (atacamite) free from carbonate. There was found in it neither arsenic, antimony, tin, or zinc, but a trace of lead. This substance, after drying in the stove, contained $Cl = 19{\cdot}6$.

This oxychloride results from the action of the brackish waters of the soil in the midst of which the blade has been lying for so many centuries. When once the object is brought in contact with the air, the presence of the alkaline chlorides and atacamite threaten a total disaggregation in consequence of its progressive conversion into super-copper oxide. This aggregation results from a certain series of reactions, set up by a small quantity of sodium chloride with the intermediation of atacamite, which I have defined by direct experiment (*Annales de Chimie et Physique*, Series 7, vol. iv., p. 552). Most of the statues of copper found in the same excavations are undergoing this same decomposition at the Museum. They are wrongly labelled "*Objects of Bronze*," as they consist of pure copper.

2. Hatchet with a socket formed of red metal. Broken fragments coated with a greenish patina. A similar instrument is represented in the hands of Chaldean personages on the monuments from the epoch of Our-Nina to that of Goudea, that is, from the year 4000 to the year 3000 before our era.

The fragments which I have analysed consist essentially of metallic copper associated with a little cupric oxide. No tin, lead, zinc, arsenic, or antimony. The hatchet has therefore not been formed of bronze, but of copper sensibly pure.

3. Entire hatchet, red, with a sharp edge, horizontal and socketed. It has been found with its handle below the ancient construction of the king Our-Nina. M. Heuzey regards it as perhaps the most ancient relic met with in these excavations. The metal is hard, of pure copper, free from tin, lead, or zinc, but contains traces of arsenic and phosphorus. It seems to have been hardened by the concourse of these latter elements. But we do not possess the ores which have served in the manufacture of the Chaldean objects, and we cannot assert, as is the case of the specimens from Sinai, that the presence of arsenic is due to the addition of some substance foreign to the copper ore properly so called. In any case I must here repeat that we have to do with copper, and not bronze, as the Chaldean tools, &c., contain no tin.

4. Egg-shaped article, of a metallic aspect, weighing 121 grms., found along with the Chaldean remains. The filings consisted of iron partially oxidised, without arsenic, zinc, or alumina.

5. Ingot and filings (ancient) of a white metal, found with the Chaldean remains in an urn of coarse pottery. The filings of the ingot contain:—Silver, 95·1; copper, a small quantity; notable patina; no lead.

6. Leaf of yellow gold, of Chaldean or Assyrian origin. This gold contains neither copper, lead, nor iron in sensible proportion. It contains a considerable quantity of silver, which the minimal weight of the sample at my disposal did not permit me to determine with precision. In this and other cases it is always the antique alloy of gold and silver known under the name of *asem*. The manner of purifying native gold was not well understood in Egypt and Chaldea in those remote ages.

The existence of successive degrees in the use of the purification of the metals, both common and precious, appears from these analyses. In particular, the use of pure copper for arms and tools was common in Chaldea about the year 4000 B.C. It preceded the use of bronze, *i. e.*, copper alloyed with tin, which is found in later articles both in Egypt and Chaldea. We may even add that the form of hatchets with handles, the processes of moulding and manufacture, and even the practical uses to which the tools were destined, have been the same both for the pure hatchets of copper in Chaldea and for the prehistoric hatchets of Europe and Siberia.—*Comptes Rendus*, cxxiv., p. 328.

CARBIDE OF CALCIUM.

IN consequence of the growing importance of carbide of calcium, and the fact that the mere contact of moisture with this material causes a dangerous evolution of the highly inflammable gas known as Acetylene, the Home Secretary has caused inquiries to be made into the subject, with the result that an Order in Council has to-day been made under the 14th Section of the "Petroleum Act, 1871," bringing carbide of calcium within the operation of that Act.

Accordingly, from the date on which such Order comes into force, viz., 1st April, 1897, it will be unlawful to keep carbide of calcium except in virtue of a license to be obtained from the Local Authority under the "Petroleum Act."

Any Local Authority to whom application may be made for a license to keep carbide of calcium can, if it so desires, obtain, on application to the Home Office, a Memorandum showing the character of the risks to be guarded against, and containing suggestions as to the nature of the precautions likely to be most effectual for securing safety.

Whitehall, 26th February, 1897.

DETERMINATION OF SULPHUR IN IRONS.

By OTTO HERTING.

IN the laboratories of many iron works it is customary to be content with Wiborgh's method (colorimetric), as the determination by the bromine method is tedious, and very unpleasant where the ventilation arrangements are imperfect. I will by no means deny the value of the colorimetric method, but wish to point out that the results are frequently very inaccurate, owing to imperfectly constructed apparatus or to escapes at the joints. The latter we may best detect by means of nitro-prusside papers. A disadvantage in Wiborgh's method which cannot be overlooked is, that we are compelled to use a very small quantity of material (0·2 to at most 0·8 grm.) of borings, which is far too small a quantity. The most expeditious quantitative method which yields perfectly satisfactory results, is, in my opinion, the following, which E. F. Wood (of the Homestead Steel Works) publishes briefly in Blair's "Analysis of Iron" p. 71:—5 or 10 grms. of borings are treated with hydrochloric acid; the hydrogen sulphide evolved is conducted into an ammoniacal cadmium salt (acetate or chloride); the cadmium sulphide is collected on a small filter, shaken out with cold water in an Erlenmeyer flask, mixed with *n*/20 solution of iodine in excess, which is then titrated back with a corresponding solution of thiosulphate. The entire operation can be completed in one hour.

About two years ago Prof. de Koninck proposed to determine sulphur in irons, adding a small quantity of stannous chloride to the hydrochloric solution to prevent the formation of ferric chloride. I am now of De Koninck's opinion, that the oxygen of the air in 1 litre does not react so quickly upon hydrogen sulphide as to occasion a separation of sulphur which might thus escape determination. Hence it is not necessary to expel the air of the flask by the introduction of a current of hydrogen or carbon dioxide.—*Chemiker Zeitung*, Feb. 6.

THIRD ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS.
RESULTS PUBLISHED DURING 1895.[*]

By F. W. CLARKE.

(Concluded from p. 101).

Helium and Argon.—The true atomic weights of these remarkable gases are still in doubt, and so far can only be inferred from their specific gravities. For argon, the discoverers, Rayleigh and Ramsay (*Phil. Trans.*, clxxxvi., 220—223) give various determinations of density, ranging H=1) from 19·48 to 20·6. The value 19·9 they regard as approximately correct.

For helium, Ramsay (*Journ. Chem. Soc.*, iii., 684) gives the density 218, while Langlet (*Ztschr. Anorg. Chem.*, x., 289) finds the somewhat lower value 2·00.

From one set of physical data both gases appear to be monatomic, but from other considerations they are supposably diatomic. Upon this question, controversy has been most active, and no final settlement has yet been reached. If diatomic, argon and helium have approximately the atomic weights 2 and 20 respectively; if monatomic, these values must be doubled. In either case helium is an element lying between hydrogen and lithium; but argon is most difficult to classify. With the atomic weight 20, argon fills in the eighth column of the periodic system, between fluorine and sodium; but if it is 40, the position of the gas is anomalous. A slightly lower value would place it between chlorine and potassium, and again in the eighth column of Mendeleeff's table, but for the number 40 no opening can be found.

It must be noted that neither gas, so far, has been proved to be absolutely homogeneous; and it is quite possible that both may contain admixtures of other things. This consideration has been repeatedly urged by various writers. If argon is monatomic, a small impurity of greater density, say of a unknown element falling between bromine and rubidium, would account for the abnormality of its atomic weight, and tend towards the reduction of the latter. If the element is diatomic, its classification is easy enough on the basis of existing data. Its resemblance

	H = 1.	O = 16.
Aluminum..	26·91	27·11
Antimony	119·52	120·43
Argon..	?	?
Arsenic	74·52	75·09
Barium	136·40	137·43
Bismuth	206·54	208·11
Boron..	10·86	10·95
Bromine	79·34	79·95
Cadmium	111·08	111·93
Cæsium	131·89	132 89
Calcium	39·78	40·08
Carbon	11·92	12·01
Cerium	139·1	140·2
Chlorine	35·18	35·45
Chromium..	51·74	52·14
Cobalt	58·49	58·93
Columbium	93·3	94·0
Copper	63·12	63·60
Erbium	165·0	166·3
Fluorine	18·89	19·03
Gadolinium	154·9	156·1
Gallium	68·5	69·0
Germanium	71·75	72·3
Glucinum	9·01	9·08
Gold	195·74	197·24
Helium	?	?
Hydrogen	1·00	1·008
Indium	112·8	113·7
Iodine	125·89	126·85
Iridium	191·66	193·12
Iron	55·60	56·02
Lanthanum	137·6	138·6
Lead	205·36	206·92
Lithium	6·97	7·03
Magnesium	24·11	24·29
Manganese	54·57	54·99
Mercury	198·5	200·0
Molybdenum	95·26	95·98
Neodymium	139·4	140·5
Nickel	58·24	58 69
Nitrogen	13·94	14·04
Osmium	189·55	190·99
Oxygen	15·879	16·00
Palladium	105·56	106·36
Phosphorus	30 79	31·02
Platinum	193·41	194·89
Potassium..	38·82	39·11
Praseodymium.. ..	142·4	143·5
Rhodium	102·23	103 01
Rubidium	84·78	85·43
Ruthenium	100·91	101·68
Samarium	148·9	150·0
Scandium	43·7	44·0
Selenium	78·4	79·0
Silicon	28·18	28 40
Silver..	107·11	107·92
Sodium	22·88	23·05
Strontium	86·95	87·61
Sulphur	31·83	32·07
Tantalum	181·2	182·6
Tellurium	126·1 ?	127·0 ?
Terbium	158·8	160·0
Thallium	202·60	204·15
Thorium	230·87	232·63
Thulium	169·4	170·7
Tin	118·15	119·05
Titanium	47·79	48·15
Tungsten	183·44	184·84
Uranium	237·77	239·59
Vanadium	50·99	51·38
Ytterbium	171·7	173·0
Yttrium	88·28	88·95
Zinc	64·91	65·41
Zirconium..	89·9	90·6

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[*] Read at the Cleveland Meeting, December 31, 1895. From the *Journal of the American Chemical Society*, xviii., No. 3.

to nitrogen, as regards density, boiling-point, difficulty of liquefaction, &c., lead me personally to favour the lower figure for its atomic weight, and the same considerations may apply to helium also. Until further evidence is furnished, therefore, I shall assume the values 2 and 20 as approximately true for the atomic weight of helium and argon.

Carbon.—Wanklyn (Chem. News, lxxii., 164; see also *Phil. Mag.*, August, 1895; also the reports of this committee for 1893 and 1894), on the basis of his investigations into the composition of hydrocarbons, reiterates his belief that the atomic weight of carbon is not 12 but 6. This question is one which falls rather outside the scope of this report and needs no further discussion here. If Wanklyn's contention is sustained, the value assigned to carbon in the table accompanying this paper should be divided by two.

In the accompanying table of atomic weights, the values are given according to both standards, $H=1$ and $O=16$. Many of the figures are the results of new and complete re-calculation from all available data, made in the preparation of a new edition of my "Re-calculation of the Atomic Weights."

ELECTRIC SHADOWS AND LUMINESCENCE.*

By Prof. SILVANUS P. THOMPSON, D.Sc., F.R.S., M.R.I.

(Continued from p. 106).

And now let me remark that not one of all the tubes shown since the first one is capable of showing a shadow upon the fluorescent screen outside, or of taking a photograph through a sheet of aluminium. Even the brilliant tube which showed so excellently the shadow of the cross, fails to show any result after hours of vain waiting. It yields no rays that will penetrate aluminium. For experiments with Röntgen rays it is absolutely necessary that the process of exhaustion should be carried beyond the stage that suffices for the production of kathode shadows; it must be pushed to about that limit which Crookes himself described as his unit for the degreee of vacuum, namely, one-millionth of an atmosphere. I do not say that with long exposures photographs cannot be taken when the degree of exhaustion is lower. Something depends, too, upon the degree to which the electric discharge is stimulated, and something also depends upon the shape and structure of the tube and upon the size and shape of the kathode. But on none of these things does the emission of X-rays depend so much as upon the degree of vacuum. The highly exhausted vacuum is the one real essential.

So soon as Crookes's researches upon electric shadows had become known, electricians set to work to try to produce electric shadows in ordinary air without any vacuum. One of the ablest of experimenters, Prof. W. Holtz, was successful, using as a source of electric discharge the electrified wind which is given off by a metal point attached to the pole of an influence machine. If in a perfectly dark room such a point is placed opposite and at a few inches from a wooden disc covered with white silk and connected at its back or edges to the other pole of the machine, it will be observed to show a pale luminosity over a circular patch where it is struck by the electric wind. If then the object is brought between the disc and the point a shadow will be observed to be cast upon the white surface. Non-conductors do not cast shadows as well as conductors do. A piece of thin mica scarcely casts a shadow at all until it is moistened. Double shadows can be got by using two disks covered with silk facing one another; any conducting object introduced between them casts a shadow on both. If such a shadow from an electrified point is cast downward upon a sheet of ebonite or pitch, the parts not shaded are found afterwards to remain electrified, and can be discovered by scattering over them Lichtenberg's mixed powders of red-lead and lycopodium, thus perpetuating the shadow.

But now it is possible to produce electric shadows in another way, photograpically, as has been known for some years (*Proc. Phys. Soc. Lond.*, xi., 353, 1892), from metal objects such as coins, by simply laying them down upon a photographic dry-plate (a gelatino-bromide plate) and sending an electric spark (from an induction-coil) into them.

Fig. 3 shows the arrangement adopted by the Rev. F. J. Smith, who is kind enough to exhibit in the library to-night some scores of his beautiful "inductoscript" photographs. Upon the screen I throw a few samples, including a print of one of the Jubilee coins (Fig. 4). These curious photographs are produed simply by the chemical action of the electric discharges which stream off from all the projecting portions, and so roughly reproduce an image of the coin. Since Röntgen's discovery many persons have announced their supposed discovery of the production of electric shadow-pictures without the aid of a Crookes tube. What they have really observed is, however, totally different. They have not been producing X-rays at all, but have merely re-discovered these inductoscript shadows.

Between the researches of Crookes, however, and those of Röntgen, there came in a very remarkable body of researches in Germany. I have but to name Goldstein, Puluj, Hertz, Wiedemann, and Lenard (See Note), amongst the workers, to show what interest has been concentrated on the subject. Hertz, whose loss Science has not ceased to lament, observed that a part at least of the kathode rays were capable of passing through thin aluminium sheet, a property which confirmed him in his previous doubt as to the material nature of the kathodic discharge. His pupil, Philipp Lenard, now Prof. Lenard, of Aachen, took up the point. He fitted up a tube with a small window of aluminium foil opposite the kathode, its form being that shown in Fig. 5. The kathode was a flat disk on the end of a glass-covered wire stem. The anode was a cylindrical tube of brass surrounding the kathode. Upon the further end of the tube a brass cap was fixed by means of vacuum-tight cement. Over a small orifice in this brass cap was set the aluminium window of foil only 1-400th m.m. thick. By this means he was able to do what had previously been supposed impossible—bring the kathode rays out into the open air. Or, at least, that is what he appears to have considered that he was doing. Certainly he succeeded in bringing out from the vacuum tube rays that, if not actual prolongations of the kathode rays, were closely identified with them. He examined their properties both in the open air and in gases contained in a second chamber beyond the window, and found them to be capable of producing photographic impressions on sensitive plates. He further examined the question whether they can be deflected by a magnet. Fig. 6, which is copied from Lenard's paper, shows the results. The row of spots on the left side shows the photographic effect under various different conditions of experiment when there was no magnet present. The spots in the right-hand row show the effects obtained when a magnet was present. For example, in the third row from the top it is seen that the bundle of rays when subjected to the influence of the magnet is partially dispersed, the spot being enlarged sideways and having a kind of nebulous tail. This proves that through the aluminium window there came some rays which were deflected by a magnet, and some rays also which were not deflected by a magnet. The question naturally arises whether the rays which Lenard had thus succeeded in bringing out into the open air are the same thing as the rays with which Crookes had been working with inside the vacuum. To that question the final answer cannot yet be given. Certainly some of the Lenard rays resemble the interior kathode rays; but some

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* A Lecture delivered at the Royal Institution of Great Britain, Friday, May 8, 1896.

differ in the crucial respect of deflectability by the magnet. The higher the degree of vacuum, the less are the rays deflected.

NOTE.

Goldstein, in his "Researches on the Reflection of Electric (*i.e.*, Kathode) Rays," in *Wiedemann's Annalen* (xv., 246, 1882), came very near to the discovery of the Röntgen rays. After pointing out that Hittorf had held the opinion that the kathode rays end at the place where they strike upon a solid wall, and that they are unable to proceed in any direction at all from thence, Goldstein directs attention to the circumstance that fluorescent patches are sometimes seen at the end of crooked tubes, where they could not have been caused by the direct impact of kathode discharges. He discusses the question whether this is due to reflection or to a deflection caused by the spot where impact first took place having become electrified negatively, and therefore acting as a secondary kathode. The latter hypothesis is rendered untenable by his observation that if the spot of first impact is made an anode the effect still occurs. He then shows that the phenomena are inconsistent with a specular reflection, but are explained by supposing that there is a diffuse reflection. He then sums up as follows:—"A bundle of kathode rays does not end, at least under those circumstances under which it excites phosphorescence, at the place where it strikes upon a solid wall, but from the place of impact on the wall there proceed electric rays in every direction in the gaseous space. These rays may be considered as reflected. Any solid wall of any property whatever may serve as a reflecting surface. It is immaterial whether or not it is capable of phosphorescence, or whether it consists of an insulator or of a conductor. The reflection is diffuse, no matter whether the surface is dull or most highly polished. An anode reflects the kathode rays sensibly as well as a neutral conductor or an insulator. The reflected rays have, like the direct kathode rays, the property to excite phosphorescence at their ends. They are subject to deflection, and their ends are deviated in the same sense as the ends of kathode rays, which would extend from the reflecting surface toward the place hit by the reflected rays."

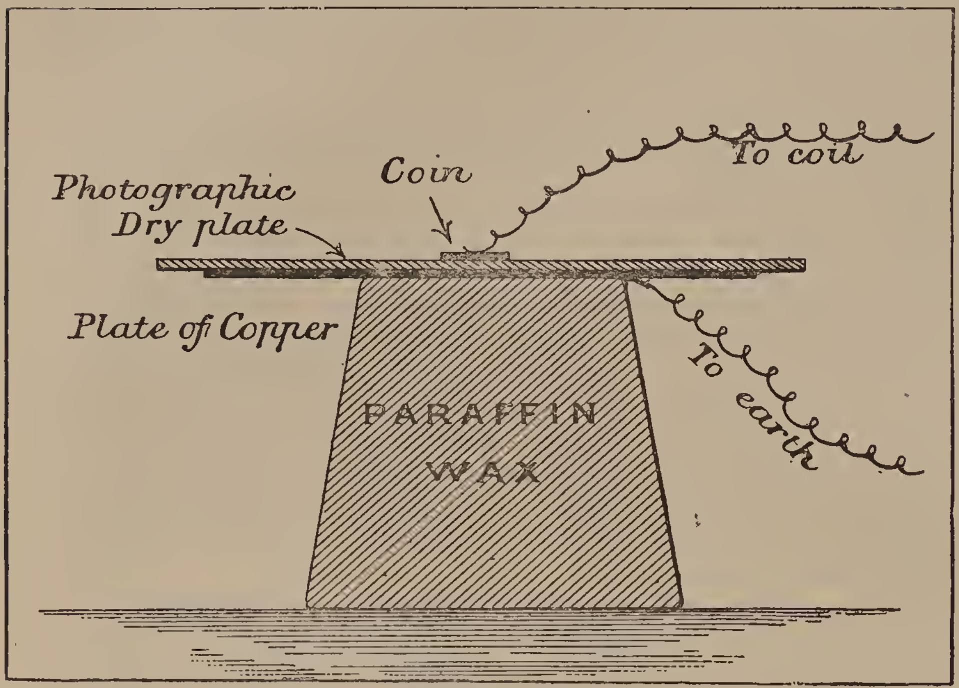

FIG. 3.

FIG. 4.

Puluj, "Radiant Electrode Matter, and the so-called Fourth State." Published in vol. i. of "Physical Memoirs," by the Physical Society of London, 1889. These are translated from papers published in 1883 in the *Memoirs of the Imperial Academy of Sciences at Vienna.*

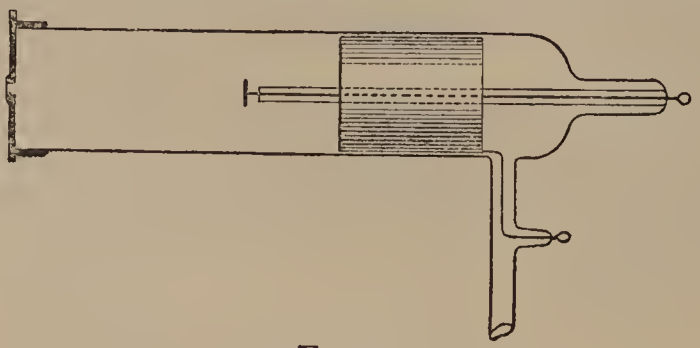

FIG. 5.

H. Hertz. "Researches on the Glow-Discharge," *Wied. Ann.*, xix., 782, 1883. Hertz regards the kathode rays as a property of the ether, not as consisting of moving particles. He finds the kathode rays to consist of a heterogeneous variety of kinds which differ from one another in their properties of causing phosphorescence, of being absorbed, and of being deflected by the magnet.

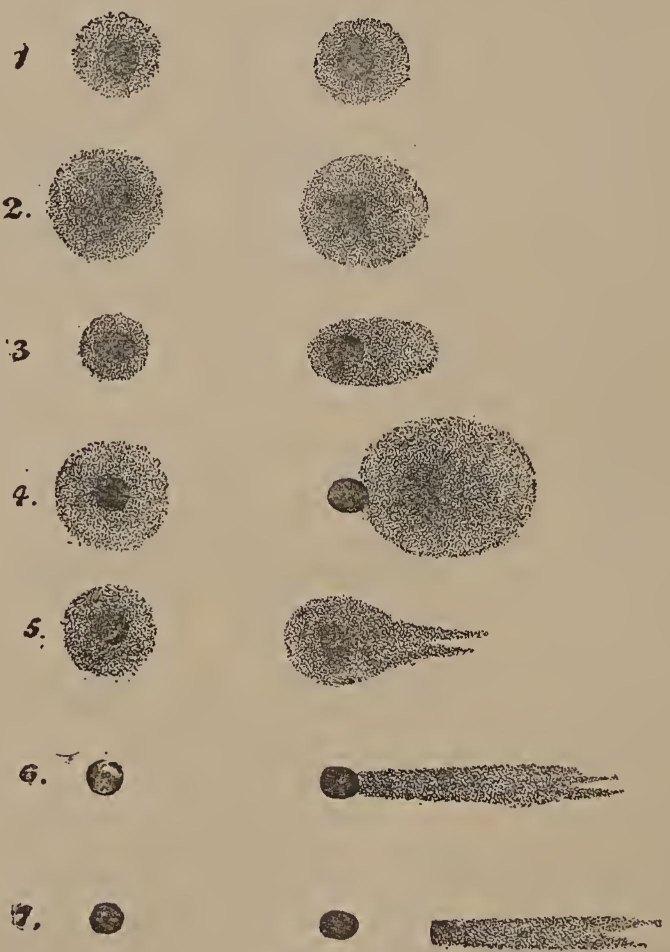

FIG. 6.

"On the Transmission of the Kathode Rays through Thin Layers of Metal" (xlv., 28, 1892), Hertz finds that glass fluoresces in kathode rays, even if covered with gold-leaf or thin films of various metals, though not if covered with thin mica. Aluminium was found best, and allowed fluorescence to occur even when a sheet of aluminium-leaf was used so thick as to be opaque to light. A diaphragm of thin aluminium-leaf on a metal frame placed inside a Crookes tube at 20 c.m. from the kathode, permitted enough rays to pass to give a tolerably bright and even fluorescence over the whole of the further end of the tube. These rays, after passing through the leaf of metal, still showed rectilinear propagation (with some diffusion), and had not lost the property of being deflected by the magnet.

E. Wiedemann's papers, which are of special importance, have mostly appeared in *Wiedemann's Annalen.* The following are the chief of them. Some of the later have been written in collaboration with Prof. H. Ebert.

"On the Phosphorescent Light excited by Electric Discharges" (*Wied. Ann.*, ix., 157, 1880).

"On Electric Discharges in Gases" (xx., 756, 1881).

"On Fluorescence and Phosphorescence," Pt. I (xxxiv., 446, 1888).

"On the Mechanism of Luminosity" (xxxvii., 177, 1889).

"On Kathodo- and Photo-Luminescence of Glasses" (xxxviii., 488, 1889).

"On Electric Discharges in Gases and Flames" (xxxv., 209, 220, 234, 237, 255, 1888).

"On Electric Discharges" (xxxvi., 643, 1889).

"On the Apparent Repulsion of Parallel Kathode Rays" (xlvi., 158, 1892).

"On Electric Discharges; Excitation of Electric Oscillations and the Relation of Discharge-tubes to the same" (xlviii., 549, and xlix., 1, 1893).

"Researches on Electrodynamic Screening-action and Electric Shadows" (xlix., 32, 1893).

"Luminous Phenomena in Electrode-less Rarefied Spaces under the Influence of Rapidly-alternating Electric Fields" (l., 1, 221, 1893).

With J. B. Messerschmitt, "On Fluorescence and Phosphorescence, Pt. II., Validity of Talbot's Law" (xxxiv., 463, 1888).

With H. Ebert, "On the Transparency of Kathode Deposits," *Sitzber. d. Phys.-Med. Soc. zu Erlangen*, Dec. 14, 1891.

Lenard's Papers are:—

"Note on a Phosphoroscope, with Spark Illumination" (*Wied. Ann.*, xxxiv., 918, 1888).

With M. Wolf, "Luminescence of Pyrogallic Acid" (xxxiv., 918, 1888).

With V. Klatt, "On the Phosphorescence of Copper, Bismuth, and Manganese in the Sulphides of Alkaline Earths" (xxxviii., 90, 1889).

"On Kathode Rays in Gases at Atmospheric Pressure, and in the most Extreme Vacuum" (li., 225, 1894).

"On the Magnetic Deflexion of the Kathode Rays" (lii., 22, 1894).

"On the Absorption of the Kathode Rays" (lvi., 255, 1895).

(To be continued).

THE OXALATES OF ZIRCONIUM.

By F. P. VENABLE and CHARLES BASKERVILLE.

The text-books of chemistry make either very little or no reference to the oxalates of zirconium. Beyond an occasional reference to the oxalate or basic oxalate gotten by precipitating with oxalic acid or an oxalate, we can find little mention of these compounds. Behrens, in his microchemical work, speaks of an oxalate prepared as colourless pyramids by precipitating a solution of zirconium sulphate with potassium binoxalate, but no analyses are given, and the crystals could scarcely have been the pure oxalate. Paykull ("Ofv. af. Vet. Ak. Förhandl.," ref. in *Ber. d. Chem. Ges.*, xii., 1719) speaks of double oxalates being prepared with the alkaline oxalates (1 : 2) and his failure to prepare the neutral oxalate. His methods, and indeed full results, are unknown to us, as we did not have access to the original paper.

We may summarise the work which follows in the succeeding pages by saying that we found it possible to prepare the basic oxalates by precipitation. This was usually in the form of $Zr(C_2O_4)_2.Zr(OH)_4$, though other ratios were gotten. The neutral oxalate we did not succeed in preparing, but instead the tendency seems to be toward the formation of the acid oxalate,—

$$Zr(C_2O_4)_2.H_2C_2O_4{\cdot}8H_2O.$$

This tendency toward the formation of acid salts was shown also in the double oxalates. Two of these were prepared. For sodium,—

$$Zr(C_2O_4)_2.3NaC_2O_4.H_2C_2O_4.5H_2O,$$

and for potassium the salt—

$$[Zr(C_2O_4)_2]_2.(K_2C_2O_4)_2.H_2C_2O_4.8H_2O.$$

The oxalate with ammonium as a constituent was not so easy of preparation in a pure state. The compound secured was $Zr(C_2O_4)_2.2(NH_4)_2C_2O_4$. The experiments and analyses are given in detail.

Zirconium Oxalates.

The Oxalate Gotten by Precipitation.—On the addition of a saturated solution of oxalic acid to a slightly acid solution of zirconium chloride until no further precipitation occurred, a gelatinous precipitate formed which had very nearly the composition $Zr(C_2O_4)_2\ 2Zr(OH)_4$. Analysis I. gave Zr 46·39, and C_2O_4 30·89, instead of the theoretical 46·40 and 30·93 respectively. The filtrate from this was turbid, and on standing yielded another precipitate which had nearly the composition $2Zr(C_2O_4)_2.3Zr(OH)_4$.

These basic oxalates are very difficultly soluble in acids, and of extremely fine subdivision, settling slowly and passing through even the best filters. It does not seem probable that they could be secured of very constant composition. Probably basic oxalates with many different ratios between the oxalate and the hydroxide might be secured. On drying at 100°, or even a little lower, the oxalic acid is gradually volatilised and lost. This is true of all the oxalates and double oxalates prepared, so that the only mode of drying these preparations was between filter-paper.

The Acid Oxalate prepared by Crystallisation.—In preparing this oxalate, zirconium hydroxide was dissolved in oxalic acid. The hydroxide is quite soluble in oxalic acid, and a concentrated solution is readily obtained. A considerable excess of the acid is required to hold the oxalate thus formed in solution. If this solution be acidified by means of hydrochloric acid a very fine precipitate is obtained, settling very slowly, easily passing through the best filter-papers, and insoluble even in a considerable excess of the acid, but soluble in concentrated sulphuric acid. This precipitate was not analysed, nor were the exact conditions of its formation determined, as its examination did not promise results of sufficient importance to justify overcoming the difficulties in the way.

On evaporating the acid solution of the oxalate the excess of oxalic acid first crystallises out. In the various preparations made, the first one or two crops of long crystals were found to be nearly pure oxalic acid, and were rejected. Then the form of the crystals changed to small granular or prismatic masses, and with each succeeding crop of crystals the percentage of zirconium increased, reaching speedily an approximately constant ratio. No difference in the form of the crystals in these different crops could be detected on superficial examination, and hence it was impossible to distinguish between the zirconium oxalate and the oxalic acid almost free of zirconium, except by analysis. In no case was the normal oxalate secured. The analyses showed a tendency toward the formation of an acid oxalate and to mixtures of this with the normal oxalate. These mixtures were gotten in the later crystallisations, but the last crystallisation, when nearly the whole would solidify into a crystalline mass, showed decreased percentages of zirconium. It is possible that larger amounts than we had at our disposal would enable one so to fraction the crystallisation as to secure a pure oxalate. It is, however, questionable whether the normal oxalate can exist in solution without admixture with some oxalic acid.

Four series of crystallisations were made, and in two cases fairly abundant crops of crystals corresponding to the acid oxalate were obtained. In each series enough of the zirconium hydroxide was taken to form about 20 grms. of the oxalate.

	First series. Sixth fraction. II.	Second series. Fifth fraction. III.	$Zr(C_2O_4)_2.H_2C_2O_4$.
Zr	25·44	25·28	25·53
C_2O_4	74·55	74·72	74·47

These are calculated upon the water-free basis. The crystals contained 29·34 and 29·27 per cent of water respectively, where the salt $Zr(C_2O_4)_2.H_2C_2O_4.8H_2O$ contains 28·90 per cent. Other crops of crystals contained percentages of zirconium not varying greatly from these given above as 28·14, 27·62, 24·9, 23·83. The percentage of zirconium in the normal oxalate is 33·96.

Zirconium Sodium Oxalate.

The addition of sodium oxalate to a slightly acid solution of zirconium chloride gives a gelatinous white precipitate. Most of this dissolves in an excess of the oxalate. The undissolved portion settles to the bottom, and after prolonged standing a second layer of a more powdery appearance forms. This can also be gotten by concentration of the filtrate from the first precipitate. Analysis showed that the first gelatinous precipitate was chiefly $Zr(OH)_4$. The second precipitate was a double oxalate of zirconium and sodium, but was either of inconstant composition (varying ratios of sodium to the zirconium), or was decomposed by the washing.

The analyses, calculated on the dry basis, gave:—

	IV.	V.	VI.
Zr	53·12	46·86	41·98
Na	9·16	4·10	1·07
C_2O_4	38·06	39·64	42·95

If the solution made with the excess of sodium oxalate was diluted considerably with water, a gelatinous precipitate was formed, very fine and insoluble. Precipitates were also formed by the addition of hydrochloric acid. This mode of forming the double oxalate was abandoned, and the following method was adopted with greater success. Zirconium hydroxide was dissolved in an excess of oxalic acid, and to this a concentrated solution of sodium hydroxide was added, bringing it nearly to neutralisation. When the solution was concentrated, an abundant crop of crystals was obtained on cooling, a good deal of heat being evolved in the mixing. Further evaporation yielded other crops of crystals. These were washed, dried between filter-paper, and analysed. The results are given in the following table:—

	VII.	VIII.	IX.	Calculated.
Na	18·14	17·46	17·75	18·19
Zr	12·59	12·66	12·78	11·93
C_2O_4	69·27	66·89	69·47	69·88

These results show a somewhat wide variation from those calculated. This probably arises from the fact that the fractions were not composed of the crystals of a single kind of oxalate, but had other oxalates mixed with them in small amounts. Examined under a magnifying glass they seemed to be homogeneous, but the different crops could not be distinguished from one another. They were all small, hard prismatic crystals, somewhat difficultly soluble in water. One set of crystals, the analysis of which is reported under VII. in the above table, was re-dissolved in water and re-crystallised. On analysis it yielded the following results:—

	VII.	XI.
Na..	18·14	18·19
Zr	12·59	12·71
C_2O_4	69·27	69·10

These were calculated upon a water-free basis. The crystals from the various crops mentioned above did not contain a very constant amount of water, but ranged from 9·13 to 11·06. The calculated amount of water in $Zr(C_2O_4)_2.3Na_2C_2O_4.H_2C_2O_4.5H_2O$ is 10·62. It would seem, therefore, that the tendency, when this method of formation is adopted, is toward the formation of crystals containing free oxalic acid and with the sodium and zirconium oxalates bearing a ratio of three to one.

Zirconium Potassium Oxalate.

The curdy precipitate gotten by precipitating zirconium chloride with normal potassium oxalate is insoluble in an excess of either of the substances. The precipitate first obtained is an impure zirconium hydroxide, containing only small amounts of oxalic acid. The supernatant liquid, on concentration, yields needle-like crystals of potassium oxalate, carrying only traces of zirconium. After the separation of a good deal of this potassium oxalate, further concentration yielded a gelatinous substance having the composition (XII.): Zr, 39·34; K, 5·06; C_2O_4, 43·05; which seems to be a basic zirconium oxalate, mixed or united with a small proportion of potassium oxalate. If the potassium be calculated as potassium oxalate and subtracted, the composition of the remainder would be approximately $Zr(OH)_4.Zr(C_2O_4)_2$.

On adding potassium binoxalate to a solution of zirconium chloride a white curdy precipitate was obtained which was not completely soluble in excess of the binoxalate. The somewhat turbid solution was filtered and evaporated. Large crystals resembling those of oxalic acid formed. These were separated, and on analysis proved to be oxalic acid. At the same time a number of small crystals were formed, which were mechanically separated, washed, and dried. These were analysed, and are reported under XIII. A further crop was gotten from the mother-liquor, and the analysis is given under XIV.

	XIII.	XIV.
Zr..	19·59	17·99
K	16·18	13·91
C_2O_4	64·23	68·09

The curdy precipitate which first formed was also examined, and found to have the composition $Zr(C_2O_4)_2.2Zr(OH)_4$.

The addition of a solution of potassium tetroxalate to zirconium chloride gave a gelatinous precipitate of zirconium oxalate (basic), carrying a little potassium oxalate. Subtracting the potassium oxalate, the percentages (XVI.) Zr 39·09, and C_2O_4 38·63, are left, which are not very different from the figures gotten for the precipitate from potassium oxalate (neutral).

This curdy gelatinous precipitate was dissolved in excess of tetroxalate, and the solution placed over sulphuric acid to crystallise, and yielded crystals having the composition (XVII.): Zr 20·85, K 16·72, and C_2O_4 62·31. As will be seen, these are not far from the 1 : 2 zirconium potassium oxalate, with excess of oxalic acid.

When potassium hydroxide was added to a solution of zirconium oxalate in oxalic acid until nearly neutral, and then set aside for crystallisation, various crops of crystals were gotten, as in the case of the double sodium oxalates. These crops of crystals were similar in appearance to the sodium crystals. They were analysed and showed fairly constant composition.

	XVIII.	XIX.	XX.	XXI.	$(Zr(C_2O_4)_2)_2.(K_2C_2O_4)_2.H_2C_2O_4$
Zr..	18·08	19·25	19·83	18·47	18·95
K ..	16·41	16·35	14·84	14·46	16·34
C_2O_4	66·51	64·40	65·33	67·07	64·71

The three previous analyses may also be referred to here as having approximately the same composition. (See Analyses XIII., XIV., XVII.). These are calculated as water-free. In the Analyses XVIII. and XIX. the percentages of water were 12·99 and 12·38. These would correspond to the formula—

$$(Zr(C_2O_4)_2)_2.(K_2C_2O_4)_2.H_2C_2O_4.8H_2O.$$

In this case, as in the zirconium oxalates and the sodium oxalates, the crystals seem to form only along with free oxalic acid, giving acid salts.

Zirconium Ammonium Oxalates.

The addition of a solution of ammonium oxalate to the slightly acid solution of zirconium chloride gave a heavy gelatinous precipitate which was soluble in excess of ammonium oxalate, and proved to be zirconium hydroxide with more or less zirconium oxalate and small amounts of ammonia. The filtrate from this precipitate was evaporated slowly and a fine crystalline powder obtained. This contained (XXII.) Zr 42·17 per cent, and C_2O_4 39·86 per cent. This is in fair agreement with—

$$Zr(C_2O_3)_2.Zr(OH)_4.$$

When ammonium oxalate is added until the first gelatinous precipitate is re-dissolved, and then evaporated to crystallisation, different crops of crystals can be gotten containing various amounts of ammonia. These did not seem to have any regular composition in our experiments, and were looked upon as basic zirconium oxalates with varying amounts of ammonium oxalate present. Thus for one of these the figures (XVIII.) Zr 31·48, NH_3 7·14, and C_2O_4 61·38 were gotten.

Abandoning this method, and using the one adopted in the cases of the sodium and potassium double oxalates, a more favourable result was obtained. Zirconium hydroxide was dissolved in excess of oxalic acid, and then this was nearly neutralised by means of ammonium hydroxide. Analyses of these crops of crystals follow:—

	XXIV.	XXV.	$Zr(C_2O_4)_2.2(NH_4)_2C_2O_4$.
Zr	16·55	16·66	17·58
NH_3 ..	14·46	13·35	13·28
C_2O_4 ..	69·99	69·99	68·94

While these do not show that the crystals had been thoroughly purified, the results indicate that the composition is one zirconium oxalate to two ammonium oxalate. On re-crystallising one of these crops of crystals, zirconium hydroxide was observed to separate when the solution was heated (to evaporate to crystallisation), and the crystals which were obtained consisted of ammonium oxalate alone.

In general it may be stated that the zirconium oxalate fails to show any decided tendency to enter into clearly-defined combinations with the alkaline oxalates, exhibiting rather a power of crystallising along with them in mixtures of any proportions. It can only be said at best that under the conditions of our experiments certain ratios seem to be preferred, and appeared more persistently. In all cases the crystals formed from oxalic acid solutions, and this free oxalic acid crystallised with them, giving acid oxalates.—*Journ. Amer. Chem. Soc.*, xix., p. 12.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on March 1st, Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—F. J. Beaumont, Major C. T. Blewitt, R.A., J. F. L. Brunner, James Cadett, J. C. Carter, John Cohen, Mrs. Thomas Collier, J. G. Craggs, T. Donaldson, Henry Edmunds, Mrs. Henry Edmunds, G. S. Elliot, W. A. Frost, F.R.C.S., W. T. Garnett, J.P., H. A. Harben, Dr. F. Hewitt, F. W. Hildyard, Mrs. George King, H. Leitner, the Rev. J. D. Parker, E. M. Preston, J. M. Richards, Colonel G. Sartorius, F. H. Schwann, Dr. W. R. Smith, H. A. Stern, C. J. Stewart, G. L. Stewart, Mrs. A. D. Waller, and Mrs. J. Lawson Walton.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 26th, 1897.

Mr. Shelford Bidwell, President, in the Chair.

Mr. J. H. Vincent read a paper on the "*Photography of Ripples.*"

If mercury is used as the medium, all waves less than 1·3 c.m. long come under Lord Kelvin's definition of a ripple; that is to say, they are waves whose lengths are less than such as are propagated with minimum velocity. Vibrations in mercury of about 200 per second and upwards generate waves whose propagation is controlled almost entirely by surface tension, and these waves are therefore classed as "capillary ripples." Their speed of propagation is of the order of about one foot per second. They are invisible, owing to their high frequency, not in consequence of the velocity of their propagation. It is usual to examine them by some stereoscopic method.

Mr. Vincent obtains photographs of the disturbed mercury surface by the sudden illumination of an electric spark. The spark is about half a centimetre in length, and it lasts about one two-hundred-thousandth part of a second. Its brightness is increased by an auxiliary spark-gap. The optical arrangement consists of two lenses, one in the path of the incident light, and another to converge the reflected light from the mercury surface into a photographic camera. Ripples are set up in the mercury by a stylus attached to a tuning fork. For this purpose it is generally sufficient to give a slight blow to the prongs; but when continuous vibration is required the tuning-fork can be connected by a thread to an electrically driven fork, as suggested by Mr. Watson.

The first photograph shows a series of circular waves, set up by a single stylus attached to a fork vibrating 180 times a second. Fixed points at known distance, just above the mercury surface, enable the wave-lengths to be deduced from the photographs; and, as the frequency is known, the surface tension may be easily calculated.

In a second photograph, two styluses are attached to the same prong. Dark lines are seen to radiate from the region between the centres of oscillation; these are the lines of minimum disturbance—hypberolas, of which the centres of disturbance are the foci. This photograph illustrates "interference" similarly to the optical method of Young and Fresnel.

A third photograph shows the formation of elliptical curves of disturbance, being the loci of the intersection of two series of circles, corresponding one to each of the two centres of vibration. Unlike the system of hyperbolas, these ellipses are not at rest, but travel outward from the sources. In order to render these ellipses stationary, it would be necessary to change one of the *sources* into a *sink*, towards which the circular waves might converge; the photograph would then correspond to the optical device of M. Meslin, who obtains interference fringes by means of a screen placed between two point centres, one a *source*, and the other a *sink*.

The phenomena of interference and diffraction are well shown in a photograph of a point source and a reflecting line. The reflector here is one side of a triangular piece of microscope cover-glass. The interference lines are due to the mutual action of incident and reflected rays; they are analogous to Lloyd's single-mirror fringes. Other photographs exhibit analogues of "spherical aberration" and "forced vibration."

Mr. Vincent acknowledged his indebtedness to Mr. Boys for the recommendation of attempting the photography of capillary ripples.

Mr. Boys congratulated the author upon the way in which the experimental difficulties had been overcome. The results would bear a good deal of close examination, and they would be found to present analogues of the greatest service in demonstrating the phenomena of acoustics and optics. Such photographs were far better than geometrical pictures drawn by instruments. For example, in the photograph illustrating the regions of minimum disturbance by lines radiating from a two-point source, it was easy to make out the positions where the two series of waves were half a period behind one another. The crests and troughs appeared as a set of dark and light concentric alternating circles, broken up into short arcs by radiating lines—the loci of minimum disturbance; all the crests on one side of any particular radiating line were seen to correspond to troughs on the other side, so that the field of disturbance was mapped out as in acoustics. One set of phenomena yet awaited illustration by this photographic method, and that was "diffraction" from a grating. It might be possible to use as an exciter a comb with chisel-shaped points. He did not think it would be possible to go quite so far as to reproduce analogues of spectral analysis. Since wave-length varies with surface tension, it was possible to vary the wave-length by dropping a little ox-gall or soap solution upon the mercury surface.

Mr. Blakesley asked why no reflections occurred from the sides of the mercury retainer.

Mr. Boys said the waves were lost at the edges of the meniscus. The mercury was kept in position by an annular ring of thin glass.

Mr. Appleyard suggested that the analogue of refraction might be obtained by an alteration of the surface-tension over a small area by amalgamation or other means.

Mr. Vincent thought this could be done, but that it would be very difficult.

The President proposed a vote of thanks to the author.

Mr. Elder then read a paper by Mr. Beckit Burnie on "*The Thermo-electric Properties of some Liquid Metals.*"

The investigation was made with a view to determining the effect of melting upon the thermo-electric properties of certain metals. The metal to be tested is contained in a W-shaped glass tube, of which one limb can be cooled and the other heated. Thus one limb can contain molten, and the other solid, metal. Copper wires are plunged one into each limb, and through these connection is made with a galvanometer. The thermal junctions, therefore, are copper-hot metal and copper-cold metal. The temperature is deduced from a separate thermal couple, calibrated by a mercurial thermometer. Curves are drawn co-ordinating temperature and electromotive force. It is found that their slope depends upon the rate of cooling or heating of the metals; this is particularly the case with bismuth. The effect is attributed to the variation in crystalline structure of the metal under test at different rates of solidification. With tin the change is less marked, and with lead it is unnoticeable. At or about the melting-points there is considerable change of slope in the curves. Here, again, the effect is smallest for lead; somewhat greater with tin; and remarkably large with bismuth, the latter changing from an exceedingly active thermo-electric metal to one resembling lead. A great change occurs also with mercury at the melting-point, indicating a difference in the Peltier effect between solid and molten metals.

A vote of thanks to Mr. Beckit Burnie was proposed by the President, and the meeting adjourned until March 12th.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Fifth Ordinary Meeting, February 8th, 1897.

Dr. J. E. Mackenzie in the Chair.

Mr. W. W. Taylor, M.A., B.Sc., read a paper on the "*Electrolytic Dissociation of Water.*"

The author began by describing the main principles of the theory of electrolytic dissociation.

The work of Kohlrausch in determining the actual conductivity of pure water was described in detail.

The method adopted by Wijs for arriving at the dissociation grade from the hydrolysis of methyl acetate; that of Arrhenius and others from the balance between aniline acetate and water; and, lastly, the numbers got by Ostwald and Nernst from the electromotive force of a gas battery consisting of hydrogen electrodes in acid and alkali, were all treated of and carefully explained.

Sixth Ordinary Meeting, February 22nd, 1897.

Mr. W. W. Taylor in the Chair.

Dr. Marshall gave a lecture on "*Electrolysis.*"

A historical sketch of the subject from the end of last century till the present time was first given; the invention of the electric pile by Volta, the decomposition of water by Nicholson and Carlisle, Davy's discoveries, and those of Berzelius, Faraday's laws, and the work of Daniell and Hittorf; finally, the theory proposed by Arrhenius.

The uses of electrolysis in chemical analysis were then considered, various examples being taken to illustrate this in reference to quantitative electrolysis.

A brief mention was then made of the uses of electrolysis in electrotyping, electro-metallurgy, and the purification of such metals as copper.

A selection was made both from inorganic and organic substances to show how certain syntheses could be conducted by electrolytic means.

NOTICES OF BOOKS.

A Practical Treatise on Animal and Vegetable Fats and Oils. By W. T. Brannt. (Second Notice). Vol. II. Philadelphia: H. C. Baird and Co. London: Sampson Low, Marston, and Co., Ltd. 1896.

We find here firstly the conclusion of the account of the non-volatile or fatty oils. The efficacy of boiling as applied to linseed oil is traced to the expulsion of mucilage. It is remarkable that in some parts of Russia and Germany cold-drawn linseed oil is used as a table-oil and in cookery.

The production of sunflower oil for industrial uses in Russia is steadily increasing.

Nut-oil, expressed from the walnut, dries better even than linseed oil, and is preferred for artistic uses. Sperm oil has an advantage over most oils, as its sophistication is exceedingly difficult. The nature of ambergris is still a disputed question; some authorities considering it as a pathological secretion of the urinary bladder, whilst others regard it as merely the indurated fæces of the animal.

The remarkable penetrative power of doeglic oil was put on record as early as 1250. The credit of first obtaining cod-liver oil, colourless, not in virtue of any artificial bleaching, but of the total freedom from putrefaction, seems to belong to Peter Möller. Eulachon oil is preferred by some physicians as being more digestible than cod-liver oil.

Fish-waste is a most valuable source of artificial manure, and is capable of much extension. It is conducted chiefly in the Lofoten Isles, at Newfoundland, and on the coasts of the United States.

Borneo tallow, obtained from trees of the genus *Hopea*, is a lubricating agent far preferable even to olive oil. The cultivation of the tree deserves attention.

Cacao-butter, one of the products of *Theobroma cacao*, and not of *Cocas mucifera* or of *Elæis guineensis*, has an exceptional power of resisting rancidity, but it is scandalously sophisticated with products which have no such properties. The original home of the cocoa-nut (better, to avoid confusion, *cocos-nut*) is correctly stated as being the Malay and the South Sea Archipelago.

It is satisfactory to find that the leading manufacturers and merchants are discouraging the term "refined lard" as applied to adulterated products.

On the subject of butters, as judged by Hehner's test, our author holds that samples with 88 per cent of insoluble fatty acids may be pronounced "pure," those with a higher percentage "suspicious," and with over 89·73 per cent "adulterated." We regret to find "titer" used in place of "standard."

Among the waxes, next to bees-wax, Chinese wax (*ceryl cerotate*) is said to possess "ten times the illuminating power of ordinary candles."

Waste fats include a variety of industrial products, one of the most important being the Yorkshire grease recovered from the waste waters of fulling mills. Its removal from the town sewage, and ultimately from the streams, is a necessary preliminary to the purification of the latter.

The bleaching of fixed oils and fats is explained very carefully. The chemical procedures were first introduced by Berthollet, though chlorine, which he proposed, has since been superseded by hydrogen peroxide, and in some cases by chromates mixed with hydrochloric acid. Animal charcoal is not well adapted for bleaching oils.

The successful application of feeble electric currents for bleaching oils seems to be due to L. Levat, of Aix. Acids could not be entirely removed in this manner from inferior lubricating oils.

Artificial butter was first produced by Mège-Mourier, under the auspices of Napoleon III. It is somewhat remarkable that whilst the Governments of France and Germany have encouraged the manufacture and sale of margarine, of course, under the proper regulations to prevent fraud, in the United States it has been opposed and persecuted in every practicable way. Eminent chemists, physiologists, and physicians, after long and careful courses of experiment, have decided that margarine has no unwholesome properties, and that it is less disposed to turn rancid than normal cow-butter.

Into the essential or volatile oils, their preparation and their distinctive characters, space does not allow us to enter.

We can strongly recommend this work to the vast and varied industries with which it is concerned.

The Chemistry of Dairying; An Outline of the Chemical and Applied Changes which takes place in Milk and in the Manufacture of Butter and Cheese; and the Rational Feeding of Dairy Stock. By Harry Snyder, B.S., Professor of Agricultural Chemistry, University of Minnesota, and Chemist of the Minnesota Experiment Station. Easton, Pennsylvania: Chemical Publishing Co. 1897.

The appearance of this book is explained and justified by the change which, within the last few years, has occurred in dairying. From a mere rule-of-thumb trade to an industry which, to be successful, must be conducted on scientific principles, or, at least, in accordance with facts scientifically determined.

In the chapter on the "General Composition of Milk," the reader is reminded that milk-fat and butter are not identical. Milk-fat is the pure dry fat, free from water, casein, or salt, all of which are present in butter to the extent of about 17 per cent.

For testing milk the Babcock method is recommended as trustworthy for whole milk, but as less reliable for butter-milk and skim-milk. Milk when partially frozen is not in a condition to be sampled.

The use of pure cultures, or as they are here called "starters," seems to be attracting attention in America for the ripening of cream.

The results of the lactometer are shown as liable to error on account of the complex composition of milk. Cream itself is variable, as it may contain as much as 60 per cent of fat. The higher the temperature reached in churning, washing, and working, the less is the proportion of water retained in the butter.

We find here no mention of the vegetable matters which in cheese-making may be used as substitutes for rennet.

It will be remarked here that in America a difference seems to be made between oleo-margarine and butterin, the former being harder and less fusible. With us this difference does not obtain, oleo-margarine being the name recognised by the law. It may here be noted that the butter now obtained from the milk of the cocoa-nut is more digestible than cow-butter.

This very useful manual is addressed not to experts, but to young men preparing themselves for the position of the dairy-farmer.

Engineering Chemistry; A Manual of Quantitative Chemical Analysis for the Use of Students, Chemists, and Engineers. By Thomas B. Stillman, M.Sc., Ph.D., Professor of Analytical Chemistry in the Stevens Institute of Technology. With 154 illustrations. Easton, Pennsylvania: Chemical Publishing Company.

The Publishing Company of Pennsylvania is decidedly earning a high and well-merited regulation for the production of works on technical chemistry. The title of the volume might with advantage be somewhat modified. Perhaps we might suggest "Manual of Quantitative Analysis, especially arranged for the Use of Engineers." But there is one section which could not be legitimately placed under such a caption. We refer, of course, to the copious and ably-written instructions for the sanitary analysis of water, a subject belonging to the medical practitioner, or the chemist truly so-called, rather than to the engineer. Here, however, we find no mention of the "tintometer" which is generally found preferable to the various calorimeters. Much of the matter on soaps can scarcely be called engineering chemistry.

On the other hand, something might have been usefully added to the remarks on filters. The Pasteur filter, which is generally found the best—at least for work on a domestic scale—does not seem to be mentioned.

The reader will be fully aware that the weights used in the United States of America are identical with the British standards. But this agreement unfortunately does not extend to the measures for liquids. The American gallon is about equal to the old English wine gallon. The obstinacy with which America, like France and Germany, clings to Baumé's hydrometer is painful. If there is any occult reason why commercial men should not or cannot use the direct specific gravity scale, why not use Twaddle, which exists only in one type, and which is easily and simply re-calculated into direct specific gravity?

Engineers will find this book a most useful and trustworthy guide.

Report on the Teaching of Chemistry by a Special Sub-Committee appointed by the Technical Education Board of the London County Council, November 23rd, 1896.

We hope that in our endeavours to realise a worthy standard of education in this country, we shall not remind the world of the too many cooks who spoiled the broth. We can scarcely enumerate the various public and semi-public bodies who have their fingers in John Bull's pie. Some boards and committees concerned are, if we consider their origin, little likely to play a very salutary part. But some of the gentlemen whose opinions are here put on record are fully qualified to speak on higher education, and deserve a respectful hearing. Thus, Mr. D. Howard, Dr. Armstrong, and Dr. Tilden do not consider that examination selects the best students. "The best thing to be done in London to promote this higher instruction is to extend the system of senior scholarships." These scholarships should on no account be awarded as the results of an examination, but as the personal recommendation of the professors upon whom the responsibility must be thrown of nominating only students of promise. Such scholars after about two years of special training in research should be able to work by themselves." "A person who is studying for the B.Sc. degree is handicapped as far as practical work is concerned, as he has to cram for his examinations. The boys cannot be picked out by mere examination, but by careful observation of their work. Scholarships gained by examination have done higher education a good deal of injury."

In short, a careful survey of the opinions expressed by the authorities here quoted shows more than ever that the blind reliance on examinations as a test of merit is nearing its end. "The selection should rather be determined by the recommendation of the head master of the school from which a pupil may proceed, based on the work of the candidate throughout his whole school career.

This is substantially the system which has worked so successfully in Germany.

The conclusions drawn from the evidence submitted are :—

1. That chemistry is a valuable subject for school teaching.
2. That it should be preceded by elementary courses of physics.
3. That the work should be always largely practical.
4. That no attempt should be made to impart in schools any knowledge of the application of chemistry for commercial purposes.
5. That in selecting candidates for the higher science training a written examination is insufficient and inadvisable.

This report is worth the most careful attention of all who are or aim at becoming authorities on national instruction.

Selection of Procedures for the Analysis of Fuels, Iron Ores, Castings, Steels, and Irons. (Recueil de Procédés de Dosage pour l'Analyse des Combustibles, des Minerais de Fer, des Fontes, des Aciers, et des Fers). By G. Arth, (Professeur de Chimie Industrielle à la Faculté des Sciences de Nancy. Paris : G. Carré and C. Naud. 8vo., pp. 313. 1897.

The present development of the iron and steel manufactures, and the extension of the industrial applications, has naturally led to the appearance of such works as that before us.

The author tells us in this preface that he does not offer a treatise on analysis, but merely a selection of the procedures in use in the principal siderurgical establishments and of other methods which it may be useful to know. He remarks that industrial analyses are of two different kinds. On the one hand easy and rapid methods for daily use, and on the other difficult procedures for establishing the composition of substances taken as types, or for checking doubtful results or such as have been the subject of dispute.

No fewer than 60 pages are here devoted to the assay and analysis of fuels. The exact difference between assay and analysis is scarcely as clear as it might be desirable. "Assay" may mean either a qualitative operation, or perhaps the determination of some leading ingredient. He determines phosphorus in the ashes of the fuel by means of the molybdenum method.

He determines the calorific power of a fuel by calorimetric methods, using the bombs of Hempel, of Mahler, and Berthelot. A whole page plate shows the installation of the bomb at the Chemical Institute of Nancy, whilst a table exemplifies the calculation.

There is also an account of the determination of calorimetric power by evaporation, and experiments in the boilers of industrial establishments. Three steam units may be employed, those of Rankine, Brix, and Hartig, equal respectively to 537, 540·6, and 552·2 cal. Then follows an account of the values of gaseous fuels ; to wit, the gases of gazogens, of blast furnaces, the gaseous mixtures of the Dawson system. A chapter is also devoted to gas analysis, *i.e.*, gases not employed as fuels but still summed up under the head assay and analyses of combustibles.

The second part is occupied with the "assay and analysis of ores," mainly, of course, those of iron. The analysis of titaniferous irons is, however, explained at some length according to the indication of Posti. It is remarked that the presence of titanic acid introduces several causes of error in determinations executed in the ordinary manner. It is also stated that oxygenated water is an excellent reagent for detecting the presence of titanic acid, as in acid solutions containing this titanic acid it produces a fine orange-yellow.

A third part of the work discusses the analysis of metallic products, iron castings, and steels. There is also the procedure of T. Parry and J. J. Morgan for the analysis of titanium, and the determination of phosphoric acid in basic slags.

Bread and Panification ; Chemistry and Technology of Baking and Grinding. ("Le Pain et la Panification Chimie et Technologie de la Boulangerie et de la Meunerie"). By Léon Boutroux, Professeur de Chemie Doyen de la Faculté des Sciences de Besançon. Paris : J. B. Baillière et Fils. Pp. 358. 1897.

France has long been distinguished for its eminence in the art of baking and all the collateral branches.

Hence, an author who combines the traditional skill of his country with a full insight into the results of of modern Science is well worthy of our careful attention. Professor Boutroux, moreover, has not confined his studies to French authorities, but has utilised the treatises of Birnbaum and Jago, so that he is able to lay before his readers the full results of the experience of the day.

From an analysis here given of wheats as produced in different countries we find the highest rank in percentage of gluten and albumen belongs to a Polish wheat, namely, 21·5 per cent, whilst the second place falls to Egyptian wheat with 20·6 per cent. If we contrast these figures with the white provincial wheat of 9·8, we shall not conclude that temperature and latitude are main factors in the growth of superior wheats. In a dry season, however, the nitrogen is much higher than in medium and moist years.

The different parts of the grain are by no means chemically identical, and vary in consequence in their physiological activity. The "entire flour" so much valued in Britain owes its laxative properties—annoying and even dangerous to some persons if beneficial to others—to the soluble matter of its coatings.

The use of rollers in milling was first applied in Hungary about 1874, and established itself in Western Europe since 1878.

The theory of panary fermentation is thus summed up. It consists essentially in an alcoholic fermentation by means of yeast and of the sugar pre-existing in the flour.

According to Bibra's analyses of bread the composition and even the reactions differ greatly. Some white breads, *e.g.*, those of St. Petersburg, are neutral. The rye bread of Nüremburg and of Stockholm is acid ; so is also the notorious pumpernickel of Westphalia, a whole-meal bread containing a little extra bran. A still inferior bread, Keilchen, is made in some parts of Saxony and Silesia.

The frauds committed by, or ascribed to, bakers are classified as—(1) The use of an excess of water; (2) the use of damaged flours; (3) the addition of alien flours; and lastly (4), the addition of saline waters other than sodium chloride.

This book will prove very valuable to public analysts, medical officers of health, and pharmacists.

Conspectus of Chemical Analysis. Part I.—Qualitative Analysis. ("Précis d'Analyse Chimique." Première Partie.—Analyse Qualitative). By E. Fink, Chef des Travaux Pratiques d'Analyse à l'Ecole de Physique et de Chimie Industrielle à la Ville de Paris. Paris: Georges Carres. 1896.

This little manual describes, in the first place, the reactions in the dry way, and then the reagents employed in the solid and in the liquid state. The author then proceeds to the assay, and in the dry way, including the use of the spectroscope. Next follows a classification of the metals from an analytical point of view, in which we perceive that not a few of the rarer substances are omitted. Next we come to the reactions of the acids, classified as the sulphuric, the hydrochloric, the nitric, the oxalic, the succinic, and acetic groups.

What may be called an Appendix treats of the preparation of the substances to be analysed, the systematic procedure for the detection of bases and acids, and the arrangement of the results.

CORRESPONDENCE

HOW SOON SHALL STUDENTS BEGIN THE STUDY OF QUALITATIVE ANALYSIS?

A Rejoinder.

To the Editor of the Chemical News.

Sir,—We perused Mr. Beebe's article on the above question with interest, but we are quite unable to agree with the conclusions he draws.

Mr. Beebe has three objections to the student beginning his laboratory course with the study of the preparation and properties of simple gases, &c. We take these objections in order.

1. "*The experiments are dangerous.*" Quite true, if the *manipulation is careless;* but is not a careless student just as likely in qualitative analysis to send half a test-tube of hot acid into his neighbour's face, as to blow him up with a flask of impure hydrogen when preparing that gas? And if a spirit of recklessness is abroad in the laboratory, whose fault is it? Mr. Beebe mentions hydrogen and phosphorus especially, in this connection. If the former be prepared in a *small* flask, and not a Woulff's bottle, the danger is lessened. All experiments, too, can be performed with *small quantities* of the gas; and the combustion of hydrogen, to show the production of water, is of course left till late in the lesson, when the flasks are free from air. Students should be *warned* of any dangerous practice.

Phosphorus need not be burned in oxygen, since carbon and sulphur could be used, but small fragments may very well be given out by the demonstrator *as required*, and the experiment performed.

Here, in an organised science school, we have classes of boys and girls, from eleven to fourteen years of age, working two lessons a week, and no accident whatever has occurred under the new Science Syllabus for the past two years.

But, assuming that such a course is dangerous, we fail to see that practice in warming liquids in test-tubes, or in filtering off precipitates, trains a student to handle the evolution flask or the deflagrating spoon. An hour's drill in the fitting up and correct use of apparatus would accomplish far more in this respect.

2. *Unconnectedness.* By this term Mr. Beebe would apparently have us understand that opportunities for revision are wanting in the course he condemns. His ideal seems to be after a "This-is-the-house-that-Jack-built" principle. A series of lessons dealing with non-metallic elements can be made to follow one another in logical sequence, and when twelve have been covered it is a good plan to repeat them. But the constant repetition, such as is obtained in qualitative analysis, soon produces mechanical work, and has then little educational value.

3. *Interest.* This can certainly be well maintained by the course Mr. Beebe criticises. Variety is always interesting, and the preparation of simple gases, supplemented by easy quantitative experiments, gives far more scope in this direction than does qualitative analysis. Our young students give unmistakable proofs that they find their work here interesting.

Again, Mr. Beebe says that the student should have a good knowledge of the preparation and properties of non-metallic elements before—or at any rate while—he is engaged in qualitative analysis. Our experience is that this knowlege is very slowly gained from "lectures," no matter how ably "illustrated by experiments" they may be. What things of mystery our chemical lectures were to us as youngsters twenty years ago! But directly a student begins to *do* the experiments for himself, and record his own observations and inferences in his note-book, the assimilation of this knowledge proceeds apace.

Finally, is there nothing to be said as to the relative educational value of the two systems? We would train our pupils to be deft in manipulation, keen to observe and discriminate, and accurate in drawing an inference.

The use of test-tubes and reagent bottles, the colours and appearances of precipitates, do not carry us far towards such a goal, while the "inferences" are mainly matters of memory. That which by constant repetition is performed mechanically ceases to have any value as a mental exercise, and young students soon acquire a very mechanical way of "getting out" salts.

But, on the other hand, in determining the properties of a common gas, the pupil's attention is kept on the *qui vive* all the lesson; he has fresh observations to chronicle and new inferences to draw continually, while the arrangement and fitting up of his varied apparatus cultivates his manipulative powers. Nor must the quantitative side be forgotten. A lad of twelve, who has worked with us six months, with one practice lesson weekly, has just found experimentally that 145 m.grms. of mercuric oxide, when heated in a combustion-tube, give off 6·2 c.c. of oxygen, and leave a residue of mercury weighing 133 m.grms. Such an exercise has done more for his education than the qualitative analysis of half-a-dozen simple salts.—I am, &c.,

H. Wigley, B.A., F.C.S.

Winsford.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 5, February 1, 1897.

Constitution of the Combination of Antipyrine with the Phenols.—G. Patein.—The author infers that—1. Monomethylphenyl pyrazolone does not combine either with phenols or acid phenols. 2. Of the two atoms of nitrogen in antipyrine, the nitrogen 1, being entirely in the same relations in the mols. of dimethyl pyrazolone and of monomethyl pyrazolone, antipyrine fixes the phenols by means of nitrogen 2. 3. The existence of the combinations of antipyrine and the phenols cannot be reconciled with the supposition of E. von Meyer, according to which antipyrine might be considered as a sort of betaine.

Determination of Lipase.—MM. Hanriot and Camus.

Separation of Glycerin in Wines by Elimination in Watery Vapours.—MM. F. Bordas and Sigoda Raczkonski.

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.

Purifying Mercury.—I shall be obliged if any correspondent can tell me how to purify a quantity of mercury I have got. Some zinc has been dissolved in it. I have no apparatus for distilling the mercury properly, so that method is impracticable. At present the mercury adheres to glass, and so is useless for a large number of experiments.—J. MacGregor.

MEETINGS FOR THE WEEK.

Tuesday, 9th.—Royal Institution, 3. "Animal Electricity," by Prof. A. D. Waller, F.R.S.

Wednesday, 10th.—Society of Arts, 8. "The Prevention of Fires Due to the Leakage of Electricity," by Frederick Bathurst.

Thursday, 11th.—Royal Institution, 3. "Greek History and Extant Monuments," by Prof. Percy Gardner, F.S.A.

—— Society of Arts, 4.30. "Prevention of Famine in India," by Sir Charles A. Elliott, K.C.S.I.

Friday, 12th.—Royal Institution, 9. "The Source of Light in Flames," by Arthur Smithells, B.Sc., F.I.C.

—— Physical, 5. "Mechanical Cause of Homogeneity of Structure and Symmetry Geometrically investigated, with special application to Crystals and Chemical Combination," by William Barlow.

Saturday, 13th.—Royal Institution, 3. "Electricity and Electrical Vibrations," by Right Hon. Lord Rayleigh, M.A., F.R.S.

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THE CHEMICAL NEWS.

Vol. LXXV., No. 1946.

VOLUMETRIC ESTIMATION OF SULPHUR IN IRON, STEEL, AND SULPHIDES OF IRON.

By G. G. BOUCHER.

There is only one volumetric process, I believe, for the estimation of sulphur in iron and steel in general use, viz., the iodine method. It is fairly accurate and quick, but has one great disadvantage—the solutions do not keep well. If kept for any length of time they lose their strength, especially if exposed to sunlight, and consequently have to be frequently re-standardised. It occurred to me that if it were possible to obtain a process where only one solution is used, and that one a solution which would keep its strength for any length of time, it would be a distinct advantage.

This I found could easily be done; and the following process will, with care, be found to give very good results, which will compare well with those given by the iodine method.

The apparatus used in this method is the same as that used in the iodine process.

From 10 to 15, or even 20, grms. of iron or steel are weighed out into a flask, which is then connected to the U-tube. Fifteen c.c. of a solution (strength 5E) of NaHO are run into the U-tube, and then sufficient HCl (strength 5E) run into the flask to dissolve the iron. The flask and contents are gently heated, and when the metal has completely dissolved the solution is heated to boiling. The U-tube is now disconnected, and the contents run slowly into an acid solution of Fe_2Cl_6. H_2S is liberated, and a portion of the iron is reduced. The reduced iron is then estimated by a standard solution of $K_2Cr_2O_7$, and it will be evident from the formulæ below that each c.c. of $K_2Cr_2O_7$ used will be equivalent to a certain quantity of sulphur.

$$(1).\ Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S.$$

$$(2).\ 6FeCl_2 + K_2Cr_2O_7 + 14HCl = 3Fe_2Cl_6 + 2KCl + Cr_2Cl_6 + 7H_2O.$$

By dissolving 3·065 grms. of $K_2Cr_2O_7$ in 1000 c.c. of distilled water, a solution is obtained 1 c.c. of which is equivalent to 0·001 grm. sulphur. A solution of twice this strength is used for the estimation of small quantities, but when the sulphur is believed to be above 0·15 per cent, it is advisable to use a stronger solution, and the standard solution used in the analysis of iron ores is used, 1 c.c. = 0·00571 grm. of sulphur.

The ferric chloride solution used is made by adding a solution of ferric chloride, containing 0·1 grm. of iron in 1 c.c., to 50 c.c. of hot HCl (strength 5E). The amount of ferric chloride required should be calculated, as it is not advisable to have a large excess; about 0·5 or 1 c.c. is usually found sufficient.

The bichromate solution can be standardised by pure iron wire or ferrous ammonium sulphate, but a better method is to dissolve about 15 grms. of iron or steel, in which the sulphur has already been determined gravimetrically, and treat the metal as described above. The amount of bichromate required to oxidise the reduced iron, divided by the amount of sulphur known to be present in the 15 grms. weighed out will give the value of each c.c. in sulphur.

Sulphur in Sulphides of Iron.

If the sulphide is soluble in HCl, 0·5 grm. is weighed out into a 300 c.c. flask, dissolved in about 40 c.c. HCl (strength 5E), and treated in the same way as iron. If the sulphide is insoluble in HCl, 0·5 grm. is weighed out into a porcelain crucible and mixed with an excess of pure iron (6 grms.). The crucible is then filled up with ground charcoal, covered with a lid, and heated to redness in a muffle with a closed door for ten or fifteen minutes. The crucible is then taken out, allowed to cool, the contents emptied into a 300 c.c. flask and treated as soluble sulphide.

It is advisable to make a blank experiment, using the same quantity of iron, &c., required by this method. The iron is sure to contain a little sulphur, which would make the results appear higher than they should be. Below I give some analyses by this method.

	Gravimetric method. S per cent.	$K_2Cr_2O_7$ method. S per cent.
Bessemer Iron.		
Sample 1	0·041	0·038
„ 2	0·015	0·017
„ 3	0·020	0·023
„ 4	0·028	0·030
Mottled Iron.		
Sample 1	0·312	0·320
„ 2	0·411	0·399
„ 3	0·295	0·296
„ 4	0·384	0·387
Sulphides of Iron (Insoluble).		
Sample 1	48·61	49·25
„ 2	30·68	30·97
„ 3	32·56	32·14
„ 4	51·0	51·10
„ 5	0·707	0·773

The process is a quick one; an analysis of iron, steel, or sulphide for sulphur can be made comfortably in about half or three-quarters of an hour. When the percentage of sulphur is very low considerable care is required at the finish of the process; the indicator should show no sign of any blue colour for the space of one minute.

I tried this method on a sample of copper sulphide with the object of seeing whether it would be possible to determine the sulphur volumetrically. I expected that some of the sulphur would be detained by the copper, but thought the experiment worth trying. The copper sulphide was first heated with pure iron in a muffle, and afterwards treated just as sulphide of iron. The results I give below:—

Copper Sulphide.

	Gravimetric process. S per cent.	Volumetric process. S per cent.
Experiment 1.. ..	24·0	22·30
„ 2.. ..	24·0	22·74

The idea of heating the iron sulphide with pure iron in a muffle is not mine; it is a process devised by F. P. Treadwell, and can be found in the *Journal of the Chemical Society*, vol. lx.

Laboratory, North Lonsdale Iron Works,
Ulverston.

ESTIMATION OF BORIC ACID IN FOODS.

By L. de KONINGH.

The estimation of boric acid, at one time very troublesome, has become quite an easy matter since the discovery that it may be accurately titrated in presence of glycerol with phenolphthalein as indicator. To apply the process to articles of food (and I will confine myself for the present to milk and uncooked eggs) some few precautions must, however, be taken.

Boric acid is seldom used alone, but mostly in admixture with borax, a mixture of three parts of the acid with one part of ground borax, constituting the article known as *glacialine*. In practice it is, however, in my opinion, not necessary to make a distinction between the acid and its sodium salt, as both are no doubt equally harmless in small quantities; but if the amount of either reaches 1 per cent or more the time has come for a protest.

When testing uncooked eggs (the entire contents beaten up) for boric acid, I take 5 grms. of the sample, add one drop of sodium hydroxide (1 : 1), dry, and finally incinerate. The char is then powdered, boiled with water, and the residual black mass again burnt. The ash is also boiled with water, and the two solutions are united. The liquid is now faintly coloured by methyl orange, and tenth-normal sulphuric acid is added until a faint pink is obtained. The solution is now boiled for a minute to expel carbon dioxide, cooled, mixed with one-half of its bulk of glycerol, and titrated with tenth-normal sodium hydroxide, with phenolphthalein as indicator. Although it is now admitted that in presence of glycerol the amount of acid may be calculated from the number of c.c. of sodium hydroxide used, I prefer to check my sodium hydroxide with pure crystallised boric acid, using about the same quantity as present in the sample, and mixing this up with exactly the same amount of glycerol and water. Working in this manner the estimation of boric acid is, as regards accuracy, second to none.

It must, however, be remembered that eggs contain a small quantity of alkaline phosphates, and that phosphoric acid behaves somewhat like the boric acid. A method of removing this acid has already been proposed and is based on the insolubility of calcium phosphate and the *comparatively* large solubility of the borate. I find, however, that in uncooked eggs there is just enough phosphoric acid to account for 3 c.c. tenth-normal sodium hydroxide, when working on 5 grms. of sample, so I now propose to deduct 3 c.c. of sodium hydroxide from the number of c.c. taken by the sample. I scarcely need point out the necessity of proving the acid by the alcohol test. As a rule the presence may be ascertained by simply stirring some of the sample with a drop of sulphuric acid and a little spirits of wine and then setting fire to it.

When dealing with milk I allow 1 c.c. of sodium hydroxide for every 10 grms. of the sample. If the amount of acid is, as usual, very small, no particular accuracy can be claimed for the process; but if present in larger, and consequently harmful, quantity, the results are all that may be desired.—*Journal of the American Chemical Society*, xix., No. 1, p. 55.

ELECTRIC SHADOWS AND LUMINESCENCE.*

By Prof. SILVANUS P. THOMPSON, D.Sc., F.R.S., M.R.I.

(Continued from p. 113).

Having touched all too briefly upon the researches of Lenard, it remains for me to speak of those of Wiedemann, of Erlangen, who for many years has made a study both of the phenomena of electric discharge and of those of fluorescence and phosphorescence. In a research made in the year 1895 he attained some results of singular interest. He had been making electric discharges, in collaboration with Prof. Ebert, by a special apparatus for producing electric oscillations of high frequency. This apparatus, in the modified form given to it by Ebert (*Wiedemann's Annalen*, liii., p. 144, 1894), stands on the table before you. It is an apparatus of the same class as that described here some years ago by Oliver Lodge, for producing Hertzian waves. An oscillating spark is produced between two polished balls set between two condensers, A and B, each made of plates of sheet zinc (Fig. 7) a few m.m. apart. Their external circuit is however, led into the primary of a small induction-coil, the secondary of which goes to a third condenser, C. When sparks from the Apps coil are sent to the spark-gap, the oscillations of the two primary condensers set up secondary oscillations in the third condenser, to which a vacuum tube can be connected. If, now, by adjusting the distances between the plates of condensers, we tune the primary and secondary circuits together, the electric oscillations that result will persist much longer than if the circuits are not so tuned. Though each oscillation may last less than the 100-millionth of a second, there will be at each spark some 20,000 or 30,000 oscillations before they have died out. Wiedemann and Ebert have found that these persistent oscillations are specially adapted to excite luminescence. To illustrate the point I select here an old Geissler tube with a comparatively poor vacuum. When stimulated by ordinary sparks directly from the Apps coil through the platinum electrodes at its ends, it

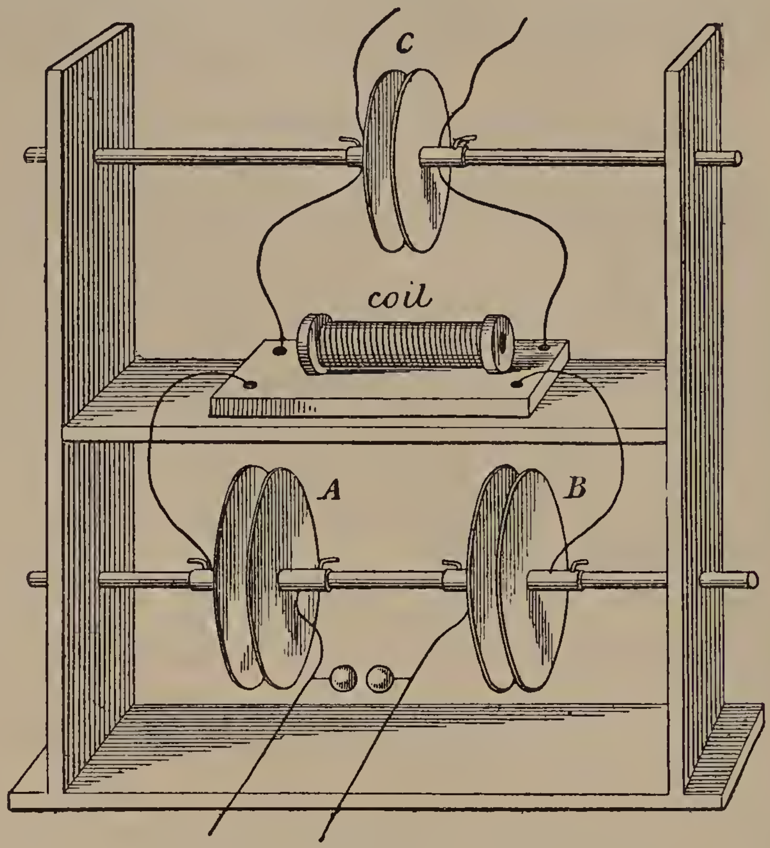

Fig. 7.

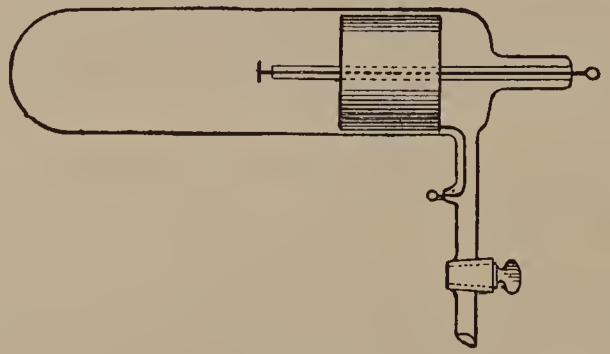

Fig. 8.

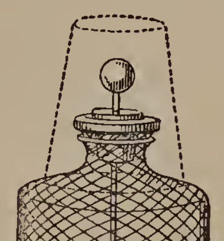

Fig. 9.

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* A Lecture delivered at the Royal Institution of Great Britain, Friday, May 8, 1896.

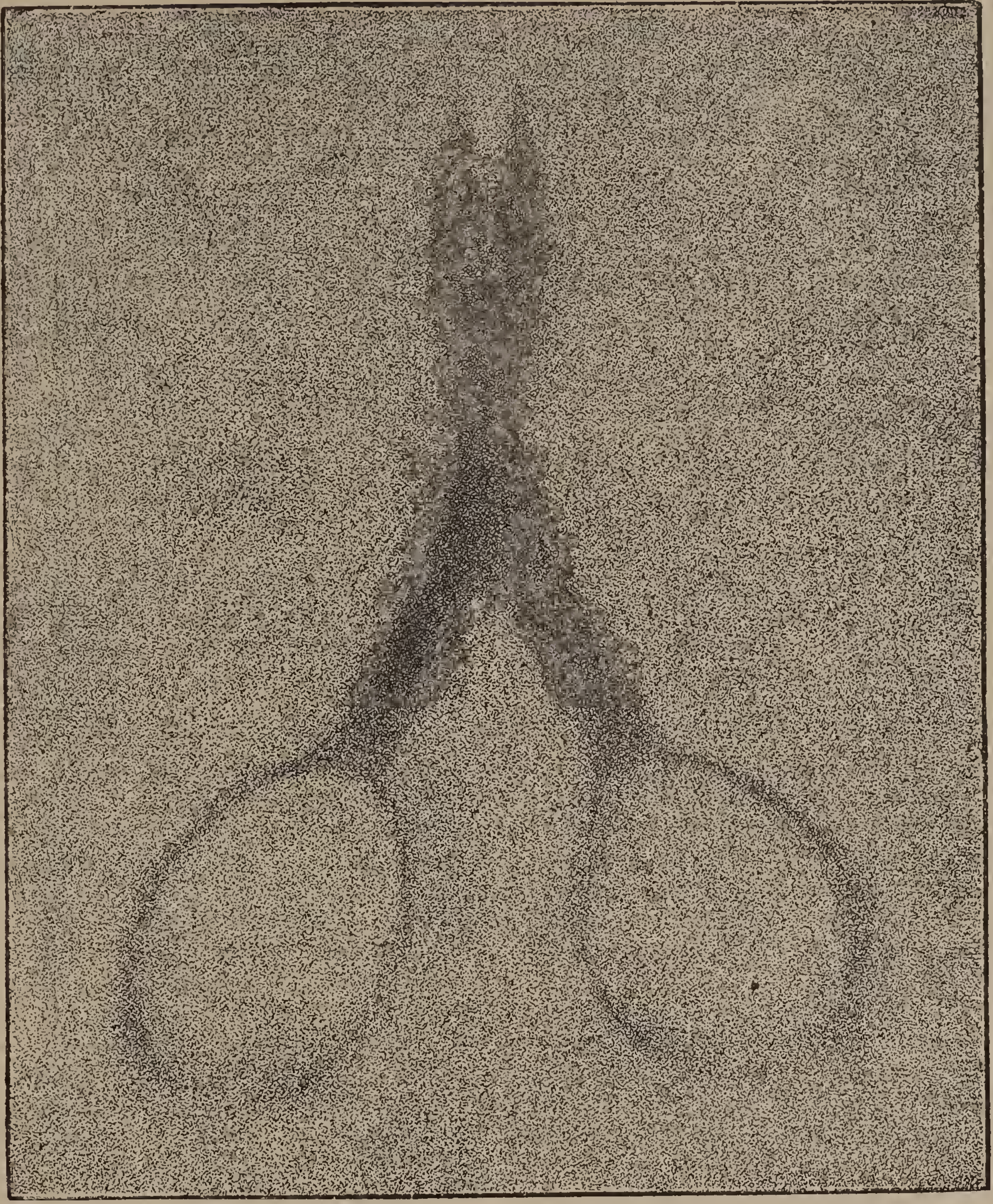

Fig. 10.

shows the usual features of Geissler tubes: there is a luminous column extending through the central bulb with stratifications along its length, while around the kathode is the usual violet glow. The glass shows no fluorescence. I now charge the connections, uniting the wires from Eber's apparatus, not to the terminal electrodes of the tube, but to two patches of tin-foil stuck upon the outside of the central bulb. Under these conditions the electric oscillations illuminate the central bulb with a glow quite different from that previously seen. Beneath each patch of foil you can discern the bluish kathode discharge, and the glass now shines with characteristic apple-green fluorescence. By moving one plate of one of the condensers in or out, I alter the conditions of resonance in the circuit, and when the tuning is best the fluorescence is at its brightest. Now Wiedemann observed (*Zeitschr. fur Elektrochemie*, July, 1895, p. 159) that the light so generated is capable of exercising a photographic action, and of other effects, but is incapable either of passing through a thin plate of fluor-spar or of being deflected by a magnet. These rays differed, therefore, both from ultra-violet light and from kathode rays; hence Wiedemann pronounced then to consist of a new species which he named "Entladungsstrahlen," or discharge-rays. It is again a matter for research to determine whether Wiedemann's rays are the same as Lenard's, or as Röntgen's rays. Wiedemann's coadjutor Ebert went on with the research, and produced on this principle a little

Table I.

Kind of rays.	Cause luminescence.	Penetrate aluminium.	Cause photographic action.	Cause combination of H and Cl.	Deflected by magnet.	Discharge electrification.	Affect spark length.	Change Nature of electric discharge.	Restore thermoluminescence.	Capable of being polarised.	Capable of refraction, &c.
Ultra-violet light	Yes	—	Yes	Yes	No	If –	Yes	—	Yes	Yes	Yes
Infra-red light ..	No	No	—	No	No	No	—	—	No	Yes	Yes
Hertzian waves .	No	No	—	No	No	—	Yes	—	No	Yes	Yes
Kathode rays ..	Yes	If thin	Yes	—	Yes	Charge violently	—	—	—	—	—
Lenard rays ..	Yes	Yes	Yes	—	Partly	Yes	Yes	Yes	—	—	—
Wiedemann rays	Yes	Yes	Yes	—	No	—	—	—	Yes	—	—
Röntgen rays ..	Yes	Yes	Yes	—	No	Yes	Yes	Yes	Yes	No	No
Becquerel rays..	—	Yes	Yes	—	No	Yes	—	—	—	Yes	—
Electric effluve..	Yes	No	Yes	Yes	?	—	—	—	Yes	No	No

"luminescence lamp" having two external rings of foil as electrodes; and within the vacuum bulb a small pastille of phosphorescent stuff, which, when excited by the oscillations of the tuned circuits, glows with a small bright light. Ebert claims that its efficiency is many times greater than that of the ordinary glow lamp.

Returning now to Röntgen's researches, we will take a glance at the kind of tube (Fig. 8) which he was employing when he made his discovery of the X-rays. Its general resemblance to previous tubes* is self-evident. The anode was a piece of aluminium tube through which passed the glass-covered kathode wire, with a small flat aluminium plate on its extremity. From this flat plate kathode rays shot forward against the bulging end of the tube, and, without any aluminium window rays which were capable of exciting fluorescence, found their way through the glass walls. Lenard had so boxed up his tube with brass cap and metal case, that if anything in the way of rays struggled through the glass walls of his tube he might not notice it. Possibly he never looked for it. Röntgen made the fortunate observation that when his tube was closely covered with opaque black card it still could cause fluorescence on a screen covered with platino-cyanide of barium on which shadows were cast. From seeing the shadows thus to securing their imprint permanently on a photographic plate was but s small step, and the discovery that they could pass freely through a sheet of the metal aluminium was the natural result of an inquiry as to the transparency of different materials. Aluminium is to these rays much more transparent than ordinary glass. No lens can focus them, nor mirror reflect them, and, unlike the kathode rays within the tube, they are not deflected by the magnet.

The criterion which we have at present as to whether any rays from any other source are or are not the same as the X-rays is that they shall be able to fulfil the following fourfold test:—They must be capable of exciting luminescence; they must be capable of impressing an image on a photographic plate; they must be capable of passing through aluminium; and they must be incapable of being deflected by a magnet. In addition they must—so far as present evidence goes—be incapable of being either refracted or polarised. Any rays that will fulfil these tests must for the present be considered identical with X-rays.

Now it has been suggested that the X-rays are the same as ultra-violet light. This is certainly not so, for ultra-violet light, as known to us by the researches of Stokes, Tyndall, Becquerel, and Cornu, will not go through aluminium and is not deflected by a magnet, though it will excite luminescence and take photographs. Furthermore, ultra-violet light can be refracted and polarised.

It has also been suggested that the X-rays are merely invisible heat-rays. But this is certainly untrue also, because although Abney has succeeded in taking photographs by heat-rays, they will not go through aluminium, are not deflected by the magnet, and instead of exciting phosphorescence they destroy it, as Goethe found out nearly a hundred years ago.

Neither are they Hertzian waves of longer period than the heat waves.

So far as is at present known there is no other way of producing the X-rays than that of employing the highly exhausted vacuum tube. They are not found in the light of ordinary electric sparks in air. They are not discoverable amongst the rays emitted by ordinary Geissler tubes with a low exhaustion. They are not found in sunlight or any artificial light. The arc light, though it yields rays that will give photographic shadows through a thin pinewood board, yields no rays that will pass through aluminium. The only other rays that seem to come within reasonable possibility of being X rays are the Lenard rays, some of which are probably identical with Röntgen's; the Wiedemann rays, which are, so far as yet investigated, entirely similar; and the Becquerel rays, to which some allusion will presently be made. It will, however, be convenient here to present a synoptic table (see Table I.) of the various kinds of rays and their respective physical properties.

One other physical property of the X-rays has been discovered since the publication of Röntgen's research. It was discovered simultaneously in Cambridge (by Prof. J. J. Thomson), in Paris, in Bologna, and in St. Petersburg, that these X-rays will cause the diselectrification of an electrified body, no matter whether it is positively or negatively charged.* That ultra-violet light can diselectrify bodies that have been negatively charged was previously known from the researches of Hertz, and of Elster and Geitel. This fresh discovery that X-rays will also discharge a positive electrification sets up a new physical test. Let me show you a simple piece of apparatus which I have found very convenient for the purpose of demonstrating this discovery. It is an aluminium-leaf electroscope (Fig. 9) entirely shielded from all external electrostatic influences by being enclosed in transparent metallic gauze. It is so well shielded that even when the cap is removed it cannot be charged in the ordinary inductive way, but must be electrified by direct conduction. The aluminium-leaves hang at the side of a fixed central plate as in Exner's electroscope. The containing vessel is of thin Bohemian glass. On exciting the instrument positively from a rod of rubbed glass, or negatively from a rod of rubbed celluloid, the leaves diverge. In either case, as soon as the X-rays are caused to shine upon the instrument, the leaves fall.

It occurred to me that by the aid of this property of diselectrification it might be possible to produce electric shadows without having resort to any photography. You are aware that if the surface or any part of the surface of a body is electrified, the fact that it is electrified can be ascertained by dusting over it mixed powders of red-lead and sulphur (or red-lead and lycopodium). With the aid of Mr. Miles Walker, who has worked with me all through this matter, I have succeeded in producing, on this plan, well defined shadows which will now be demonstrated to you. A clean sheet of ebonite, freed from all traces of previous electrification by being passed through a spirit flame, is laid on a properly prepared metal table. On it stands a small tray of thin aluminium, supported on four insulating legs. In this tray is placed the object whose shadow is to be cast,—for example, a pair of scissors or an object cut out in sheet lead. Over this again is placed a leaden cover with an opening above the tray, the leaden cover being designed to cut off electrostatic influences which might interfere. The tray is then electrified by a small influence machine, and while it is so electrified X-rays are sent downwards from a Crookes tube placed above. They pass down through the aluminium tray and carry its electrification to the ebonite sheet, which therefore becomes electrified all over except in the parts which are shielded by the scissors or other metallic object. The sheet of ebonite is then removed from the leaden enclosure, the aluminium tray lifted off, and the mixed powders are dusted over, adhering to the surface of the ebonite and revealing the otherwise invisible electric shadow. Fig. 10 is a shadow taken in this way. It is but right to mention that Prof. Righi, of Bologna, has independently obtained electric dust shadows in a very similar way since these experiments of mine were begun.

(To be continued).

Ammoniacal Silver Chlorides.—R. Jary.—In the case of ammoniacal chlorides the dissociation in a space occupied by water ensues in the same manner as in a vacuum.—*Comptes Rendus*, cxxiv., No. 6.

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* It is, in fact, identical with the form described by Hertz in 1883. See *Wiedemann's Annalen*, xix., p. 810.

* It is of great interest to note that this identical property had been observed by Lenard a year previously as an effect of his rays. He found they would discharge an electroscope enclosed in a metal chamber, with an aluminium sheet in front, whether positively or negatively charged, and at a distance of 30 centimetres from his tube.

VOLUMETRIC DETERMINATION OF MOLYBDENUM AND VANADIUM.*

By CARL FRIEDHEIM.

(Concluded from p. 91).

Hence they (*i.e.*, Gooch and Fairbanks) recommend to effect the whole operation in a current of carbon dioxide free from atmospheric air, for which, instead of the simple and convenient Bunsen apparatus, a more complicated distillatory apparatus is requisite, which, on account of its greater capacity, must give greater errors except we work with carbon dioxide. That better results cannot be obtained has been already mentioned.

A further reason which Gooch and Fairbanks advance for the necessity of their proposed alteration of my method cannot hold good. They consider it necessary that the solution to be decomposed during the operation should be evaporated down from a given initial volume to a fixed final volume, interrupting the process as soon as the latter is reached. They were led to this *modus operandi* "because it is not sufficient to indicate that the ebullition must be interrupted when the liquid has taken a clear green colour, and when a vapour of the colour of iodine ceases to pass over, for the green colour of the solution is formed very slowly, and we (Gooch and Fairbanks) were able to show iodine in the residue long after the green colour had been perfectly developed."

The latter phenomenon certainly takes place, but has nothing whatever to do with the reduction of the molybdenum teroxide, but must be referred to the fact that if the contents of the flask are brought in contact with the air the hydriodic acid is at once oxidised. The longer such a solution is left in contact with carbon disulphide with access of air the more intensely it is coloured, which does not ensue if air is excluded.

The appearance of the green tinge and the disappearance of the iodine colouration shows sharply the end of the reaction, as it is manifest from results already published, even for substances whose proportion of molybdenum is unknown, and gives a more trustworthy basis than boiling down the solution to a certain volume, which is suitable only for the weights used by Gooch and Fairbanks, and cannot be at once transferred to substances whose proportion of molybdenum is unknown.

In the same connection we must notice another proposal made by the same authors. It is well known that vanadium pentoxide can be quantitatively reduced to tetroxide by potassium bromide and hydrochloric acid, and that an excellent volumetric method for determining vanadium can be secured (Holverscheidt's method) by receiving the liberated halogen in potassium iodide, and titrating the iodine set at liberty. In concert with Euler I have showed that on boiling vanadium pentoxide with potassium iodide and hydrochloric acid, the reduction can likewise be carried almost quantitatively as far as vanadium tetroxide, whilst vanadium teroxide is formed quantitatively on the addition of syrupy phosphoric acid. Of course, we have not utilised this result for a volumetric investigation of pure vanadates, for which there was no need, since the potassium bromide method is simpler, more convenient, and more trustworthy. Ph. E. Browning (*Zeit. Anorg. Chemie*) now proposes to modify this method of reduction so that the reduction of the vanadates is effected under certain conditions in open vessels with potassium iodate and sulphuric acid; the solution, after the iodine has been expelled by boiling is neutralised with alkaline hydroxide mixed with tartaric acid and bicarbonate, and the vanadium tetroxide existing in solution is determined with a standard solution of iodine, titrating back with arsenious acid.

As an advantage over the convenient method of distillation, it is alleged that the complicated distillatory apparatus is superfluous. To this it may be replied that the manipulation of the compendious Bunsen apparatus is the most convenient conceivable, that the supercession of a smooth titration with thiosulphate by titration with two standard solutions, in one case with a blue liquid, does not mean any progress, and that, finally, in Browning's method, the determination of the bases (*e.g.*, lead and barium) in the residue of the distillation is rendered impossible and much more difficult.

Exactly the same objections must be urged against the modification of my method for the determination of molybdenum as proposed by Gooch and Fairbanks, which consists in decomposing the molybdate in an open method and titrating it on Browning's principle.

In a subsequent memoir (*Zeit. Anorg. Chemie*) A. [illegible] banks proposes to determine the phosphorus in the yellow ammonium phospho-molybdate indirectly, the molybdenum in the compound being ascertained according to the Gooch-Fairbanks-Browning method. The authors here overlook to mention that I have already recommended the volumetric determination of the molybdenum in phospho-molybdates, and the method which I have described, and that I connected with it Hundeshagen's method for titrating the total method by alkali hydroxide, therefore determining the phosphoric acid as difference. This method is, however, of interest only for the general examination of the so-called white phospho-molybdates; for the determination of the phosphorus in the yellow compound the gravimetric method of Hundeshagen-Pemberton is far simpler and more convenient than that proposed by Fairbanks.

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* *Berichte d. D. Chem. Gesell.*

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 21st, 1897.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Messrs. Charles A. Hill, Arthur Marshall, and William H. Sodeau were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Arbuckle, 34, Moore Street, Cadogan Square, S.W.; Masumi Chikashigé, B.Sc., Kumamoto, Japan; Alfred Foster Cholerton, Lyndum House, Lincoln Street, Leicester; Clarence Hamilton Creasey, 78, Baggeholme Road, Lincoln; James Crowther, B.Sc., West Field, Lightcliffe, Halifax; William Alfred Davis, 108, Gordon Road, Peckham, S.E., Ernest Goulding, 18, Mercer's Road, Holloway, N; Charles Heppenstall, Ferrybank, Arklow, Co. Wicklow; Harold Johnson, 5, Boulevard Clovis, Bruxelles; William Robert Lang, B.Sc., 5, Crown Gardens, Glasgow; Barker North, 3, Manor Terrace, Felixstowe; Herbert Spindler Pullar, Rosebank, Perth, N.B.; William Ralston, B.Sc., 337, Cathcart Road, Glasgow; John Stewart Remington, Dromore, Milverton, Leamington; Leonard Sumner, B Sc., Butt Hill, Prestwich, near Manchester; Andrew Turnbull, Ph.D., Daldowie, Broomhouse, near Glasgow.

The certificates of the following candidates, recommended by the Council, under Bye-law I., par. 3, were also read:—

Thomas Hannibal Aquino, Gadag, Dharwar District, India; Alfred Rutter, Broken Hill, N.S.W.; Rustomji Navroji Unwalla, Bhaunagar, Kathiawar, India.

The following is the text of the letter which has been received from Professor Stanislao Cannizzaro, acknowledging the address presented to him by the Society on the occasion of his jubilee.

To the Council and Fellows of the Chemical Society of London.

Gentlemen,—I beg to offer to your Society the report of the celebration of my seventieth birthday, together with the volume containing some of my writings which were reprinted on that occasion, and a copy in bronze of the gold medal which was presented to me.

At the same time, I beg to convey to my colleagues the expression of my heartfelt gratitude for their very flattering address, which I have received with the greatest satisfaction.

The Chemical Society won my devotion, when, in 1862, they added my name to the restricted roll of their foreign members; and again in 1872 when they honoured me by intrusting to me the delivery of the Faraday Lecture.

A further proof of their high consideration is now offered to me in this address, in which I find my labours for Science appreciated and valued in so very high a degree by authority so competent: I feel I am indebted for this favourable estimate of my merits to the extreme kindness which my English colleagues have always shown to me, and for which I now desire to express my profound gratitude.

Great is the pleasure which this fresh manifestation of their affectionate esteem has afforded me, thus assuring me that their estimate of me has in no way lessened.

Your ever true and affectionate colleague,
Stanislao Cannizzaro.

December, 1896.

Of the following papers those marked * were read:—

*1. "*Observations on the Properties of some Highly Purified Substances.*" By W. A. Shenstone.

1. The author has compared the behaviour of oxygen under the influence of the silent discharge of electricity when saturated with water vapour, and when carefully dried. The results show that, contrary to the statement of previous investigators, oxygen is most freely converted into ozone when wet, and that well dried oxygen yields only a very minute percentage of ozone. The results obtained also shows that the ozone in ozonised oxygen is far more stable in the presence of water vapour than in its absence. That is to say, the change by which ozone is converted into oxygen is very greatly retarded by the presence of moisture.

2. Chlorine prepared by the electrolyis of silver chloride, and also carefully purified bromine and iodine, have been dried by very thorough treatment with prepared phosphoric oxide, and then presented to the action of mercury prepared for the purpose by several distinct methods and thoroughly dried. In every case the metal and the halogen interacted instantly and rapidly.

3. Highly purified chlorine, when submitted to the silent discharge of electricity, does not undergo condensation.

4. The abnormal expansion of chlorine which has been described by several observers appears to depend upon the presence of impurities in the chlorine.

Incidentally, a new vacuum tap and other novel apparatus are described in this paper.

Discussion.

The President, Mr. H. B. Baker, and Professor Tilden expressed their admiration of the skill and resource which Mr. Shenstone had brought to bear in investigating a difficult problem.

Dr. Thorpe stated that he had witnessed Dr. Budde's experiments at Bonn, which were conducted with great care, and he had watched the expansion of chlorine under the influence of the violet and ultra-violet rays. The chlorine had been prepared by the oxidation of hydrochloric acid, and was believed to be pure. Some subsequent observers had confirmed Dr. Budde's results, but others had failed to do so—as was now the case with Mr. Shenstone, whose painstaking enquiry, he hoped, might be the means of finally settling the question.

Dr. Thorne stated that he had observed on a large scale the instability of ozone when in contact with an alkali.

Mr. Shenstone, in reply, stated that he did not doubt the correctness of Dr. Budde's observations with chlorine prepared and purified as he had described. He considered, however, that such chlorine could not be regarded as highly purified, and that moisture was almost certainly present.

*2. "*The Action of Diastase on Starch.*" By Arthur R. Ling and Julian L. Baker.

The authors show that maltose when heated with Fehling's solution, under the conditions prescribed by Wein, reduces 1·079 grms. of copper per grm. of sugar. The table of Wein, therefore, gives results which are 4·5 per cent too low, a result also arrived at by Brown, Morris, and Millar.

They have examined in detail the products of the limited action of diastase on starch at 70°, and have separated maltose and the following unfermentable substances, which were purified to such an extent as to free them from all extraneous matter.

Maltodextrin α, $C_{36}H_{62}O_{31}$, identical with Brown and Morris's maltodextrin, but having the properties $[\alpha]_D=180 : R=32 \cdot 81$.

Maltodextrin β, $C_{24}H_{42}O_{21}$, identical with Prior's "achroodextrin III.," and having the properties $[\alpha]_D=171 \cdot 6$ and $R=43$.

A substance, $C_{12}H_{22}O_{11}$, isomeric with maltose, and obtained from the unfermentable residue of that particular fraction previously called isomaltose by Lintner. It had the constants $[\alpha]_D=156$ and $R=62 \cdot 5$, and may consist of the simple "dextrin," $C_{12}H_{20}O_{10}+H_2O$, the existence of which the authors' previous work foreshadowed. Inasmuch as it gave a small amount of crystalline osazone, it perhaps contained maltose.

When the three substances above named are treated with an excess of diastase at 60° for a few hours, the approximate reducing powers of the products are $R=90$; $91 \cdot 5$; 94, respectively.

There are now ample data to conclude that starch, when hydrolysed by diastase, is converted into a series of maltodextrins of gradually decreasing molecular weight and optical rotatory power, and of increasing reducing power. These appear to have the optical and reducing properties of mixtures of the original starch and maltose.

Discussion.

Dr. G. H. Morris regretted that Messrs. Ling and Baker had given no particulars of the substances they described beyond the constants $[\alpha]_D$ and R. He had therefore no means of judging whether the substances agreed with the maltodextrin described by Mr. H. T. Brown and himself, nor was it possible to follow the authors' line of work. The constants given for maltodextrin α agreed fairly with the law of definite relation as formulated by Mr. Brown and himself; but the maltodextrin β (Prior's achroodextrin III.) did not, and the purity of this substance is therefore doubtful. He wished to learn more about the unfermentable residue of isomaltose, which the authors appeared to regard as one of the end-products of the action of diastase on starch. He did not think it necessary to enunciate a new theory of starch conversion whilst there was still so much dispute as to facts.

Mr. Ling, in reply to Mr. Chapman, said he saw no reason for assuming the presence of a "stable" dextrin among the products of starch hydrolysis; ultimately maltose was the sole product. In reply to Dr. Morris, he said that much more information would be found in the paper than it had been possible to give an account of in the brief time at his disposal. It would be seen that the formulæ of the maltodextrins could *not* be calculated from the percentages of apparent maltose which they yielded.

*3. "*The Solution Density and Cupric-Reducing Power of Dextrose, Lævulose, and Invert-Sugar.*" By Horace T. Browne, F.R.S., G. Harris Morris, Ph.D., and J. H. Millar.

The authors have extended the methods described in their previous paper (*Proc.*, 1896, xii., 241) to the examination of the solution density and cupric-reduction of dextrose, lævulose, and invert-sugar. They find that the solution densities of the two former differ considerably with the same concentration of the solution, but that the volume occupied in solution by a unit of weight of each is less at lower than at higher concentrations, consequently the divisor to be applied to the specific gravity decreases with the concentration. The solution density of invert-sugar was calculated from those of dextrose and lævulose, and the results so obtained were confirmed at various points by direct experiments.

They also find that the cupric-reducing powers of the three sugars, when determined under their standard conditions, are, for dextrose, $\kappa=117$ to 105; for lævulose, $\kappa=107{\cdot}5$ to 101; and for invert sugar, $\kappa=111$ to 103. The higher numbers are obtained when a small amount of cuprous oxide is precipitated, and the lower when reduction is carried nearly to the maximum. When the experimental numbers are expressed in the form of a curve, it is found that at the one end, taking the cupric-reduction of dextrose at 100, lævulose is represented by 91·3, and invert-sugar by 94·2; at the other end of the curve the ratio is 100, 94·6, and 97·5; whilst at an intermediate point, which corresponds to the amount of cuprous oxide usually reduced, the relation is, dextrose 100, lævulose 92·3, and invert-sugar 96·15.

4. "*Derivatives of Maclurin.*" Part II. By A. G. PERKIN.

From maclurin which yields a pentabenzoyl derivative (König and Kostanechi, *Ber.*, 1894, xxvii., 1996), a pentacetyl compound has not yet been obtained, for by acetylisation in the ordinary way only sticky products result, and when excess of sodium acetate is employed (Ciamician and Silber, *Ber.*, 1894, xxvii., 1628), there is formed a peculiar substance having the composition of pentacetyl maclurin less 1 molecule of water. Judging from the stability of maclurin-azo-benzene,

$$C_{13}H_8O_6(N_2{\cdot}C_6H_5)_2,$$

described in a previous communication (Bedford and Perkin, *Trans.*, 1895, lxvii., 933), when compared with that of maclurin itself, it appeared probable that this on acetylisation might behave normally, which was found to be the case.

Triacetyl-maclurin-azobenzene,

$$C_{13}H_5O_6(C_2H_3O)_3(N_2{\cdot}C_6H_5)_2,$$

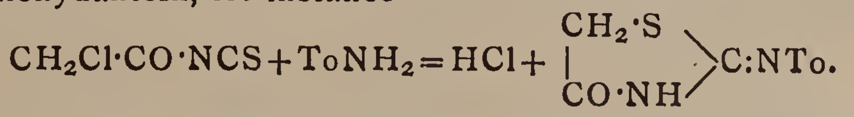
orange-yellow needles, m.p. 240—243°, is insoluble in cold alkaline solutions, but decomposed by them on boiling. Suspended in acetic acid and treated with sulphuric acid, a quantitative yield of maclurin-azobenzene is produced. Phloroglucin-azobene similarly yields a *monacetyl* derivative, $C_6H_3O_3(C_2H_3O)(N_2C_6H_5)_2$, orange-red needles, m.p. 222—223°, also quantitatively decomposed by sulphuric acid into the azo-compound. These substances furnished no higher acetyl derivatives, two hydroxyls present in the original molecules of maclurin and phloroglucinol having assumed in their diazobenzene compounds the ketonic condition. This method is being applied for the estimation of hydroxyl groups in certain analogous substances, particularly catechin and cyanomaclurin, which combine readily with diazobenzene, but do not give normal products on acetylisation by the usual method.

Mention is made of a second product closely resembling luteolin trimethyl ether, and formed at the same time, during the methylation of luteolin. This, though isolated many months since, was not mentioned at the time, believing that the work then published was sufficient to establish priority for the further study of this reaction. The author wishes to reserve this to himself for further examination.

5. "*Halogen-substituted Acidic Thiocarbimides and their Derivatives; a Contribution to the Chemistry of the Thiohydantoïns.*" By AUGUSTUS EDWARD DIXON, M.D.

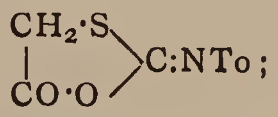
Continuing his previous work on the acidylthiocarbimides (*Trans.*, 1895, lxvii., 1040; 1896, lxix., 855; *ibid.*, 1593, &c.), the author endeavoured to prepare halogen substitution derivatives of certain members of the fatty acid class, in the hope that, by combination with organic bases, glycolylthioureas would be obtained of known structure, whose relations to the thiohydantoïns produced by other methods would serve to decide the constitution of the latter.

The derivatives in question were obtained by heating a mixture of sand and lead thiocyanate with the α-halogenised acid chloride (or bromide), dissolved in anhydrous toluene; as a rule, the yield amounted to only about 60 per cent of the theoretical. On bringing the products into contact with primary or (secondary) amines, interaction occurred spontaneously, with elimination of the halogen, and formation of the corresponding substituted thiohydantoïn, for instance—



$$CH_2Cl{\cdot}CO{\cdot}NCS+ToNH_2=HCl+\left.\begin{array}{l}CH_2{\cdot}S\\ |\\ CO{\cdot}NH\end{array}\right\rangle C{:}NTo.$$

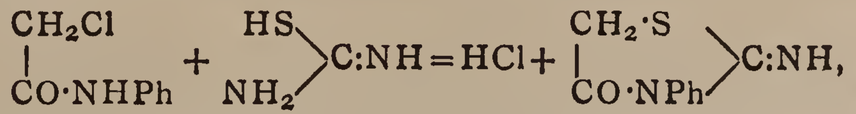
By prolonged boiling with hydrochloric acid, the latter compound is hydrolysed, ammonia being formed, together with a substance (melting at 119—120°) identical with the "orthotolylthiocarbimidoglycolide" obtained by Völtzkow (*Ber.*, 1880, xiii., 1580) from EtOH,ToNCS and $CH_2Cl{\cdot}COOH$. Since the nitrogenised organic group, introduced by the base in the formation of the thiohydantoïn, does not form an integral portion of its ring, whilst, on the other hand, the nitrogen withdrawn by hydrolysis holds no organic radicle in combination, it follows that the ring must exchange its NH for oxygen, thereby becoming—



$$\left.\begin{array}{l}CH_2{\cdot}S\\ |\\ CO{\cdot}O\end{array}\right\rangle C{:}NTo;$$

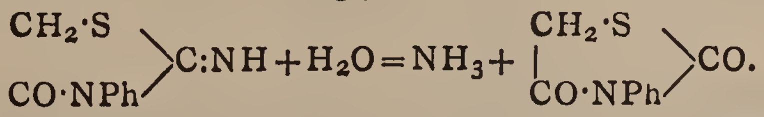
thus, by an entirely different method, the formula is corroborated, which Evers assigns to the corresponding phenyl derivative (*Ber.*, 1888, xxi., 975). From orthotolylthiourea and ethylic chloracetate, a thiohydantoïn was obtained, agreeing in properties with that produced from the thiocarbimide; on hydrolysis, it afforded the same glycolide, m. p. 119—120°.

On the other hand, thiourea, when treated with a substituted chloracetamide (*e.g.*, chloracetanilide) yielded (P. Meyer, *Ber.*, 1877, x., 1965) thiohydantoïn, together with a substitution derivative; the phenylthiohydantoïn so obtained was apparently identical with that produced from phenylthiourea and ethylic chloracetate. The essential interaction he explained substantially as follows:—



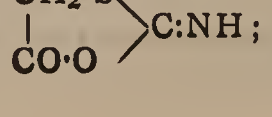
$$\begin{array}{l}CH_2Cl\\ |\\ CO{\cdot}NHPh\end{array}+\left.\begin{array}{r}HS\\ \\ NH_2\end{array}\right\rangle C{:}NH=HCl+\left.\begin{array}{l}CH_2{\cdot}S\\ |\\ CO{\cdot}NPh\end{array}\right\rangle C{:}NH,$$

and the fact that ammonia and phenylthiocarbimidoglycolide were formed on hydrolysis, appeared to agree satisfactorily with the above view of its constitution, as well as to fix that of the glycolide,—



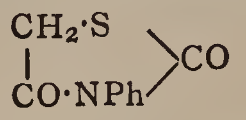
$$\left.\begin{array}{l}CH_2{\cdot}S\\ \\ CO{\cdot}NPh\end{array}\right\rangle C{:}NH+H_2O=NH_3+\left.\begin{array}{l}CH_2{\cdot}S\\ |\\ CO{\cdot}NPh\end{array}\right\rangle CO.$$

It would seem, however, from Meyer's paper, that the particular phenylthiohydantoïn obtained from chloracetanilide was not used in preparing the related phenylthiocarbimidoglycolide; it was conceivable, therefore, that the former might, though melting at the same temperature, be really isomeric with that produced by the other methods. This could be ascertained by examining the products of hydrolysis, for the withdrawal from the ring of its nitrogenised group would afford aniline, together with "thiocarbimidoglycolide,"—



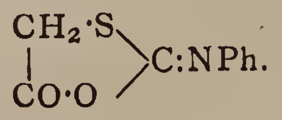
$$\left.\begin{array}{l}CH_2{\cdot}S\\ |\\ CO{\cdot}O\end{array}\right\rangle C{:}NH;$$

whilst, even if the phenyl group should be retained, and ammonia formed instead, the product—



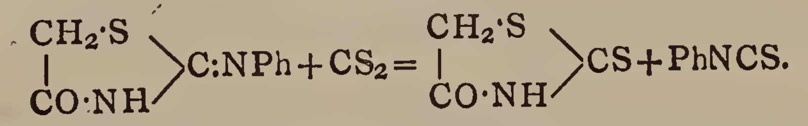
$$\begin{array}{l}\mathrm{CH_2{\cdot}S}\\ \;|\\ \mathrm{CO{\cdot}NPh}\end{array}\!>\mathrm{CO}$$

would still be an isomeride of the true phenyl thiocarbimidoglycolide,—



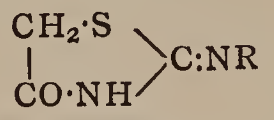
$$\begin{array}{l}\mathrm{CH_2{\cdot}S}\\ \;|\\ \mathrm{CO{\cdot}O}\end{array}\!>\mathrm{C{:}NPh.}$$

But, on experiment, the products of hydrolysis, and hence the thiohydantoïn itself, were found to be identical with those obtained in other ways. Finally, the compound was decomposed by carbon disulphide at 180°, phenylthiocarbimide being obtained, together with rhodanic acid, but not a trace of thiocyanic acid; and hence the interaction follows the course—



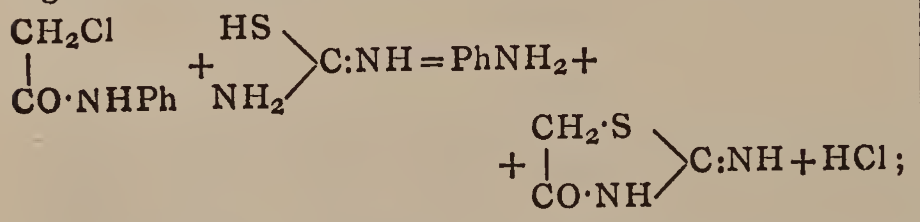
$$\begin{array}{l}\mathrm{CH_2{\cdot}S}\\ \;|\\ \mathrm{CO{\cdot}NH}\end{array}\!>\mathrm{C{:}NPh}+\mathrm{CS_2}=\begin{array}{l}\mathrm{CH_2{\cdot}S}\\ \;|\\ \mathrm{CO{\cdot}NH}\end{array}\!>\mathrm{CS}+\mathrm{PhNCS.}$$

The author therefore regards the known monosubstituted thiohydantoïns in which the radicle is attached to nitrogen, as constituted on the type—



$$\begin{array}{l}\mathrm{CH_2{\cdot}S}\\ \;|\\ \mathrm{CO{\cdot}NH}\end{array}\!>\mathrm{C{:}NR}$$

and suggests that the formation of the phenylic member from thiourea and chloracetanilide may be due to a secondary action, for thiohydantoïn is also produced, together with aniline,—

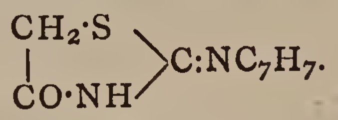


$$\begin{array}{l}\mathrm{CH_2Cl}\\ \;|\\ \mathrm{CO{\cdot}NHPh}\end{array}+\begin{array}{l}\mathrm{HS}\\ \\ \mathrm{NH_2}\end{array}\!>\mathrm{C{:}NH}=\mathrm{PhNH_2}+\begin{array}{l}\mathrm{CH_2{\cdot}S}\\ \;|\\ \mathrm{CO{\cdot}NH}\end{array}\!>\mathrm{C{:}NH}+\mathrm{HCl};$$

and from these, by mutual interaction, ammonia and phenylthiohydantoïn might result. Ammonia was, in fact, expelled, when aniline and thiohydantoïn were heated together with alcohol; and a substance produced, which appeared, judging from its melting-point, to be its phenylic derivative, but the quantity obtained was insufficient for analysis.

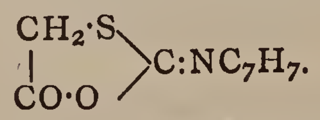
The following compounds are described:—

Orthotolylthiohydantoïn,—



$$\begin{array}{l}\mathrm{CH_2{\cdot}S}\\ \;|\\ \mathrm{CO{\cdot}NH}\end{array}\!>\mathrm{C{:}NC_7H_7.}$$

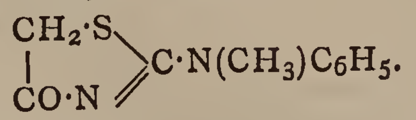
—From chloracetylthiocarbimide and orthotoluidine; white prisms, melting at 144—145° (corr.). When boiled with baryta-water it yields thioglycolic acid; by boiling, dilute hydrochloric acid, it is slowly decomposed into ammonia and "orthotolylthiocarbimidoglycolide,"—



$$\begin{array}{l}\mathrm{CH_2{\cdot}S}\\ \;|\\ \mathrm{CO{\cdot}O}\end{array}\!>\mathrm{C{:}NC_7H_7.}$$

The same thiohydantoïn is produced from orthotolylthiourea and ethylic monochloracetate; its *hydrochloride* melts at 212·5—213·5° (uncorr.).

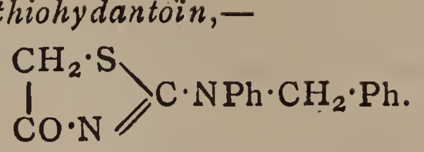
Methylphenylthiohydantoïn,—



$$\begin{array}{l}\mathrm{CH_2{\cdot}S}\\ \;|\\ \mathrm{CO{\cdot}N}\end{array}\!\gg\mathrm{C{\cdot}N(CH_3)C_6H_5.}$$

—From the thiocarbimide and methylaniline; flattened needles, melting at 129—130° (corr.), and decomposed by boiling with caustic alkali or baryta-water, into ammonia, methylaniline, and thioglycollic acid. It is also obtained by heating αα-methylphenylthiourea, in alcohol, with ethylic monochloracetate; the *hydrochloride* melts at 193—194°.

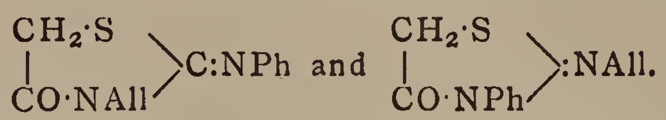
Benzylphenylthiohydantoïn,—



$$\begin{array}{l}\mathrm{CH_2{\cdot}S}\\ \;|\\ \mathrm{CO{\cdot}N}\end{array}\!\gg\mathrm{C{\cdot}NPh{\cdot}CH_2{\cdot}Ph.}$$

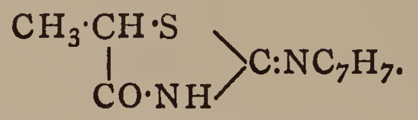
—From benzylaniline; it melts at 118—119°, and is decomposed by prolonged boiling with hydrochloric acid, into benzylaniline, and a substance melting at about 123—124°, probably "thiocarbimidoglycolide."

Allylphenylthiohydantoïn.—From allylphenylthiocarbamide and monochloracetamide an oil was obtained; it appears to be a mixture of the two forms—



$$\begin{array}{l}\mathrm{CH_2{\cdot}S}\\ \;|\\ \mathrm{CO{\cdot}NAll}\end{array}\!>\mathrm{C{:}NPh}\text{ and }\begin{array}{l}\mathrm{CH_2{\cdot}S}\\ \;|\\ \mathrm{CO{\cdot}NPh}\end{array}\!>\mathrm{C{:}NAll.}$$

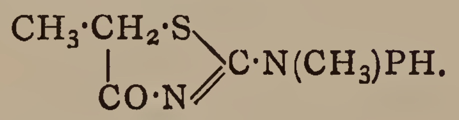
α *Bromopropionylthiocarbimide*, $\mathrm{CH_3{\cdot}CHBr{\cdot}CO{\cdot}NCS}$, when treated with orthotoluidine, affords *methylorthotolylthiohydantoïn*,—



$$\begin{array}{l}\mathrm{CH_3{\cdot}CH{\cdot}S}\\ \quad\;|\\ \quad\mathrm{CO{\cdot}NH}\end{array}\!>\mathrm{C{:}NC_7H_7.}$$

Crystalline powder, melting at 72—73°, and decomposed by boiling dilute alkali, with formation of α-thiolactic acid, $\mathrm{CH_3{\cdot}CH(SH){\cdot}CO_2H}$.

Dimethylphenylthiohydantoïn,—



$$\begin{array}{l}\mathrm{CH_3{\cdot}CH_2{\cdot}S}\\ \quad\;|\\ \quad\mathrm{CO{\cdot}N}\end{array}\!\gg\mathrm{C{\cdot}N(CH_3)PH.}$$

—From the above thiocarbimide and methylaniline; vitreous plates, melting at 129—130°.

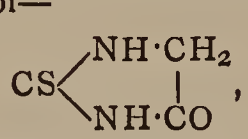
α-Bromobutyrylthiocarbimide, $\mathrm{CH_3{\cdot}CH_2{\cdot}CHBr{\cdot}CO{\cdot}NCS}$' by combination with aniline, yielded *ethylphenylthiohydantoin*,—

$$\begin{array}{l}\mathrm{CH_3{\cdot}CH_2{\cdot}CH{\cdot}S}\\ \qquad\;|\\ \qquad\mathrm{CO{\cdot}NH}\end{array}\!>\mathrm{C{:}NC_6H_5.}$$

White needles, m. p. 148—149° (corr.).

Ethylorthotolylthiohydantoin.—A sandy white powder, melting at 95—96°, to a turbid liquid, clearing at 98°; the *hydrochloride* forms white needles, m. p. 224—225° (corr.). When boiled with alkali, then acidified and mixed with ferric chloride, followed by ammonia, a purplish colouration is produced, due, probably, to the presence of α-thiobutyric acid.

For greater convenience and precision in naming "thiohydantoïns" of the above types, and the corresponding derivatives of—



$$\mathrm{CS}\!<\!\begin{array}{l}\mathrm{NH{\cdot}CH_2}\\ \qquad\;|\\ \mathrm{NH{\cdot}CO}\end{array},$$

together with the related "thiohydantoïc" acids, the author proposes a modification of the nomenclature at present employed.

6. "*The Amyl* (*Secondary butyl-methyl*) *Derivatives of Glyceric, Diacetylglyceric, and Dibenzoylglyceric Acids, Active and Inactive.*" By Percy Frankland, Ph.D., B.Sc., F.R.S., and Thomas Slater Price, B.Sc.

The authors describe the preparation and properties of amyl (lævo-active) glycerate (dextro-active), amyl (inactive) glycerate (dextro-active), amyl (lævo-active) glycerate (inactive), as well as of the corresponding diacetyl and dibenzoylglycerates. The interest attaching to these bodies depends, firstly, on those compounds with the inactive amyl and active acid radicle filling gaps in the series of active glycerates, diacetylglycerates, and dibenzoylglycerates already prepared, and described by one of the authors. The position of the maximum rotation in these series becomes thus more precisely localised. Secondly, the influence of one asymmetric carbon atom on another in the same molecule can be ascertained, and the principle of the superposition of the optical effects of the asymmetric carbon atoms is put to the test and found to hold good. Thus the authors show how the optical properties of the eight possible active amylglycerates can be calculated from a knowledge of the optical properties of two particular ones, and similarly in the case of the eight active amyl diacetylglycerates, and the eight active amyl dibenzoylglycerates.

In the series of the dibenzoylglycerates, of which now the methyl, ethyl, propyl, and amyl terms are known, the rotation diminishes from the methyl to the amyl compound, and there is every probability that in this series the rotation will be found to pass through a minimum.

The influence of temperature on the rotation of all the compounds described has been also investigated, with the result that, as before, the rotation of the glycerates was found to be but little sensitive to temperature, the rotation of the diacetylglycerates much more sensitive, and that of the dibenzoylglycerates still more sensitive to temperature. Again, as before, it was found that the negative rotation of the diacetylglycerates increased, whilst the positive rotation of the dibenzoylglycerates diminished with rise of temperature. It was, however, further found that the compounds in which the amyl alone was active, viz., amyl (lævo-active) glycerate (inactive), amyl (lævo-active) diacetylglycerate (inactive), and amyl (lævo-active) dibenzoylglycerate (inactive), had their rotation practically unaffected by temperature, the sensitiveness to temperature being thus confined to the rotation dependent on the asymmetric carbon atom belonging to the glyceric acid part of the molecule.

7. "*The Refraction Constants of Crystallised Salts.*" By Alfred E. Tutton.

This communication is in reply to certain criticisms of Pope (*Trans.*, 1896, lxix., 1530) concerning the author's work on the refraction constants of the sulphates and double sulphates containing potassium, rubidium, and cæsium (*Trans.*, 1896, lxix., 502). It is first shown that the claim of Pope to originality, in showing that the molecular refractions of solid salts are the sums of the atomic or equivalent refractions of the components, is unfounded, and that the whole of the conclusions published in the author's memoir, with regard to this subject, in connection with the entire twenty-two double sulphates investigated, were based upon the assumption of this rule. The second point is with regard to the criticism that the mean molecular refractions of the salts given were not the mean of the three values corresponding to all three refractive indices of the biaxial crystals in each case, but the mean of the two extreme values; and with regard to the re-calculated results presented by Pope taking the intermediate value into account, which Pope appears to show exhibit far greater accordance than the author's values. The author points out that the course pursued was taken after careful consideration, with full knowledge of the problem, and for the sufficient reason that the whole of the salts in question were so extremely feebly doubly refractive, and the extreme values consequently so close together, that he judged that the difference between the results of the two processes would be within the range of experimental error. He then shows that grave errors occur in Pope's re-calculations; there are numerous errors in Table III., two of them being whole numbers, one of which amounts to a fifth of the total value, and Table IV., is entirely wrong in consequence. When the errors are corrected, the latter table, in which the two whole-number errors also appear, assumes quite a different aspect, the results of the two modes of calculation become nearly identical, the differences between them being then well within the range of the experimental error, and amply justify the author's course. The author finally shows that the two cases, rubidium sulphate and cæsium sulphate, quoted by Pope as adverse to the author's statement that "the matter in a crystal has, for refraction purposes, the same average effect as the same matter uncrystallised," lead to diametrically opposite conclusions; and, moreover, that such conclusions are of no value, as the differences in question between the values for solution and for the crystallised condition are well within the range of experimental error.

8. "*The Refraction Constants of Crystalline Salts.*" A Correction. By William Jackson Pope.

The author regrets to find, notwithstanding that the numbers used in his paper (*Trans.*, 1896, lxix., 1530) were several times checked, an error of a unit in two numbers in Table III. which vitiates the first line of Table IV. (*loc. cit.*, p. 1537); the first, third, seventh, and ninth numbers in the line in question should be 5·11, 5·26, 14·5, and 15·00, and in the fourth column of Table III. the numbers 4·25 and 13·51 should each be increased by unity. The comparison made in the six lines following Table IV. is consequently unjustifiable.

The error, although to be regretted, in no way affects the general argument, but, if left uncorrected, tells unfairly against the method of calculation used by Tutton.

9. "*On the Wide Dissemination of some of the Rarer Elements and the Mode of their Association in Common Ores and Minerals.*" By W. N. Hartley, F.R.S., and Hugh Ramage.

By means of spectrographic analysis the authors have examined about 170 specimens of ores and minerals, comprising oxides, carbonates, and sulphides. Half a grm. of each substance, finely powdered, was heated in the oxyhydrogen flame. The following elements and their compounds yield spectra under these conditions which are easily observed.

(*a*) In very small quantity—

Na, Ca, Pb, Ni, K, Se, Bi, Cu, Ba, Cr, Rb, Ga, Mn, Ag, In, Fe, Cs, Tl, Co.

(*b*) In small quantity—

Li, Au, Cd, Sb, and Sn.

(*c*) In such quantity as to indicate that the substance is a principal constituent of the mineral—

Be, B, Di, Te, Rh ?, Mg, Al, S, Pd ?, Zn, Ce, Se, Ru ?.

Some of the metallic elements in the list (*c*) under special conditions yield oxyhydrogen flame spectra, which are easily observed even in small quantity. Other elements than the above have not been sought for in this research.

In almost every case the locality from which the specimens of ores and minerals came is recorded, and the results of the spectrographic analysis have been tabulated. Several novel and interesting facts are disclosed, which may be stated very briefly as follows:—

Clay Iron-stones and Black-band Ores. — Fifty-one specimens examined. All contain sodium, potassium, copper, calcium, and manganese; 47 contain silver; 32, lead; 21, gallium; 13, nickel; 12, chromium; 1, strontium; and 1, thallium. Probably all contain rubidium, but it is difficult to recognise owing to the multitude of iron lines. Three specimens undoubtedly contain it.

Brown Hæmatites.—Six specimens examined. All contain sodium, potassium, copper, calcium, and manganese; 5 contain silver; 5, lead; and 5, nickel; 3, chromium; 2, gallium; 2, thallium; and 1, indium. Probably all contain rubidium; in one it is undoubtedly present.

Limonites.—Five specimens examined. All contain sodium, potassium, silver, manganese, and apparently rubidium; 4 contain calcium; 4, lead; 3, copper; 3, nickel; 1, gallium; 1, thallium; and 1, chromium.

Red Hæmatites.—Eighteen specimens examined. All contain sodium and potassium; 17 contain copper; 14, manganese; 13, silver; 12, lead; 12, calcium; 3 contain gallium; 3, indium; 3, nickel; 2, chromium; 1, rubidium; and 1, thallium.

Magnetites.—Seven specimens examined. All contain sodium, potassium, copper, silver, calcium, gallium, lead, and manganese. Four appear to contain rubidium; 2, nickel; and 1 contains indium.

Siderites.—Five specimens examined. All contain sodium, potassium, copper, silver, calcium, indium, and manganese; 3 contain lead; 1 contains rubidium; 1, gallium; 1, cobalt; 1, nickel; and 1, bismuth.

Aluminous Minerals, such as Bauxites.—Seventeen specimens. All contain sodium, potassium, copper, calcium, and iron; 16 contain gallium; 15, chromium; 13, nickel; 12, manganese; 9, silver; 3, lead; and 2, rubidium.

Manganese Ores and Minerals.—Eleven specimens examined. All contain sodium, potassium, copper, calcium, and iron; 10 contain silver; 5, rubidium, and 5, nickel; 4, gallium; 4, lead; and 4, strontium; 2, barium; 1, indium; and 1, cobalt.

Blendes.—Fourteen specimens examined. All contain sodium, copper, silver, and iron; 13, potassium; 12, gallium; 12, lead; 10, silver; 10, manganese; 9, indium; 7, cadmium; 4, thallium; 2, nickel; and 1, chromium. The zinc was observed in only 8 specimens, the spectrum being hidden by other lines.

Nickel and Cobalt Ores.—Nine specimens examined. All contain sodium, potassium, copper, calcium, iron, and nickel; 6 contain cobalt; 6, lead; 4, chromium; 3, silver; 1, barium; and 1, strontium.

Tin Ores.—Five specimens examined. All contain sodium, indium, and iron; 4 contain potassium; 3, copper; 3, calcium; 3, lead; 2, silver; and 2, manganese.

Galenas.—Eight specimens. All contain sodium, potassium, copper, silver, and iron; 4 contain manganese; and 3, calcium.

Pyrites.—Thirteen specimens. All contain sodium, potassium, copper, silver, calcium, and iron; 11 contain lead; 10, manganese; 5, indium; 5, thallium; 5, nickel; and 1, gallium.

Out of 168 ores and minerals examined, gallium occurs in 68; indium in 30; and thallium in 17. Rubidium occurs probably in 70, but unquestionably in 13. All the carbonates of iron and all the tin ores, without exception, contain indium. With one single exception, all the bauxites contain gallium.

Silver, copper, calcium, potassium, and sodium are very widely disseminated through all ores and minerals.

The authors draw deductions as to the formation of beds and lodes of ore from the following facts, which they claim to have established:—First, that certain groups of ores and minerals are pervaded by small quantities of the same metals as common impurities. Secondly, the rare metals, more particularly rubidium, gallium, indium, and thallium, are associated with the same groups of minerals, and also with allied groups.

It is easy to trace the association of similarly constituted compounds to their connection with elements related to each other, as determined by the periodic system of classification. These compounds have certain properties in common, distinctive of the groups of elements and compounds to which they belong; hence in a given course of chemical changes, similar compounds are formed and thrown together by precipitation or otherwise. All the minerals mentioned have undoubtedly had an aqueous origin.

The presence of the alkali metals in all the specimens, but in variable proportions, has a special significance.

In the analysis of many different precipitates, obtained both in neutral and even strongly acid solutions, the alkali metals have been found in combination with the precipitated substance. It has long been known that manganese, aluminium, and iron in the state of hydroxides, combine with more or less of the alkalis, but in a great measure such combinations have been disregarded.

Anniversary Meeting.

The Anniversary Meeting will be held on Wednesday, March 31st, at 3 o'clock in the afternoon.

Anniversary Dinner.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Criterion Restaurant on Wednesday, March 31st, at 6.30 for 7 p.m.

OBITUARY.

THE LATE GEORGES VILLE.

It is our very painful duty to put on record the death of our valued friend Georges Ville, who closed his most useful and honourable career on February 22nd. The deceased held the Chair of Vegetable Physiology in the Museum of the Jardin des Plantes. His life has been essentially devoted to a practical study of the vital conditions of plants, and especially of our food-plants.

Professor Ville pointed out the necessity of keeping cultivated lands adequately supplied with those constituents of plant-food which are most readily exhausted by the crops. As such, in addition to phosphoric acid, potassium salt, and nitrogen, he laid great weight on lime in the form of gypsum. This recommendation, we need scarcely say, though borne out by his experiments, is not ratified by British practice. To keep cattle for the production of manure—as is done by too many farmers in this country—he humorously compared to the conduct of a supposed iron manufacturer who should plant and keep up forests to supply his work with fuel. He shows that all the elements of plant-food can be obtained at less cost from mineral sources. But it is a gross misunderstanding to say that Prof. Ville denounced the use of animal manures.

He introduced in France the method of trial-plots of arable land, thus making the plant analyse the soil for itself. The process which he names sideration is simply ploughing in crops which are of no value in themselves, but which serve to enrich the soil especially by fixing atmospheric nitrogen in states suitable for the nourishment of succeeding crops.

His published works, some of which have been translated into English, are of great but unequal value. His lectures on agriculture, delivered in Belgium as well as in France, cannot fail to rouse up the agricultural mind, though they carry ideas which in England would be quite out of place. But he has done an incalculable service to France, and to the civilised world in general, by exposing the worn-out fallacy that organic matter by passing through the bodies of horses or of oxen acquires some novel and mysterious virtue which it had not before.

Ville's chief works are:—"Artificial Manures" (Longmans and Co.), and "The Perplexed Farmer, how is he to meet Alien Competition?" (Longmans and Co., 1891).

NOTICES OF BOOKS.

Directory of Paper Makers, January, 1897. London: Marchant, Singer, and Co.

The paper industry does not meet with an amount of attention from the outside public at all commensurate with its importance.

The work before us confines itself strictly to the conventional functions of a directory without entering at all upon the prospects, the difficulties, and possible dangers of the trade. The manufacture of filter-papers occupies the attention of eight firms, but we fear we must say that none of these takes a standing equal to that of Munktell and Co., of Sweden, and Schleicher and Schüll, of Germany.

A circumstance which we much regret is that the trade is so scantily developed in Ireland. There the air is less polluted with smoke than in most parts of England and even of Scotland; the water supply is more abundant in quantity, and we think we may say superior in purity to that on our side of St. George's Channel. Ireland has, in short, the greatest natural facilities for the development of the paper manufacture.

CORRESPONDENCE.

RELATION BETWEEN ROTATION AND REDUCING POWERS OF HYDROLYSED STARCH SOLUTIONS.

To the Editor of the Chemical News.

Sir,—I have not yet read the full paper of Browne, Morris, and Millar, a notice of which appears in the Chemical News (lxxv., p. 42).

The fact that a constant relation exists between cupric reducing and rotatory powers in hydrolysed starch solutions was pointed out by me, in a paper read before the A.A.A.S. at the Boston meeting, in 1880, and published in full in the *Proceedings* for that year, and in the *Journal of the American Chemical Society* (vol. ii., 1880, pp. 395—402). There is also an abstract of my paper in the *Berichte der Deutschen Chemischen Gesellschaft* (xiv., 1584).

From the results of my investigations, it would be only a logical conclusion to infer that similar relations exist among hydrolytic starch products in general. In the materials examined by me, the products of hydrolysis were chiefly dextrose and dextrine. In the researches made by the authors above mentioned, maltose and dextrine were the chief hydrolytic products.

In my paper the data of the examination of a large number of samples of commercial starch glucoses are found, with formulæ for calculating the percentage of reducing sugars for varying specific gravities. The calculated reducing powers obtained by these formulæ were found to agree remarkably well with the actual reducing data secured with Fehling solution. With the improved modern optical and chemical methods it is quite certain that a formula could be constructed for the hydrolytic products of starch obtained with sulphuric acid, which would give directly, from the optical observation of the solutions, practically correct figures for reducing powers.
—I am, &c.,

H. W. Wiley, Chief of Division.

United States Department of Agriculture,
Division of Chemistry, Washington, D.C.,
February 24, 1897.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 6, February 8, 1897.

M. Leidier, of Marseille, addressed to the Academy a memoir on an automatic lightning-rod for telegraphic and telephonic lines.

New Researches on the Determination of Pyrophoric Acid.—M. Berthelot and G. André.—Facts to serve towards the "History of Metaphosphoric Acid," by M. Berthelot and G. André.

Reduction of Nitrates in Arable Soil.—P. P. Dehérain.—These three papers will be inserted in full.

Certain Coloured Reactions.—E. Pineura.—These colourations are obtained with β-naphthol-sulphuric acid prepared by dissolving 0·02 grm. of β-naphthol in 1 c.c. of sulphuric acid of sp. gr. 1·83; we add from 10 to 15 drops of this reagent to about 0·5 grm. of the substance to be characterised; if the latter is in solution it is gently evaporated to dryness. Tartaric acid gives at first a blue colour, which, if we continue to heat, gradually passes to a very decided green tint; if, when the matter is cold, we add 15 to 20 times its volume of water we obtain a permanent yellowish red. Citric acid gives an intense blue, which does not turn green with prolonged application of heat. The addition of 15 to 20 times its volume of water gives a colourless solution, or one very fainly yellowish. A small quantity of tartaric acid mixed with the citric acid brings up the green tint which pure citric acid never produces; 10 to 12 per cent of tartaric acid then produces a dark greenish blue. Pure malic acid gives at once a yellowish green colour, which becomes bright yellow on prolonging the heat. The addition of water turns the colour to a bright orange. These reactions are characteristic and easy to observe; it is merely necessary to heat carefully, and to withdraw the capsule from the fire as soon as any colour is observed. If it ceases to increase in intensity, we heat afresh if requisite. Other organic substances produce similar colours, but less definite and characteristic. β-naphthol sulphuric acid also serves to distinguish the alkaline nitrites; 10 drops of this reagent, added to 0·05 grm. sodium nitrite, dissolved in a few drops of water, give rise to a very intense redness, which is not altered on the addition of water. Alkaline nitrates may be distinguished in an analogous manner by means of a solution of 0·10 grm. resorcin in 1 c.c. of sulphuric acid at 1·76. The action of this reagent upon 0·05 grm. potassium or sodium nitrate determines the appearance of a red-brown, which soon becomes a very intense violet, and which passes to orange on the addition of water.

New Method of Preparing the Primary Amines.—Marcel Delépine.—It becomes easy to have a pure primary amine, if we can combine the corresponding mineral ether with hexamethylamine.

Sanitation of the Match Trade.—M. Magitot.—The author's conclusions are:—1. The sanitation of the manufacture of matches with white phosphorus is a problem simple and easy of solution. 2. The method of sanitation consists of two orders of means based on two factors of injury, which are (*a*) phosphorism, (*b*) necrosis. 3. To phosphorism we oppose the ventilation of the work by artificial means, powerful enough to withdraw the poisonous emanations from the workers. To necrosis we oppose the principle of selection; that of recruitment and maintenance from the hands of persons entirely free from any injury of the mouth or the jaws which might furnish an opening for the chemical mischief. 4. The problem of sanitation is entirely comprised in the two terms—ventilation and selection.

Determination of Potassium Bitartrate in Wines.—Henri Gautier.—This paper will be inserted in full.

Indigenous Essence of Basil (Ocymum basilicum).—MM. Dupont and Guerlain.—The product which accompanies linalol in oil of basil is estragol (para-methoxyallylbenzene).

Argon and Nitrogen in the Blood.—P. Regnard and Th. Schlœsing.—The authors were obliged to operate on about 10 litres of blood. The blood, on leaving the veins, could not be allowed to come in contact with the air for a single instant. Whilst adhering to facts positively observed, the authors conclude that argon exists in solution in the blood.

No. 7, February 15, 1897.

The Age of Copper in Chaldea.—M. Berthelot.—Already inserted.

A Safety Receiver adapted for containing Liquefied Gases.—J. Fournier.—This paper requires the accompanying figures.

Influence of the X-Rays on the Striking Distance of the Electric Spark.—M. Guggenheimer.—The author has succeeded in establishing that:—1. At equal distances and at equal potential differences the augmentation of the striking distance of the passive spark depends on the intensity of the X-rays encountering the micrometer. 2. At an equal difference of potential (by the micrometer) and at an equal intensity of the X-rays the augmentation of the striking distance of the passive spark depends on the distance of the micrometer from the emissive wall of the tube. 3. The interposition of a fluorescent screen of barium platinocyanide, of a plate of glass, or of quartz does not appreciably change the radiation.

False Equilibria of Hydrogen Selenide.—H. Pélabon.—A mathematical paper with a diagram, not suitable for insertion.

Action of Cuprous Oxide upon Solutions of Silver Nitrate. — Paul Sabatier. — Not susceptible of useful abstraction.

On certain Derivatives of Salicylic Aldehyd.— Paul Rivals.—A thermo-chemical paper. The heat of molecular combustion is = 1589·7 cal. at constant volumes and 1590·3 cal. at a constant pressure.

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.

Dental Alloys.—Are there any books on the alloys used in dentistry? If so, who are the publishers?—Jack.

MEETINGS FOR THE WEEK.

Monday, 15th.—Society of Arts, 8. (Cantor Lectures). "Alloys," by Prof. W. Chandler Roberts Austen, F.R.S.
Tuesday, 16th.—Royal Institution, 3. "Animal Electricity," by Prof. A. D. Waller, F.R.S.
—— Society of Arts, 8. "The Progress of the British Colonies of Australasia during the Sixty Years of Her Majesty's Reign," by James Bonwick.
Wednesday, 17th.—Society of Arts, 8. "Music in England at the Queen's Accession," by J. Spencer Curwen.
Thursday, 18th.—Chemical, 8. "On the Atomic Weight of Carbon," by Alexander Scott, M.A., D.Sc. "On a New Series of Miacosulphates of the Vitriol Group," by Alexander Scott, M.A., D.Sc. "The Action of Alkyl Haloids on Aldoximes and Ketoximes," by Wyndham R. Dunstan, F.R.S., and Ernest Goulding.
—— Royal Institution, 3. "Greek History and Extant Monuments," by Prof. Percy Gardner, F.S.A.
Friday, 19th.—Royal Institution, 9. "Greek and Latin Palæography," by Sir Edward Maunde Thompson.
Saturday, 20th.—Royal Institution, 3. "Electricity and Electrical Vibrations," by Right Hon. Lord Rayleigh, M.A., F.R.S.

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An Associate of the Institute of Chemistry, who has had four years' experience with Consultant Analyst and four years at Works, desires engagement. Food and Agricultural work specialities. Unexceptional references.—Address, H. I., 27, Wellington Square, London, S.W.

Analytical Chemist, A.I.C., who has had experience in well-known Laboratory and Cement Works, seeks employment in Works or Laboratory.—Address, "Works," Chemical News Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Analytical Chemist (Ph.D.) seeks Engagement; Belgian (26); studied in Germany and Switzerland; three and a half years' experience with Agricultural Laboratory; now engaged at Aniline Colour manufactories. Thorough knowledge of English, French, German, and Dutch.—Address, "A.B.K.," care of Street and Co., 30, Cornhill, E.C.

Assistant wanted, at the end of March, in a London Analytical Laboratory. Hours, 10 to 5; Sat., 10 to 1. Annual holiday, 14 days. Applicants must be experienced in the quantitative analysis of water, food, drugs, and commercial substances generally. F.I.C. or A.I.C. preferred. Salary, paid monthly, £100 to £125 a year, according to qualifications.—Apply to A.Z., Chemical News Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Works' Chemist, A.I.C., late with large London manufacturers, well up in Plant and Building Construction, experience in management of men, and in conduction of Technical Research work, good Commercial Analyst, seeks Appointment. Moderate Salary.—Address, "Plant," Chemical News Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Wanted, in London Smelting Works, an Assistant Chemist. Must be well up in Leady and Cuprous material.—Write C. N. 929, Deacon's Advertising Offices, Leadenhall Street, London, E.C.

Young Chemist wanted as Assistant in large Manure Works. — Apply, by letter only, to Mr. Vincent Edwards, F.I.C., West End Laboratory, 55, Weymouth Street, W.

FOR SALE.—Complete set of "Journal of the Chemical Society," from 1848—1896. 70 vols., bound in half calf; good condition. Enquiries and offers to M.Sc., Chemical News Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

BOARD OF WORKS FOR THE POPLAR DISTRICT.

TO CHEMICAL MANUFACTURERS AND OTHERS.

NOTICE IS HEREBY GIVEN,
That the Board will meet at the Board Room, 117, High Street, Poplar, on Tuesday, the 16th day of March inst., at 6.30 o'clock in the evening precisely, to receive
TENDERS
for the Supply of
DISINFECTANTS
for one year, ending Lady Day, 1898, as follows, viz.,—
CARBOLISED PEAT POWDER, 15 PER CENT OF CARBOLIC, AT PER TON.
PERMANGANATE OF POTASH, AT PER Lb.
BLACK CARBOLIC ACID, 33 PER CENT OF CARBOLIC.
CHLORO-NAPTHOLEUM, IN BULK, 25 PER CENT OF CARBOLIC.
BURNETT'S DRAIN TESTS, AT PER GROSS.
KEMP'S DRAIN TESTS, AT PER GROSS.

The Board do not bind themselves to accept the lowest or any Tender.

Contractors will be required to pay Trade Union rates of wages, and to covenant not to sub-let any portion of the Contract. Compliance with these conditions will be rigidly enforced under a penalty of the sum of £5 for each breach.

Contractors will be required to furnish securities to the satisfaction of the Board, and to enter into bond with them for the due performance of Contract, and pay down the sum of £2 immediately upon acceptance of the Tender, towards the expenses of the contract and bond.

Tenders, upon the forms for that purpose, are to be delivered, in separate covers, duly marked and sealed, before Two o'clock in the afternoon of the 16th day of March, after which time no Tender will be received.

Further particulars and Forms of Tender can be had at the Office of the Surveyor, any day to the 15th day of March, between 9 a.m. and 4 p.m.

WM. HENRY FARNFIELD,
Clerk to the Board.
Board Offices,
117, High Street, Poplar, E.,
6th March, 1897.

THE CHEMICAL NEWS.

Vol. LXXV., No. 1947.

A NOTE ON THE ESTIMATION OF ZINC OXIDE.

By E. ASTON, B.Sc. (Lond.), and L. NEWTON,
University College, London.

Fresenius states that zinc oxide, when mixed with sulphur, and heated gradually to redness in a current of hydrogen gas, is quantitatively transformed into zinc sulphide.

We attempted in this way to determine the purity of zinc oxide prepared in the following manner from pure zinc, and have met with an anomaly which, we think, deserves to be placed on record. A preliminary analysis of the zinc was first made, by dissolving a weighed quantity in nitric acid, evaporating to dryness, igniting, and then weighing the zinc oxide obtained.

1·106 grms. of zinc gave 1·38075 grms. of zinc oxide. Percentage of zinc in the ZnO—*Found*, 80·29; *Calculated*, 80·24.

50 grms. of zinc, thus shown to be almost pure, were dissolved in pure nitric acid, and the solution evaporated to dryness. The residue was taken up with water, and the solution filtered. To the filtrate a few drops of ammonium sulphide were added, the liquid was allowed to stand for some hours with repeated shaking, and then filtered.

The filtrate was evaporated to dryness on a water-bath, then dried in an air-bath at 150° C., and finally ignited, first in the blowpipe, and then for three hours in a muffle furnace.

Two weighed specimens of oxide thus prepared were mixed with sulphur and gradually heated to redness in a current of hydrogen gas.

After cooling down in the gas the crucibles were weighed.

This process was repeated in the one case sixteen, in the other twenty-two times, but in neither did the quantity of zinc sulphide exceed 96 per cent of the theoretical, though it had increased generally by a small amount at each weighing.

These results might conceivably be due to impurities in the zinc oxide used, and we therefore tried another method of estimation, viz., as sulphate, in order to see whether the same result would be obtained.

A weighed quantity of the oxide was dissolved in dilute sulphuric acid in a weighed platinum crucible and evaporated to dryness; the greater part of the acid was driven off by heating in an asbestos oven to about 340° C.

The crucible was placed in a sulphur bath for about two hours, then removed and weighed. It was replaced in the bath for an equal period of time, and then re-weighed (Baubigny, *Comptes Rendus*, vol. xcvii., p. 854). The weight had not changed, and the result of the experiment was that—

0·5742 grm. of ZnO gave 1·14065 grms. of $ZnSO_4$;

hence the percentage of zinc in the zinc oxide was 80·19 instead of 80·24, the theoretical quantity.

Our zinc oxide, therefore, was pure, and, so it would seem, that the change from oxide prepared from zinc nitrate, to sulphide by heating with sulphur in a current of hydrogen, cannot be made the basis of a quantitative method.

At this point it may be advisable to give some of the numbers experimentally obtained.

(1). 0·3555 grm. of zinc oxide gave—

1st weighing	0·3735 grm. ZnS.
6th „	0·3905 „ „
10th „	0·3985 „ „
11th „	0·3985 „ „

At this stage ZnS and sulphur were ground together in an agate mortar, so as to make sure of an intimate mixture.

14th weighing	0·4065 grm. ZnS.
16th „	0·4070 „ „

At this point the quantity of ZnS obtained was 95·59 per cent of the theoretical.

(2). In this case the zinc oxide and sulphur were in each case ground together in an agate mortar, and then introduced into the crucible.

0·4685 grm. of zinc oxide gave—

1st weighing	0·5055 grm. ZnS.
12th „	0·5275 „ „
13th „	0·5280 „ „
15th „	0·53275 „ „
16th „	0·5325 „ „
22nd „	0·5374 „ „

At this point the experiment was arbitrarily stopped. The quantity of zinc sulphide obtained was 95·88 per cent of the theoretical. The compound formed appears in each case to correspond roughly to a formula $3ZnS.2ZnO$. Two points may be noted about these numbers:—

1. After the first heating with sulphur, the weight of sulphide produced is more than 85 per cent of the theoretical, being in the first case 87·7 per cent and in the second 90·10 per cent; any further increase is only by very small quantities, and cannot be due to impurities in the sulphur, which left no residue on ignition.

2. Two weighings may give exactly the same number; that is to say, a constant point is reached, and yet on repeating the process an increase is obtained. Thus it is impossible to find a point at which the change from oxide to sulphide definitely stops.

It was thought advisable to see whether, under the same circumstances, zinc oxide prepared from compounds other than the nitrate would be quantitatively changed into sulphide.

Experiments were therefore tried with—

(1) Zinc oxide prepared from zinc sulphide by ignition.
(2) „ „ „ carbonate „
(3) „ „ „ sulphate „

(1). The zinc sulphide used was prepared by dissolving some of our pure zinc oxide in acetic acid, and passing into the solution a current of sulphuretted hydrogen gas.

The precipitate was collected, washed, and then dried in a current of hydrogen gas.

That this sulphide was pure is shown by the following analyses:—

(*a*) 0·1582 grm. ZnS gave on ignition 0·1322 grm. ZnO.
(*b*) 0·11075 „ „ 0·0925 „

	Percentage of *Zn* found.	Percentage of *Zn* in ZnS calculated by theory.
(*a*)	67·052	67·010
(*b*)	67·017	67·010

0·11585 grm. of zinc oxide thus prepared was heated with sulphur in the usual manner, and gave 0·13860 grm. ZnS.

Percentage of *Zn* found.	Percentage of *Zn* in *ZnO* calculated by theory.
80·16	80·24

(2). *Zinc Oxide prepared from Zinc Carbonate.*

Some zinc oxide was dissolved in acetic acid, and precipitated with pure ammonium carbonate solution.

The precipitate was collected, washed with boiling water, and then ignited until its weight remained constant. 0·2245 grm. of zinc oxide thus prepared was mixed with sulphur and treated in the usual manner, giving 0·2685 grm. of zinc sulphide.

Percentage of Zn found.	Percentage of Zn in ZnO by theory.
80·14	80·24

(3). *Zinc Oxide prepared from Zinc Sulphate.*

The zinc oxide used in this case was prepared by igniting to a constant weight the sulphate previously obtained in the estimation of zinc oxide as sulphate.

0·140 grm. of zinc oxide gave 0·168 grm. of zinc sulphide.

Percentage of Zn found.	Percentage of Zn in ZnO calculated.
80·41	80·24

It must be pointed out that in this case the final point was only reached after three ignitions with sulphur. But after the first ignition the quantity of zinc sulphide formed was already 98·4 per cent, and therefore the case is hardly comparable to that of the oxide prepared from the nitrate.

Thus, zinc oxide prepared by ignition of the nitrate is not quantitatively transformed into sulphide by heating with sulphur in a current of hydrogen gas, as are specimens of oxide prepared in other ways.

University College, London,
March, 1897.

THE DETERMINATION OF TITANIC ACID.

By J. JAS. MORGAN.

In determining titanic acid in iron ores by the usual methods, part of it is found with the insoluble residue and part in the acid solution. Arnold, in his "Steel Works Analysis," describes a method based upon the principle that, in the presence of excess of phosphate of iron, titanic acid forms an insoluble phospho-titanate of iron, and is found with the insoluble residue, and, in the absence of sufficient phosphate of iron to fix the titanium in this form, brings about the desideratum by the addition of ammonium phosphate. The method on the whole is very satisfactory, the only drawback being the method of precipitating the titanium, which is effected by boiling the largely diluted solution (measuring 1000 c.c.) until the volume is reduced to 250 c.c. This occupies considerable time, while the precipitate not unfrequently adheres so tenaciously to the beaker as to render the complete removal a very difficult matter. The writer, therefore, prefers Blair's method of precipitation, and carries out an estimation as follows (a combination of Arnold's and Blair's methods) :—

To the weighed portion of the dry ore add 1 grm. of ammonium phosphate dissolved in a little water, and effect solution by digesting with hydrochloric acid, and, when solution is complete, evaporate to dryness and well bake. Dissolve the dry mass in hydrochloric acid, dilute, collect the insoluble residue (containing the whole of the titanic acid as phospho-titanate of iron) on a filter-paper, and wash with hot dilute hydrochloric acid and cold water until free from iron salts. Dry the filter-paper and contents, ignite the contents in a platinum crucible, and mix with about ten times its weight of potassium carbonate. Fuse, extract the fusion in a little hot water, filter off the insoluble, and well but carefully wash with hot water. Then dry filter and contents, place in a platinum crucible, ignite, mix with about 6 grms. of acid potassium sulphate, and fuse at a low red heat for half an hour. Extract the cold fusion in 10 c.c. of hydrochloric acid and 50 c.c. of sulphurous acid, filter, and wash with hot water. Dilute the filtrate, add 20 grms. of sodium acetate dissolved in water, then one-sixth the volume of acetic acid, and boil for a few minutes. Allow the resulting precipitate to settle, collect on a filter, and wash with water containing acetic acid. Dry, ignite, and weigh as TiO_2.

With pig-irons the weighed portion, after the addition of the ammonium phosphate,[*] is dissolved in nitric acid, sp. gr. 1·20, the solution taken to dryness, and baked. The dry mass, dissolved in hydrochloric acid, again taken to dryness, re-dissolved in hydrochloric acid, and, after diluting the solution, the silica, &c., filtered off; the remainder of the operation being then similar to the above.

A RECLAMATION.

We have received a communication from Prof. Dr. C. Riffenbach, bearing date "Cairo, February 18, 1897." The author mentions that we insert in the Chemical News of February 12th a reprint of a paper by M. Gomberg, of Michigan, which appeared in the *Journal of the American Chemical Society*, and which touches his region.

Prof. Riffenbach informs us that he published this research by Gomberg in the *Zeitschrift für Analyt. Chemie*, 1896, p. 466, as a Supplement, and requires us to notice his research. To this end he, simultaneously with this letter, sends a special reprint of the paper.[†]

ELECTRIC SHADOWS AND LUMINESCENCE.[‡]

By Prof. SILVANUS P. THOMPSON, D.Sc., F.R.S., M.R.I.

(Concluded from p. 124).

This will be a convenient place to mention a new effect of X-rays which I have recently observed, and which is set down in the table. When X-rays fall upon a metal object electrified by an influence machine, they produce some curious changes in the nature of the discharge into the air. If the body is already discharging itself from some edge or corner in an *aigrette* or brush discharge (visible in darkness only) the size and form of the aigrette is much altered. Under some circumstances not yet investigated, the incidence of X-rays causes the aigrette to disappear; under, others, the X-rays provoke its appearance.

Since the publication of Röntgen's research the most notable advance that has been made has been in the direction of improving the tubes. Röntgen himself has mostly employed a pear-shaped tube with a flat circular kathode near the top, producing a beautiful fluorescence of the lower part of the tube. He carefully verified the circumstance that the X-rays originate at that portion of the glass surface which receives the impact of the kathodic discharge. They appear in fact to be generated at the place where the kathode discharge first impinges upon the surface of any solid body. It is not necessary that the substance which is to act as emitter of the X-rays should become fluorescent. On the contrary, it appears that the best radiators are substances that do not fluoresce, namely the metals. I have found zinc, magnesium, aluminium, copper, iron, and platinum to answer —the last two best.[§] Mr. Porter, of University College, and Mr. Jackson, of King's College, have independently found out the merits of platinum foil, the former using

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[*] With phosphoric irons the addition of ammonium phosphate is not necessary, unless the titanium present is considerable.

[†] At the present date this reprint has not reached us.—*Ed.* C. N.

[‡] A Lecture delivered at the Royal Institution of Great Britain, Friday, May 8, 1896.

[§] (The author has since found metallic uranium to surpass all other metals).

an old Crookes tube designed for showing the heating effect of the kathode discharge when concentrated by a concave kathode. On the table are some of the experimental forms (see *Philosophical Magazine*, August, 1896, p. 162) of tubes I have used. The best results are found when the kathodic discharge is directed against an interior piece of metal—preferably platinum—which I term the antikathode (*Comptes Rendus*, cxxii., p. 807), set obliquely opposite the kathode, and which serves as a radiating surface from which the X-rays are emitted in all directions. When experimenting with various forms of tube, I have spent much time in watching, by aid of a fluorescent screen, their emissive activity during the progress of exhaustion. As already mentioned, X-rays are not emitted until the stage of minimum internal resistance has been passed. As the exhaustion advances, while resistance rises and spark length increases, there is noticed, by aid of the screen, a luminosity in the bulb, which, faint at first, seems to come both from the front face of the bit of platinum that serves as antikathode, and from the back face; an oblique dark line (Fig. 11), corresponding to the plane of the antikathode, being observed in the screen to separate the two luminous regions. On slightly increasing the exhaustion the emission of X-rays from the back of the antikathode ceases, while that from the front greatly increases (Fig. 12), and is quite bright right up to the angle delimited by the plane of the antikathode. There is something mysterious, needing careful investigation, in this lateral emission of X-rays under the impact of the kathode discharge.

Of all the many forms of tube yet produced none has been found to surpass the particular pattern devised by Mr. Sydney Jackson (Fig. 13), and known as the "focus tube." It was with such a tube that I showed you at the outset the fundamental experiments of Röntgen. A concave polished kathode of aluminium concentrates the kathodic discharge upon a small oblique sheet of platinum, which, while acting as antikathode, serves at the same time as anode. Not only does the concentration of the kathodic discharge upon the metal cause it to emit X-rays much more vigorously, but it also has the effect of causing them to be emitted from a comparatively small and definite source, with the result that the shadows cast by opaque objects are darker. (Photographs were then thrown upon the screen, those taken with "focus" tubes showing remarkable definition of detail. Some of these were by Mr. J. W. Giffen; others, showing diseased bones, &c., taken by the lecturer, and some by Mr. Campbell-Swinton and by Mr. Sydney Rowland, were also projected).

The objection has been taken that in these shadow photographs it is impossible to distinguish the parts that are behind from those that are in front. In a sense that is so. But I venture to say that the objection not only can be got over, but has been got over. I cannot show the proof of my assertion upon the screen, because I cannot put upon the screen a stereoscopic view. But here in my hand is the Röntgen stereograph of a dead tame rabbit. Two views were taken, in which the X-rays were thrown in two different directions at an angle to one another. When these two views are stereoscopically combined, you observe the rabbit's body with the lungs and liver inside in their relative positions. The soft organs, which cast faint shadows almost indistinguishable amid the detail of ribs and other tissues, now detach themselves into different planes, and are recognisable distinctly. I now send up for projection in the lantern the two photographs that were taken at the beginning of my discourse, and which have in the meantime been developed.

Turning back to the phenomena of luminescence,* permit me to draw your attention to the accompanying table of the different kinds of luminescence with which the physicist has to deal.

TABLE II.

Phenomenon.	Substance in which it occurs.
1. Chemi-luminescence ..	Phosphorus oxidising in moist air; decaying wood; decaying fish; glowworm; firefly; marine organisms, &c.
2. Photo-luminescence ..	
(*a*) *transient* = Fluorescence.	Fluor-spar; uranium-glass; quinine; scheelite; platino-cyanides of various bases; eosin, and many coal-tar products.
(*b*) *persistent* = Phosphorescence.	Bologna-stone; Canton's phosphorus and other sulphides of alkaline earths; some diamonds, &c.
3. Thermo-luminescence ..	Scheelite; fluor-spar.
4. Tribo-luminescence.. ..	Diamonds; sugar; uranyl nitrate; pentadacylpara-tolylketone.
5. Electro-luminescence ..	
(*a*) Effluvio-luminescence.	Many rarefied gases; many of the fluorescent and phosphorescent bodies.
(*b*) Kathodo-luminescence	Rubies, glass, diamonds, many gems and minerals.
6. Crystallo-luminescence ..	Arsenious acid.
7. Lyo-luminescence	Sub-chlorides of alkali-metals,
8. X-luminescence	Platino-cyanides, scheelite, &c.

You will note the names given to discriminate from one another the various sorts of luminescence. Chemi-luminescence denotes that due to chemical action, as when phosphorus oxidises, or when the glowworm emits its cold light. Then there is the photo-luminescence of the bodies which shine when they are shone upon. There is the thermo-luminescence of the bodies which shine when heated. There is tribo-luminescence caused by certain substances when they are rubbed. There is the kathodo-luminescence of the objects placed in a Crookes tube. There is the crystallo-luminescence of certain materials when they become solid; and the lyo-luminescence of certain other materials when they are dissolved. Lastly, there is the X-luminescence set up by the X-rays.

Pausing on photo-luminescence, here is an experiment to illustrate the difference between its two varieties, phosphorescence and fluorescence. Light from an arc lamp, filtered from all rays except violet and ultra-violet, is thrown upon a disc to which rapid rotation is given by an electric motor. The disc is painted with two rings, one of sulphide of calcium, the other of tungstate of calcium, Though the light falls only on one patch, you note that the sulphide shows a continuous ring of blue light, for the emission of light persists after the stuff has passed out of the illuminating rays. The tungstate, on the other hand, shows only a short trail of light, the rest of the ring being non-luminous, since tungstate has but little persistence. The light has in fact died out before the stuff has passed a quarter of an inch from the illuminating beam. This is a sort of phosphoroscope designed to show how long different materials will emit light after they have been shone upon. Those which show only a temporary luminescence are called fluorescent, while those with persistent luminescence are called phosphorescent. For many years it has been known that some diamonds are phosphorescent. Three such are here shown,* which, after exposure of one minute to the arc light, shine in the dark like glowworms. The most highly phosphorescent material yet produced is an artificial preparation of sul-

---

* This very convenient term was suggested some six years ago by Wiedemann, to denote the many phenomena known variously as fluorescence or phosphoreseence. It refers to all those cases in which light is produced, whether under the stimulus of electric discharge, of heat, of prior exposure to illumination, or of chemical action, and the like, in which the light is emitted at a lower temperature than that which would be necessary if it were to be emitted by means of incandescence.

* Kindly lent by Dr. J. H. Gladstone, F.R.S.

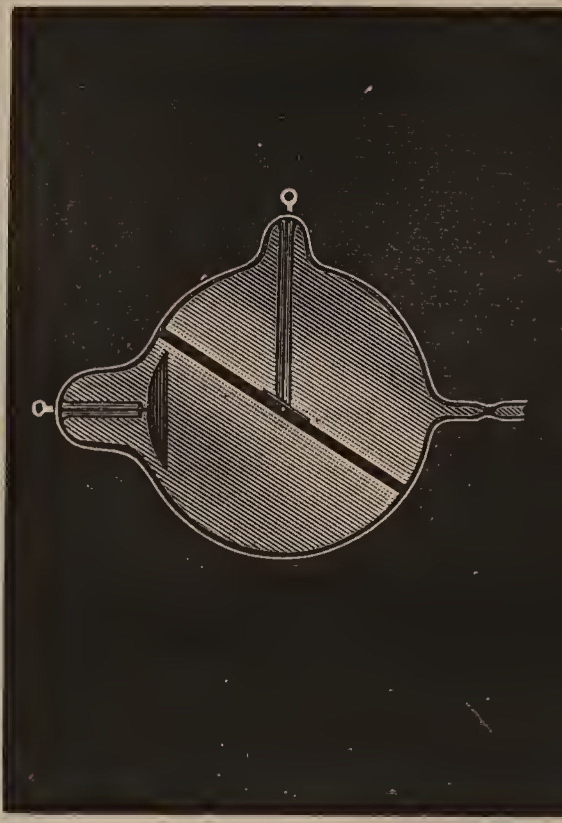


FIG. 11.

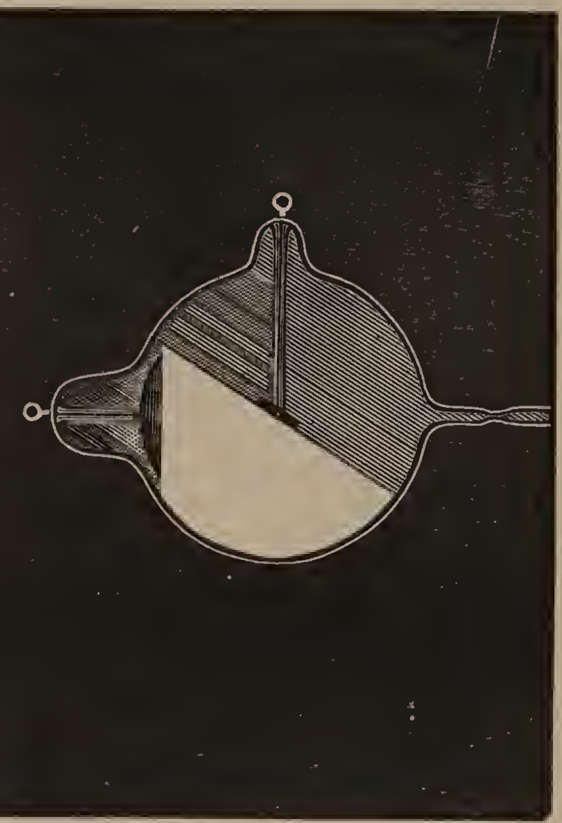


FIG. 12.

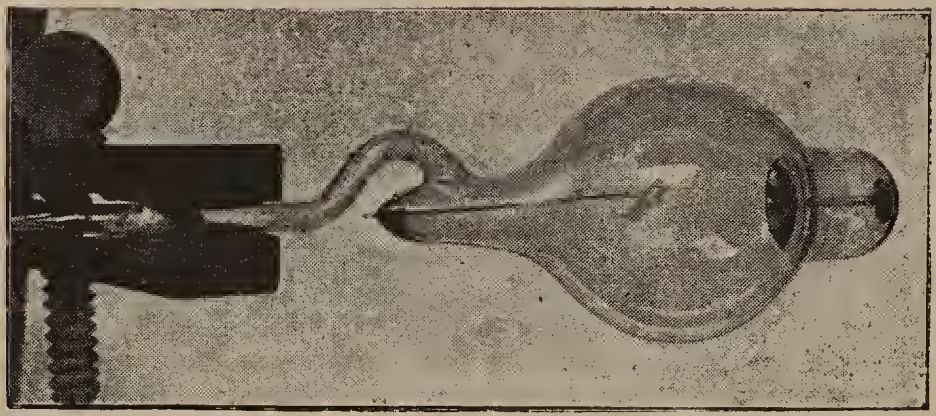


FIG. 13.

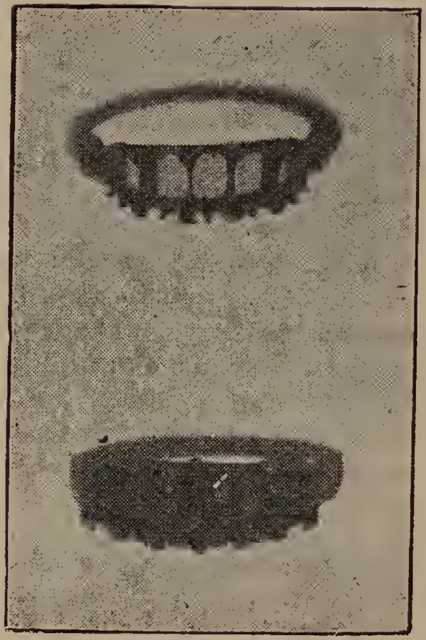


FIG. 14.

phide of calcium manufactured by Mr. Horne. The specimen exhibited has a candle-power of about $\frac{1}{10}$ candle per square inch after exposure for a few seconds to direct sunlight; but the brilliancy rapidly dies away, though there is a visible luminescence for many days. This substance is also brightly luminescent in a Crookes tube, and less brightly under the influence of X-rays.

Many substances, notably fluor-spar, have the property of thermo-luminescence, that is, they shine in the dark when warmed. Powdered fluor-spar dropped upon a hot shovel emits bright light. If, however, the spar is heated to a temperature considerably below red heat for some hours, it apparently comes to an end of its store of luminous energy, and ceases to shine. Such a specimen, even after being kept for some months, refuses to shine a second time when again heated. It has, however, long been known that the property of luminescing when warmed can be restored to the spar by passing a few electric sparks over it, or by exposing it to the silent discharge or aigrette. Wiedemann having found that the kathode rays produce a similar effect, it occurred to me to try to find out whether any of these X-rays also would revivify thermo-luminescence. I have found that on exposure for twenty minutes to X-rays, a sample of fluor-spar which had lost its thermo-luminescent property by prolonged heating was partially though not completely revivified.

I referred earlier to the rays recently discovered by M. H. Becquerel. In February last M. Becquerel, and independently I myself (see *Philosophical Magazine*, July, 1896), made the observation that uranium salts emit some rays which very closely resemble the X-rays, since they will pass through aluminium and produce photographic action. It remains to be seen whether these rays are identical with those of Röntgen.

Finally, let me briefly exhibit two results of my own work. There is now shown (Fig. 14) the photographic shadow of two half-hoop ruby rings. One of them is of real rubies, the other of imitation stones. By artificial light it is difficult to distinguish one from the other, but when viewed by the X-rays there is no mistaking the false for the true. The real rubies are highly transparent, those of glass are practically opaque.

After gaining much experience in judging by photography of the relative transparency of materials, I made a careful research (*Phil. Mag.*, August, 1896) to discover whether these rays can be polarised. At first I used tourmalines of various thicknesses and colours. More recently I have tried a number of other dichroic substances, — andalusite, sulphate of nickel, of nickel and ammonium, sulphate of cobalt, and the like. The method used for all was the following:—A slice of the crystal was broken into three parts. One part was laid down, and upon it were superposed the other two in such a way that in one the crystallographic axis was parallel, in the other perpendicular, to the crystallographic axis in the first piece. If there were any polarisation the double thickness where crossed in structure would be more opaque than the double thickness where the structure was parallel. Not the slightest trace of polarisation could I observe in any case. Of numerous other observers who have sought to find polarisation, none has yet produced a single uncontestable case of polarisation.

At the present moment interest centres around the use of luminescent screens for observing the Röntgen shadows, and in this direction some advances have been claimed of late. It should, however, not be forgotten that Röntgen's original discovery was made with a screen covered with platino-cyanide of barium. Here is a piece of card covered with patches of several different kinds of luminescent stuffs, several platino-cyanides, several sulphides, and some samples of tungstate of calcium. Of these materials the brightest in luminescence is the hydrated platino-cyanide of potassium employed by Mr. Sydney Jackson; the next brightest is a French sample of platino-cyanide of barium; platino-cyanide of strontium coming third.

Using a focus tube of Mr. Jackson's improved pattern, enclosed in a box with a cardboard front, and taking a platino-cyanide screen, I am able in conclusion to demonstrate to all those of my audience who are within a few feet of the apparatus, the facts that have so startled the world. You can see the bones of my hand and of my wrist. You can see light between the two bones of my forearm; while metal objects, keys, coins, scissors, &c., enclosed in boxes, embedded in wood blocks, or locked up in leather bags, are plainly visible to the eye.

Whatever these remarkable rays are, whether they are vortices in the ether, or longitudinal vibrations, or radiant matter that has penetrated the tube, or, lastly, whether they consist simply of ultra-violet light, their discovery affords us one more illustration of the fact that there is no finality in science. The universe around us is not only not empty, is not only not dark, but is, on the contrary, absolutely full and palpitating with light: though there be light which our eyes may never see, and sounds which our ears may never hear. But science has not yet pronounced its last word on the hearing of that which is inaudible and the seeing of that which is invisible.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 4th, 1897.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Mr. H. L. Bowman was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. John Owen Alexander, 11, Avenue Road, South Norwood Park, S.E.; John B. Ashworth, 16, Ducie Street, Prince's Park, Liverpool; John Barclay, B.Sc., Avenue Cottage, near Bromsgrove, Worcestershire; Frank Bastow, B.Sc., 1, Braithwaite, Keighley; William Dillon, 7, Laurel Place, Chapel Lane, Armley, Lancashire; E. G. Guest, M.A., The Grammar School, Kirkham, Lancashire; T. Hartley, Gatwell Street, Bruton, Somerset; John Holmes, Crewe Villa, Putney Bridge Road, S.W.; O. C. Johnson, 52, Thayer Street, Ann Arbor, Michigan, U.S.A.; H. King, B.Sc., 4, North Street, Scarborough; H. M. Lloyd, 28, Victoria Street, Merthyr; R. N. Lyne, Government Offices, Zanzibar; C. H. Parker, Manor House, Tettenhall, Wolverhampton; S. Pollitt, B.Sc., 19, Paulton Square, Chelsea, S.W.; M. Wildermann, Ph.D., Davy-Faraday Laboratory, Albemarle Street, W.

Of the following papers those marked * were read:—

*10. "*Observations upon the Oxidation of Nitrogen Gas.*" By Lord Rayleigh, F.R.S.

On the basis of Davy's assertion that the dissolved nitrogen of water is oxidised during electrolysis, various attempts were made; but they led to no useful result, even leaving it doubtful whether Davy's facts are correct.

The influence of pressure upon the oxidation of nitrogen by the electric flame was next examined. It appeared that, while in a small vessel the effect of increased pressure was favourable, but little advantage resulted when the vessel was large enough to give the maximum effect at a given pressure. The pressures compared were two atmospheres, one atmosphere, and half an atmosphere.

The remainder of the paper is devoted to a detailed description of a large scale apparatus (shown working) in which 21 litres of mixed gases enter into combination per hour, at an expenditure of about 1 horse-power.

Discussion.

Professor Armstrong, referring to Lord Rayleigh's remark as to the importance of the platinum electrodes being red-hot, enquired whether there was any evidence that the platinum played a special part in the process.

Professor Ramsay suggested, as an explanation of the better results obtained when a large vessel was employed, that nitric oxide was the first product, and that this subsequently combined with oxygen to form the peroxide.

The President considered it probable that some of the oxide of nitrogen first formed was subsequently decomposed by the heat of the flame itself, and that the large vessel, by presenting a large surface of alkaline liquid, favoured the rapid absorption of the oxide of nitrogen, and thus less was decomposed than would be the case in a smaller vessel, where the rate of absorption was smaller. He enquired with what proportion of nitrogen to oxygen combustion occurred most rapidly.

Professor M'Leod remarked that he had made an experiment in the manner originally suggested by Cavendish, and had found that nitrite as well as nitrate was formed.

Lord Rayleigh, in reply, said that the larger vessel apparently led to better results by increasing the facilities for absorption. He did not consider that the platinum played any special part in the process. The action seemed most rapid when the proportion of air to oxygen was as about 5 to 6, which corresponds with two of nitrogen to three of oxygen. He believed that both nitrite and nitrate were formed. The apparatus shown was suitable for the preliminary concentration, but not for the final purification of argon.

*11. "*On some Apparatus for Steam-distillation.*" By F. E. Matthews, Ph.D.

In this paper several forms of apparatus for automatically steam-distilling substances are described.

Some solids of high melting-point may be separated by boiling the substance mixed with water in a flask fitted with a reflux condenser; the solid substance adheres to the inside of the condenser, whence it can be removed from time to time.

For liquids heavier than water, the flask in which the mixture is boiled is connected with the side tube of an ordinary distilling-flask; this distilling-flask, filled with water up to the side-tube, serves as the receiver. Into the neck of the receiver, and passing below the surface of the water, a bent Liebig's condenser is fitted which has the peculiarity of having a hole made in it a short distance above the level of the water in the receiver. On boiling the mixture in the flask, the vapours pass up the side-tube of the receiver into the upper portion of its neck and thence through the hole in the receiver, when condensation takes place. The condensed liquids run down the condenser to the water-level in the receiver, where a drop of the heavy fluid sufficiently large to sink is formed from time to time. The condensed liquids displace their own volume of water, which flows from the receiver through the side-tube back again to the boiling-flask. In all cases in which vapour is passing in one direction in a tube, and water in the other, the advantage of perforating the tube near its lower end is pointed out.

For liquids lighter than water, the apparatus consists of the boiling-flask, which is an ordinary distilling-flask; this is connected by the upper opening to an upright tube furnished with a T-piece. The top of the upright tube is connected to the condenser, the lower end dips two or three inches into a Woulfe's bottle, containing water in sufficient quantity, which serves as the receiver. Through another neck of the Woulfe's bottle, a second tube passes from the bottom of the bottle and is connected to the side-tube of the boiling-flask. The mixed vapours pass from the boiling-flask into the upright T-tube, thence into the condenser; there becoming condensed, they fall down into the T-tube, producing a column of liquid which forces water from the bottom of the receiver back into the boiling-flask through its side-tube.

A modification of this apparatus dispenses with the necessity of having an indiarubber connection exposed to the hot vapour. In this modification the boiling-flask is an ordinary plain flask. This is connected to the condenser by a side-tube blown on to the upright tube. The water returns to the boiling-flask through another T-tube, blown on to the side-tube of the upright tube. For conveniently emptying the receiver without dismantling the apparatus, a separating funnel with two necks may replace the Woulfe's bottle of the previous apparatus.

Many liquids bump badly when boiled with water; this can generally be got over by introducing a zinc-platinum couple into the boiling-flask. The temperature of the water in the boiling-flask may be raised by dissolving suitable substances, such as sulphuric acid or calcic chloride, in it, or liquids of higher boiling-point may be used.

*12. "*Researches in the Stilbene Series.*" I. By John J. Sudborough, Ph.D.

The author has obtained benzil as one of the products of the action of zinc dust and acetic acid on benzoin; if the action is continued the benzil disappears and the chief product is deoxybenzoin. The formation of an oxidation product of benzoin by the action on it of zinc dust and acetic acid appeared so remarkable that the author has studied the action of acetic acid alone on benzoin, and he finds that small quantities of benzil are formed if benzoin is heated with six times its weight of glacial acetic acid on the water-bath for eight—nine hours.

By the action of phosphorus pentachloride on deoxybenzoin a solid chlorstilbene has been obtained, which differs from Zinin's oily compound. It melts at 45°, yields a dibromide and a dichloride, also with nitrous fumes two compounds probably represented by the formulæ $Ph{\cdot}CHNO_2{\cdot}CClNO_2{\cdot}Ph$ (m. p. 128°) and $Ph{\cdot}C(NO_2){:}C(NO_2){\cdot}Ph$ (yellow prisms, m. p. 104—105°).

An oily compound can be obtained by the action of phosphorus pentachloride on deoxybenzoin at low temperatures. The oil contains the same amount of chlorine as solid chlorstilbene.

Methyldeoxybenzoin and ethyldeoxybenzoin on treatment with phosphorus pentachloride can be made to yield both oily and crystalline compounds, analysis of which points to their being methyl- and ethyl-chlorstilbenes. Solid methylchlorstilbene melts at 124°, and the corresponding ethyl compound at 60°. The dichlorides and dibromides are also described. The question as to the nature of the oily compounds has not been settled; the author describes a method by which he proposes to determine whether they are merely slightly impure forms of the solid compound, true stereo-isomerides, or structurally isomeric with the solid compounds.

*13. "*Diortho-substituted Benzoic Acids.* III. *Hydrolysis of Substituted Benzamides.*" By John J. Sudborough, Ph.D., Percy G. Jackson, and Lorenzo L. Lloyd.

In order to determine whether diortho-substituted benzamides exhibit the same remarkable degree of stability towards hydrolysing agents as characterises the diortho-benzoyl chlorides (*Trans.*, 1895, lxvii., 587) and ethereal salts, the authors have investigated the following compounds:—

Ortho-, meta-, and para-brombenzamide; 2:4-, 2:6-, and 3:5-dibrombenzamide; 2:4:6- and 3:4:5-tribrombenzamide; 2:4:6-trichlorbenzamide; 2:4:6-trimethylbenzamide (mesitylformamide) and mesitylacetamide, $C_6H_2Me_3{\cdot}CH_2{\cdot}CONH_2$. Of the three mono-substituted brombenzamides the ortho-compound proves to be somewhat more stable in the presence of boiling (30 per cent) sulphuric acid than the meta- and para-compounds. This agrees with the properties of the corresponding methylic monobrombenzoates and of the monobrombenzoyl chlorides.

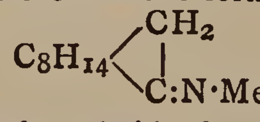
Of the three dibromamides the 2:6- or di-ortho-substituted compound proves to be the one most difficult to hydrolyse by means of 75 per cent sulphuric acid, and again of the two tribromamides the 2:4:6- or symmetrically substituted amide is much more stable than the isomeric 3:4:5-tribrombenzamide. 2:4:6-trichlorbenzamide although not hydrolysed so readily as 2:4- and 3:5-dibrom- and 3:4:5-tribrombenzamide is less stable than the corresponding 2:4:6-tribrom-compound.

The methyl derivatives could not be investigated as regards their hydrolysis with 75 per cent sulphuric acid, as they are charred and decomposed by this means. Towards 30 per cent sulphuric acid the mesitylformamide is much more stable than the corresponding acetamide.

In the course of this investigation the following new compounds have been obtained:—3:5-Dibrombenzamide, m. p. 187°; 2:4:6-tribrombenzonitrile, m. p. 127°; 2:4:6-tribrombenzamide, m. p. 193—194°; 3:4:5-tribrombenzamide, m. p. 199°; 2:4:6-trichlorbenzonitrile, m. p. 75°; 2:4:6-trichlorbenzamide, m. p. 177°; mesitylformamide, m. p. 105°; mesitylacetamide, m. p. 210°.

*14. "*Conversion of Camphoroxime into Methylcamphorimine and Camphenylnitramine.*" By M. O. Forster, Ph.D.

Further investigation of the base obtained on heating camphoroxime in sealed tubes with methylic iodide has proved it to be the methyl-derivative of Tiemann's camphorimine; it therefore has the formula—



$$C_8H_{14}\left\langle\begin{matrix}CH_2\\ |\\ C{:}N{\cdot}Me\end{matrix}\right.,$$

and not, as appeared probable from the preliminary examination (*Proc.*, 1895, xi., 145), the formula $C_{12}H_{19}N$. This is shown by its behaviour towards concentrated hydrochloric acid at 200°, giving rise to camphor and methylamine.

Methylcamphorimine hydrochloride and *methiodide* melt at 270° and 231—232° respectively; the *perbromide* has also been prepared.

The action of dilute nitric acid on camphoroxime, if interrupted after a few minutes, gives rise to *camphenylnitramine*, which is also formed when a solution of the oxime in chloroform is treated with nitrogen peroxide.

An acid solution of potassium permanganate converts camphoroxime into an unstable nitroso-derivative, which separates from the liquid as a sticky, green mass; when preserved in the desiccator the substance deliquesces, and loses its green colour, the yellow residue yielding camphor when distilled in an atmosphere of steam.

15. "*Note on Wechsler's Method for the Separation of Fatty Acids.*" By Arthur W. Crossley.

Wechsler (*Monatsh.*, 1893, xiv., 462) has described a method for the separation of fatty acids, the principle of which method is contained in the following statement.

If to a mixture of two fatty acids four-fifths of the caustic soda necessary to neutralise them be added, and the whole steam-distilled, the distillate contains the pure higher-boiling acid. From the residue of the distillation a further three-fifths of the acids are set free by addition of sulphuric acid, and the whole distilled in steam. Finally, the remaining fifth of the acid is set free, and in this case the distillate contains the lower-boiling acid in a pure condition.

The purity of the acids contained in the various distillates was proved by converting them into silver salts and subsequent analysis of these salts.

After trying this method of separation, with very unsatisfactory results, on a mixture of fatty acids obtained in a research on which Professor Perkin and the author have been engaged for some time past, it was thought advisable to test some of Wechsler's experimental data.

Accordingly, Wechsler's experiments have been carefully repeated and results obtained which do not agree with that author's.

As Wechsler always worked with equimolecular proportions of fatty acids, the results of some experiments are recorded in which varying proportions of fatty acids were employed. In every case the results were unsatisfactory, for even when using three molecules of the lower to one of the higher boiling acid, the former was not obtained pure in the last distillate, and the first distillate contained a decided mixture of the two acids.

It is therefore to be concluded that Wechsler's method does not give such good results as the author suggests, nor can it in any way be looked upon as a satisfactory method for separating mixtures of fatty acids.

16. "*On the Crystalline Structure of Gold and Platinum Nuggets and Gold Ingots.*" By A. Liversidge, LL.D., F.R.S.

In view of the theory that gold nuggets are built up of concentric layers deposited round a central nucleus, the author has examined a large number of specimens from various sources. The nuggets were ground down, or sliced through, to obtain sections, which were polished and etched by suitable solvents. They all possessed a well-marked crystalline structure, and usually enclose foreign substances. The crystalline structure is not incompatible with an aqueous origin; and the author suggests that the gold has been slowly deposited from solution, either at ordiinary or at high temperatures; the nuggets being more or less rolled masses of gold which have been set free from disintegrated veins.

17. "*On the presence of Gold in Natural Saline Deposits and Marine Plants.*" By A. Liversidge, LL.D., F.R.S.

The author gives a preliminary account of the results of the examination for gold of rock salt, sylvine, and other similar saline deposits, bittern, sea-weed, kelp, oyster-shells, &c. The process of determination used was to add from 0·5 to 5 grms. of ferrous sulphate to the unfiltered solution of 100 to 1000 grms. of the salt in water. The resulting precipitate was then scorified with lead and cupelled. The natural salts contained from 1 to 2 grains of gold per ton, whilst kelp and bittern furnished in some cases as much as from 14 to 20 grains.

Ordinary Meeting, February 18th, 1897.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Mr. E. Haynes Jeffers was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Herbert William Leyland Barlow, M.A., M.B., Holly Bank, Urmston, Manchester; Frederick Filmer de Morgan, Andely Lodge, Caeran Park, Newport, Monmouthshire; Louis Charles Deverell, Onslow House, Worthing; William James George Lasseter, B.A., 10, Stanley Road, Oxford; Harry Edward William Phillips, B.A., 47, Chalfont Road, Oxford; William Herbert Waite, B.A., Park Road, Halifax; Charles Thomas Foster Watts, 7, Cambrian Crescent, Chester; John Welsh, 12a, Seller Street, Chester.

The certificate of the following candidate, recommended by the Council under Bye-law I. (3), was also read:—

Frederic Hewlett Burton-Brown, Simla, India.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As *President*—Professor James Dewar, M.A., LL.D., F.R.S., *vice* Mr. A. G. Vernon Harcourt, M.A., D.C.L., LL.D., F.R.S. As *Vice-Presidents* — Professor W. Ramsay, Ph.D., F.R.S., and Professor J. Emerson Reynolds, M.A., F.R.S., *vice* Professor James Dewar, M.A., LL.D., F.R.S., and Mr. Horace T. Brown, F.R.S. As *Ordinary Members of Council*—Messrs. C. T. Heycock, M.A., F.R.S.; Rudolph Messel, Ph.D.; Tom Kirke Rose, D.Sc.; and Alexander Scott, M.A., D.Sc., *vice* Messrs. Bernard Dyer, D.Sc.; G. Harris Morris, Ph.D.; W. A. Shenstone; and T. Stevenson, M.D.

It was also announced that the Council had awarded the Longstaff Medal to Prof. William Ramsay, F.R.S., for the discovery of helium, and his share in the investigation of argon.

Messrs. H. Brereton Baker, F. D. Chattaway, and John Shields were appointed to audit the Society's accounts.

Of the following papers those marked * were read.

*18. "*The Formation of Dithionic Acid in the Oxidation of Sulphurous Acid by Potassium Permanganate.*" By T. S. Dymond and F. Hughes.

When a solution of sulphurous acid is titrated with a solution of potassium permanganate, decolorisation of the permanganate ceases when only 89 per cent of the quantity required to oxidise the sulphurous acid to sulphuric acid has been used. This is due to the formation of dithionic acid in addition to sulphuric acid. The proportion of dithionic acid produced is constant, and is not influenced by either the dilution or the temperature, or the acidity of the solution. Its production, therefore, appears to be an essential part of the reaction, and to be due to the weak oxidising action of the permanganate in a final stage of its reduction. The sulphuric and dithionic acids produced are in the proportion required by the supposition that manganese heptoxide is first reduced to the red oxide with production of sulphuric acid, and further reduced to the monoxide with production of dithionic acid. When, however, sulphurous acid is treated with the red oxide, sulphuric acid is the only product.

Discussion.

The President said that he had worked, a number of years ago, upon the reaction between solutions of potassium permanganate and sulphurous acid, before sodium thiosulphate had come into use for estimating iodine. In making determinations without excluding air from the water, he had found that the quantity of permanganate used was far less than the amount necessary for the complete oxidation of the sulphurous acid. He found that the sulphurous acid was oxidised by the atmospheric oxygen dissolved in the water, and so progressively as the water gradually dissolved the oxygen in the air lying over it. As the result of a number of experiments, he proved that the diminution in the quantity of permanganate required increased with the dilution of the sulphurous acid, and also that if the water was boiled until air-free the quantity of permanganate used was larger; but he had not obtained such constant results as Messrs. Dymond and Hughes. He had tried the experiment of adding a small quantity of manganous sulphate to the dilute solution, and had found that this salt also was able to determine the oxidation of sulphurous acid by atmospheric oxygen. He thought the author's experiments extremely interesting in showing the constant production of dithionic acid.

Dr. Scott thought it would be worth while to try the effect of manganic sulphate in oxidising sulphurous acid.

Prof. Dunstan suggested that it would be interesting to determine whether the formation of dithionic acid occurred at the positive electrode during the electrolysis of a solution of sulphurous acid, since it seemed possible that the dithionic acid might be formed by the oxidation of sulphurous acid in much the same way as persulphuric acid was formed by the oxidation of sulphuric acid. He understood that in the remarkable action of manganous sulphate described by the President this salt undergoes no change.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, March 12th, 1897.

Mr. Shelford Bidwell, President, in the Chair.

Mr. William Barlow read a paper on "*A Mechanical Cause of Homogeneity of Structure and Symmetry, Geometrically Investigated, with Special Application to Crystals and to Chemical Combination.*" Illustrated by Models.

The author has previously established that every homogeneous structure displays one or other of the thirty-two kinds of crystalline symmetry. He now shows that homogeneous structures possessing most, if not all, of these kinds of symmetry may be produced mechanically, as the equilibrium arrangements of assemblages of mutually-repellent particles; and, also, that these mechanical systems of particles exhibit characteristics entirely analogous to certain crystalline and other properties of matter. The fundamental concept may be summarised thus:—A number of different kinds of mutually-repellent particles dispersed through space, the amount of this repulsion being some inverse function of the distance between the particles concerned; the particles are destitute of polarity, and the difference in kind consists in a difference in the degree of mutual repulsion which two particles exercise, according to the kinds taken. It is further premised that the assemblage is agitated, so as to render unstable all but the final equilibrium arrangement; and a means is provided for linking the particles symmetrically, and unlinking them, under certain circumstances, so as to modify the repulsion between the particles affected. The data thus summarised may be regarded as merely provisional, because the making of the equilibrium arrangement one in which "closest packing" prevails, is the object primarily aimed at; and these concepts are mere devices for attaining this end. By the employment of particles of different kinds, a large amount of variety is provided for. The first step taken is to deduce the law of "closest packing," which runs thus:—Every assemblage of mutually-repellent particles will continually approximate to, or strive after, that relative arrangement of the particles composing it, in which it has come, at every part, to occupy a minimum of space under a given general pressure, or average repulsion, between the particles. This law acts on all assemblages of the nature defined, however numerous the kinds of particles composing them; but for its effects to be traceable, a very limited number of kinds must be present. Passing from assemblages consisting of a single kind of particle, the author takes a very simple case of two kinds of particles confined to a plane, and shows what type of symmetry will be produced when equilibrium is realised. Very simple cases of particles in space are then taken, and it is shown that a large number of different kinds of symmetry are displayed by the equilibrium arrangements produced when there is variety in the relations between the repulsions. To illustrate "close packing," stacks of balls of various sizes are employed; but it is pointed out that the conditions of statical equilibrium of the particles are not always adequately expressed in this way; although every case of the latter kind can be represented approximately by a case of the former kind, possessed of the same order of symmetry. Very slight variation in the relations between the repulsions alters the form of the equilibrium arrangement; sometimes merely changing the angle without affecting the type; sometimes, when it passes some critical point, bringing about an alteration in type. Changes of the first kind resemble the change in crystal form caused by variation of temperature; whilst those of the latter kind, especially when associated with re-arrangement of the particles, are analogous to polymorphism. In many cases the arrangement of the particles is such that some may be removed without affecting the distribution of the remainder, and without destroying the "close packing." If, therefore, other particles, exercising a slightly less repulsion, be substituted for the removed, *inoperative*, particles, the only resulting change consists in a diminution of the pressure on the particles surrounding them. A species of isomorphism is in this way realised.

When the particles of an assemblage are partially connected by hypothetic linking in a symmetrical manner, similar groups are formed; but, in order that the formation of such groups may not be arbitrary, the partitioning which is produced must have as complete symmetry as that of the partioned structure. In consequence of this, some kinds of groups are not directly obtainable by symmetrical partitioning of a homogeneous structure; but it is always conceivable that they may be included in the larger groups of some more complex constellation, and that they may be subsequently separated to form an assemblage by themselves. Consequently, very intricate results may be reached by successive steps. Symmetrical intermixture, linking, and unlinking, succeeding one another until complicated groups are built up, for the production of which such an agency as "close packing" appears at first sight inadequate. Having called attention to a large number of arrangements, some capable and some incapable of symmetrical partitioning into groups of a single kind, some linked and some unlinked, the author contends to have established the following two propositions:—(1) The nature of the symmetry displayed by a homogeneous assemblage of mutually-repellent particles of different kinds in equilibrium, depends on the relations subsisting between the repulsions exercised by these particles. (2) The assemblages belonging to all of the thirty-two classes of crystalline symmetry result from the fundamental law of "close packing," when the relations between the different repulsions take the widest possible range of variety. Links which restrain the action of the repulsion can be present between some of the particles in some cases. The author refers to crystal "twinning," and points out that the action of dimorphism is competent to produce analogous "twinning" of symmetrical assemblages of linked particles. A number of other properties of linked assemblages analogous to those of crystals are also described. In the domain of chemistry the author cites the continually accumulating experimental evidence of the existence of geometrical arrangement in the molecule, both that established stereochemically and that derived from the study of isomerism, as revealing a state of things precisely such as is arrived at by the law of "closest packing" in assemblages afterwards broken up into similar groups of particles. Attention is called to many groupings of the latter order fulfilling very exactly the conditions of disubstitution in the case of many carbon compounds. While he does not regard his work as throwing any light on the nature of change of state, or change of bulk, the author observes that the distribution in precise proportions of the constituents that must obviously accompany or precede a chemical combination, may fairly be claimed as a resemblance to the regular intermixture brought about according to the law of "closest packing." He further suggests that the reason why some bodies do not readily interact may be due to the "close packing" of one or both.

Prof. **Herschel** said he was particularly pleased with the models. He thought it probable that a very wide application would be found for the author's results. There was no doubt much to be learnt from models built up of spheres of two or more sizes, but it would be necessary to learn a great deal more about these symmetrical arrangements before they could be applied with any degree of certainty.

Mr. **Fletcher** said it was impossible to criticise the paper without long and careful study. From certain hypotheses the author had deduced a law of "closest packing" that seemed adequate to explain many results observed by chemists and crystallographers; at the same time admitting that the law might be presumed from other reasoning. By his models he had tried to present a picture not of the forms of atoms or molecules, but merely analogical representations of the probable structure of particles. Hitherto the research had been confined to determining the possible arrangements of particles all of one kind, but here were examples of packed spheres of various sizes. It was not quite clear how, in an elementary substance, there could be such a structure, although there certainly were cases of polymorphism awaiting explanation, as for instance with sulphur. The paper, with its 188 pages of MS., represented a vast amount of clear thinking, and many years of admirable work.

Prof. **Adams** called the attention of Fellows of the Physical Society to the Museum at King's College, where were the original models as made and used by the early investigators of this branch of Physics.

Prof. **Miers** (communicated, too late for reading)—The principle of "close packing" was not new, but Mr. Barlow was the first to extend it to explain solution, diffusion, and stereochemical problems. His remarks on the growth of curved crystals, vicinal faces, and pseudo-symmetrical crystals were open to criticism. With regard to vicinal faces, however, lencite seemed to be a mineral in accord with his hypothesis. The author regarded a crystal as consisting of mutually repellent particles of different sorts: this seemed a very right way of attacking the problem of crystal structure, and would explain some recent observations of Rinne on crystals consisting of water particles and silicate particles. Further, Mr. Barlow had considered the way in which an assemblage might be broken up by the loosening of the ties, and the change of partners, among individual members. That is to say, he had considered crystallisation and solution, features quite ignored by ordinary theories. His view of crystal structure failed to explain why crystals should have faces, and gave no hint as to the controlling forces which keep mutually-repellent particles together. Nevertheless it suggested, among other striking analogies, those bearing on the relationship between crystal structure and chemical constitution, and the irregularities of crystals, such as were commonly neglected in accepted theories. Mr. Barlow had opened up a very promising line of inquiry.

Mr. **Barlow**, in replying, said he greatly appreciated the interest shown in his work.

The **President** then proposed a vote of thanks to the author, and the meeting was adjourned until March 26th. At the invitation of Dr. S. P. Thompson, the Society will on that occasion meet at the Technical College, Leonard Street, Finsbury.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Last Ordinary Meeting of the Session, March 8th, 1897.

Mr. C. **Saintsbury** in the Chair.

Dr. J. E. **Mackenzie** read a paper "*On the Compounds of Nitrogen and Hydrogen.*"

Five such compounds are at present known:—NH_3, ammonia; N_2H_4, hydrazine; N_3H, azoimide; N_4H_4, ammonium nitride; and N_5H_5, hydrazine nitride.

Ammonia does not call for description here. The other substances are of comparatively recent discovery, the chemist to whom we owe most of our knowledge of them being Theodor Curtius. In 1883 he commenced a series of researches on amido-acids. In the course of these he obtained the hydrochloride of ethyl amido-acetate, a beautiful crystalline substance, which, on being diazotised, yielded ethyl diazo-acetate (*Ber.*, xvi., 2230):—

$$HCl{\cdot}H_2N{\cdot}CH_2{\cdot}COOC_2H_5 + NO_2H = \\ = N_2:CH{\cdot}COOC_2H_5 + 2H_2O + HCl.$$

By similar treatment other amido-acid esters yielded diazo esters (*Jour. Prak. Chemie*, [2], xxxviii., 404), these being oils, slightly soluble in water, miscible with the ordinary organic solvents, having a characteristic odour and being volatile. The diazo-acetic ester, on treatment with dilute caustic soda, gave the sodium salt, which, on being acidified with dilute sulphuric acid, split off nitrogen and formed glycollic acid,—

$$2N_2CH{\cdot}COONa + H_2SO_4 + 2H_2O = \\ = 2N_2 + 2CH_2(OH)COOH + 2Na_2SO_4.$$

On the other hand, if concentrated caustic soda were used, a polymer, triazo-acetic acid, was formed, which, by the action of acids, broke up into hydrazine and oxalic acid,—

$$(N_2CH)_3(COOH)_3 + 6H_2O = 3N_2H_4 + 3(COOH)_2.$$

Thus, in 1887, the sulphate of hydrazine was obtained. Other salts were also formed, and from them Curtius separated hydrazine hydrate, N_2H_4,H_2O, by distilling with strong bases such as CaO or NaHO. The hydrate is a colourless, fuming liquid, b.p. 119°. It destroys cork and rubber, and is a powerful reducing agent and poison.

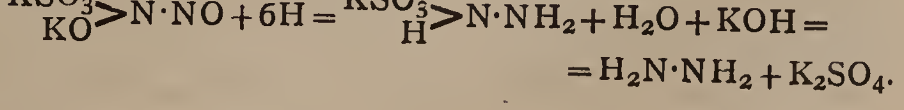
In 1895 Lobry de Bruyn isolated free hydrazine:—(*a*) by mixing anhydrous solutions of hydrazine hydrochloride and sodium methylate, separating the sodium chloride and fractionating the resulting solution under reduced pressure,—

$$N_2H_4{\cdot}HCl + NaOC_2H_3 = NaCl + CH_3OH + N_2H_4;$$

(*b*) by dehydrating the hydrate by means of barium oxide and distilling under reduced pressure.

Hydrazine melts at + 1·4° and boils at 113·5°, under 761 m.m., or at 56° under 71 m.m. pressure of mercury. It is one of the strongest reducing agents. In chlorine it takes fire spontaneously, HCl and N being formed. With sulphur it reacts in cold, with production of SH_2 and N. It displaces ammonia from solutions of ammonium salts. With acids it forms two series of salts, *e.g.*, $N_2H_4{\cdot}HCl$ and $N_2H_4,2HCl$. Its condensations with aldehyds and ketones are very important.

Other methods of preparing hydrazine are those of Pechmann (*Ber.*, xxviii., 1847 and 2374), Thiele and Duden (*Ber.*, xxvii., 3498). That of the latter is the simplest. By the action of sulphurous acid on potassium nitrite, potassium dinitroso-sulphonate is formed, which on reduction by sodium amalgam eventually affords hydrazine,—



$$\substack{KSO_3\\KO}{>}N{\cdot}NO + 6H = \substack{KSO_3\\H}{>}N{\cdot}NH_2 + H_2O + KOH = \\ = H_2N{\cdot}NH_2 + K_2SO_4.$$

In 1890 Curtius published his first paper on "Azoimide, N_3H" (*Ber.*, xxiii., 3023). By means of hydrazine benzoyl-glycollic ester is converted into benzoyl hydrazide,—

$$C_6H_5CO{\cdot}OCH_2{\cdot}COOC_2H_5+2N_2H_4=C_6H_5CO{\cdot}NH{\cdot}NH_2+ \\ +NH_2{\cdot}NH{\cdot}CH_2COOH+C_2H_5OH,$$

which on diazotising yields benzoyl azoimide,—

$$C_6H_5{\cdot}CONH{\cdot}NH_2+NOOH=C_6H_5{\cdot}CON_3+2H_2O.$$

This decomposes when boiled with caustic soda,—

$$C_6H_5CON_3+2NaOH=C_6H_5COONa+N_3Na+H_2O,$$

forming sodium nitride, from which azoimide is set free by the action of acids,—

$$N_3Na + H_2SO_4 = N_3H + NaHSO_4.$$

By careful fractionation a solution of 91 per cent N_3H was obtained, which was dehydrated by calcium chloride. Azoimide is a colourless liquid with an unbearable odour, boils at 37°, and is miscible with water and alcohol. It is frightfully explosive; 5 c.grms. exploded in a barometer tube shattering the glass to a powder and spreading the mercury as a fine dust.

Angeli's method of obtaining azoimide is probably the simplest. On mixing solutions of hydrazine sulphate and silver nitrite, silver nitride separates,—

$$N_2H_4,H_2SO_4 + AgNO_2 = N_3Ag + 2H_2O + H_2SO_4.$$

Thiele's method, starting from amido-guanidine, and Wislicenus's from sodamide, are also important.

The metallic salts of azoimide resemble those of hydrochloric acid very much, except that they are explosive. Ammonium nitride, N_3NH_4, is the most perfect explosive known; 1 kilo. is calculated to liberate 1148 litres of gas at 0° and 760 m.m. (*Bull. Soc. Chim. Paris*, xi., 744).

Hydrazine nitride, $N_3N_2H_5$, is formed by mixing hydrazine hydrate and ammonium nitride or free azoimide. It is a crystalline substance, which behaves like gun-cotton, burning quietly on exposure to flame, but exploding on detonation or sudden heating.

NOTICES OF BOOKS.

A Handbook for Brewers; being a Practical Guide to the Art of Brewing and Malting, embracing the Conclusions of Modern Research which bear upon the Practice of Brewing. By Herbert Edwards Wright, M.A., Author of a "Handbook for Young Brewers." Second Edition, thoroughly Revised. London: Crosby Lockwood and Son, 7, Stationers' Hall Court, Ludgate Hill. 1897. Small 8vo., pp. 516.

This work is of an extremely comprehensive character. It is concerned not merely with the chemistry of the brewing process, but also with the mechanical construction of brewery plant in the widest sense of the term. Micro-biology and the use of the microscope are very carefully considered. We cannot, however, agree with the author's rather unfavourable estimate of immersion lenses. Several little precautionary hints are given which prove the author to be a practical microscopist.

The controversies between Liebig, Pasteur, Traube, and Brefeld are fairly expounded.

The commercial phase of the brewer's business is next expounded.

As regards the theoretical considerations, Mr. Wright ventures on the opinion that "the final limit of subdivision has probably never been reached." The "pleomorphic craze" of A. G. Salamon and others meets with little countenance. But such questions have a very subordinate interest for the brewer, or indeed for any technical chemist.

We are glad to find the admission that Demerara sugar (when genuine) is perhaps the best and purest sugar in the world (p. 148). On the opposite page it is mentioned that sugars having a large bold crystal are not beloved by the trade, as they oppose certain difficulties to the mysterious process known as handling—which, by the way, avenges itself on the men by whom it is effected.

An entire and ably written chapter is devoted to water and its impurities. It is admitted that soluble mineral matter may be tolerated by the brewer to an extent larger than would be tolerated in a drinking or culinary water, or in that employed in the tinctorial art. The injurious action of salts of magnesium in appreciable quantities, we submit, can scarcely be contested. Nitrites in a brewing water he objects to on the authority of Emile Laurent.

The author lays little weight upon Prof. Frankland's previous sewage pollution. He attaches more weight than does Prof. Wanklyn to the possible presence of phosphoric acid in waters, and he considers that waters which after boiling and filtration—we would add *by the Chamberland-Pasteur process*—develop organisms with the Heisch test, probably contain organic matter of an albuminous character, and should be used (if at all) with great caution.

The author quotes the conclusion of Jörgensen, that for brewing purposes it is only necessary to know whether the water contains organisms capable of developing in wort or beer.

Mr. Wright reminds his readers that the presence of free carbonic acid in waters is by no means a proof of purity.

In speaking of materials used as partial substitute for malt, the author mentions that beet-sugar is far inferior to cane-sugar for brewing purposes.

This book will be found most useful not merely to brewers, whether learners or practitioners, but to technologists in general.

CORRESPONDENCE.

LOST PLATINUM.

To the Editor of the Chemical News.

Sir,—Three platinum basins have recently disappeared from this laboratory, and, as it is just possible that some amongst your numerous readers may have been buying second-hand platinum basins, I append the following particulars, in the hope—perhaps somewhat remote—that the platinum may be recovered and the thief brought to book: Basin marked A (scratched on the side), weight 21·877 grms.; basin scratched B, weight 22·412 grms.; basin scratched X, weight 59·747 grms.—I am, &c.,

S. Archd. Vasey.

Laboratory, 423, Strand, W.C.,
March 17, 1897.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 8, February 22, 1897.

M. Violle has been elected a Member of the Academy in the Section of Physics, *vice* M. Fizeau, deceased.

M. de Heen, of Liège, addresses to the Academy two notes, entitled "Existence of Anodic Rays analogous to the Cathodic Rays," and "Photography of the Electric Radiations of the Sun and of the Solar Atmosphere."

M. Breton demanded the opening of two sealed papers recently deposited by him, and relating, the one to "the use of alternating simple currents, diphasic and triphasic, for the production of X-rays;" and the other to "a radiographic phial for the refrigeration of the anticathode by a current of cold water."

M. de Sanderval addressed a paper, accompanying photographs obtained through metallic plates of different natures.

M. A. Graby, of Malange, sent the description of a new photographic procedure, rendering it possible to obtain positives in the colours without the production of a proof.

New Method for producing Transparent Crystals.—Ch. de Wateville.—If during its growth we give to a crystal a movement of rotation on itself it assumes a transparency and a lustre analogous to those of precious stones seen cut and polished whatever may be the axis of the crystal near which the rotation is effected. The movement appears not to lose any influence upon the relative development of the faces unless it is very rapid and the solution is very concentrated. If we operate, *e.g.*, upon a solution of alum saturated above 50° (and with the speed of several rotations per second), we progressively disappear the faces of the dodecahedron, and those of the cube which the crystal presents at the outset of the operation; those of the octahedron of the maximum density alone remaining. The author has obtained especially satisfactory results with potassium and ammonium alums, copper sulphate, and sodium chlorate.

On Persulphuryl Chloride.—A. Besson.—This memoir will be inserted *in extenso.*

Anethol and its Homologues.—Ch. Mouet and A. Chauvet. — The author describes a new synthesis of anethol, simpler they consider than than the procedure of Perkin. They have thus obtained two homologues of anethol (para-butenyl anisol and para-isopentenyl anisol).

Soluble Oxidising Ferment of the Cassage of Wines. — P. Cazeneuve. — Not suitable for useful abstraction.

Detection of Coal-tar Colours in White Wines and the Difference between the Colours and those of Caramel.—Alb. d'Aguilar and W. da Silva.—This memoir will be inserted in full.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxvii., No. 1.

This issue contains no chemical matter.

No. 2.

Ores of Manganese in Russia (*Chemiker Zeitung*).—It appears that in 1896 the Russian output of manganese ores was 248,000 tons, that of the rest of the world being only 66,821 tons.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. ii., No. 1.

Review of the Progress effected in the Industry of Essences and Perfumes. — A. Haller. — The author claims the production of perfumes as an art evidently French. Only the English products approach them in fineness, but they possess neither the distinction nor the delicacy of French perfumery. France, both on its southern coasts and in Algeria, possesses great natural advantages for this manufacture; but he recommends that the aid of chemical science should be carefully and eagerly sought for. He raises the question whether the French madder production might not have been saved by such means, pointing out that, in spite of artificial indigo, the yield of India has since 1886 been increased from 33,320 chests yearly to 40,510. The firm Schimmel and Co., of Leipzig, employs at present nine chemists. The English lavender (of Mitcham) cannot be estimated solely according to its percentage of linalyle acetate, and it is yet preferred to common essences of lavender which contain from 30 to 40 per cent. We cannot help expressing our deep regret that a part of the precious Mitcham soil has been allowed to fall into the hands of "Jerry." Whether the oil of lavender obtained at Sandy (Bedfordshire) is equal to the Mitcham growth we are not yet able to decide. English essence of peppermint (Mitcham) is always in demand on account of the fineness of its odour, the cause of which chemical research has not yet been able to detect.

MISCELLANEOUS.

The Chemiker Zeitung.—The issue of February 20th gives a plan and a full description of the Pharmaceutical Institute and Laboratory for Applied Chemistry in connection with the University of Munich. This journal is also discussing the possible influence of the deposit of "sealed papers" describing the details of an invention may have upon a patent subsequently obtained.

Action of Nitrogen Oxides upon Ferrous Chloride and Bromide.—V. Thomas.—The compounds obtained are inalterable in dry air, and undergo no loss of weight in a vacuum. In most cases they are capable of being split up into chloride (or bromide) and nitrogen peroxide. —*Comptes Rendus*, cxxiv., No. 8.

Action of Dilute Nitric Acid upon Nitrates in Presence of Ether. — M. Tanret. — On agitating water containing nitric acid with aqueous ether, the acid is distributed by the water and the ether so that the quantities dissolved by an equal volume of each liquid bear a constant relation to each other. This relation has been called by MM. Berthelot and Jungfleisch the *coefficient* of distribution; it is independent of the relative volume of the two liquids, but varies with their temperature and concentration.—*Comptes Rendus*, cxxiv., No. 9.

Discharge of the Röntgen Rays: Part Played by the Surfaces Struck.—Jean Perrin.—The gas effect is readily explained if we admit that the X rays at every point of their track liberate equal quantities of positive and negative electricity, movable along tubes of force which contain them. Similarly the metallic effect is readily explained by supposing that on the contact of a conductor, and in a manner variable with nature, the ionisation of the gas is very intense. I propose to call this phenomenon the superficial ionisation of the gas on contact with the conductor.—*Comptes Rendus*, cxxiv., No. 9.

The Chemical Laboratory of Wiesbaden. — The Chemical Laboratory of Prof. Dr. R. Fresenius has been attended by fifty-eight Students during the Winter Session of 1896-97. Of these, forty-three were from Germany, four from England, two from Switzerland, two from Sweden and Norway, two from the United States of North America, one from Austria, one from Roumania, one from Russia, one from Spain, and one from Brazil. There were three Assistant Demonstrators in the several teaching departments, and twenty Assistants in the Versuchsstationen (private laboratories). Besides the Director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged, as Teachers in the Establishment, Prof. Dr. H. Fresenius, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, Dr. W. Lenz, Dr. L. Grünhut, and Architect Brahm. The next Summer Term begins on the 26th of April. Throughout the Winter Session, besides various scientific researches, a great number of analyses have been undertaken in the different departments of the Laboratory for manufacturers of all kinds, in judicial cases, and in many branches of trade, mining, agriculture, and hygiene.

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.

Dental Alloys.—(Reply to "Jack").—Consult "Hunter's Mechanical Dentistry" (Longmans and Co., 3s. 6d.). Supplied by Elliot Stock, 62, Paternoster Row, E.C., for 3s. 1d.—G. A. KEYWORTH, Hastings.

MEETINGS FOR THE WEEK.

MONDAY, 22nd.—Society of Arts, 4.30. (Cantor Lectures). "Alloys," by Prof. W. Chandler Roberts-Austen, F.R.S.

TUESDAY, 23rd.—Royal Institution, 3. "Animal Electricity," by Prof. A. D. Waller, F.R.S.

WEDNESDAY, 24th.—Society of Arts, 8. "The Transmission of Power by Alternating Electric Currents," by W. B. Esson, M.Inst.C.E.

THURSDAY, 25th.—Chemical, 8. Pasteur Memorial Lecture, by Prof. P. F. Frankland, F.R.S.

— Royal Institution, 3. "The Relation of Geology to History," By Prof. W. Boyd Dawkins, M.A., F.R.S., F.G.S.

— Society of Arts, 8. "The Cultivation and Manufacture of Rhea Fibre," by Thomas Barraclough. (This meeting will be held at the Imperial Institute).

FRIDAY, 26th.—Royal Institution, 9. "Early Man in Scotland," by Sir William Turner, F.R.S.

SATURDAY, 27th.—Royal Institution, 3. "Electricity and Electrical Vibrations," by Right Hon. Lord Rayleigh, M.A., F.R.S.

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LECTURES.

Experimental Chemistry (Inorganic)	Prof. H. FRESENIUS, Ph.D.
Experimental Physics Stöchiometry	W. FRESENIUS, Ph.D.
Organic Chemistry	E. HINTZ, Ph.D.
Chemical Technology	L. GRÜNHUT, Ph.D.
Microscopy, with exercises in Microscopic work	W. LENZ, Ph.D.
Chemistry and Analysis of Foods	Prof. H. FRESENIUS, Ph.D. W. FRESENIUS, Ph.D., and E. HINTZ, Ph.D.
Hygiene Practical exercises in Bacteriology	Dr. med. G. FRANK.
Technical Drawing, with exercises	J. BRAHM.

The next Session commences on the 26th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to the undersigned.

Prof. R. FRESENIUS, Ph.D.

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ESTIMATION OF THORIA.
CHEMICAL ANALYSIS OF MONAZITE SAND.*

By CHARLES GLASER.

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

Iron oxide	3·50	per cent
Titanic acid	4·67	"
Silica	6·40	"
Monazite, by difference	85·43	"
	100·00	

The sample contained 18·38 per cent phosphoric acid, which calculated as cerium phosphate (factor 3·32) equals 61·10 per cent.

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

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

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

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

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

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

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

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

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

To determine the solubility or insolubility of the different substances left in the insoluble residue from fusions, such residue was treated with dilute hydrochloric acid, both cold and hot. The solution was found to contain all the iron and titanium, the larger part of the silica, and about one-half of the earths present; these

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* From the *Journal of the American Chemical Society*, vol. xviii., No. 9.

Table of Reactions of the Rarer Earths.

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

consisted of relatively large portions of zirconia and glucina. Thoria seems not to enter into solution, but is left with the remainder of the earths.

An attempt was made to separate thorium oxalate from the mixed precipitated oxalates, by boiling with ammonium oxalate. Such boiling, filtering, and crystallising yielded oxalates, which, after ignition, corresponded to 2·29 per cent of oxides. The earths were, however, of a deep orange colour, and contained both cerium and zirconia. The latter was present because an insufficient quantity of ammonium oxalate had been used in the first precipitation. In the oxalates of the cerium metals found insoluble in the above treatment, the presence of thoria could be distinctly proven by means of sodium hyposulphite, for which reason the work proved unsatisfactory.

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

With the view of obtaining further knowledge of the behaviour of thoria, fragments of Welsbach mantles were subjected to analysis. They weighed 0·6591 grm., which after ignition fell to 0·6552 grm. Prolonged treatment with boiling sulphuric acid left a residue of 0·0883 grm., which became soluble in water after fusion with acid potassium sulphate. The solutions thus obtained were examined by the same method, but separately, as follows:—After neutralising with ammonia the greater part of the free acid, the solutions were heated to boiling and hot solution of ammonium oxalate was added.

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

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

Upon cooling, solution I. yielded a moderate quantity of a crystalline deposit, while solution II. gave a copious one. Both precipitates were collected on one filter, washed, ignited, and weighed. They yielded 0·1124 grm. of thoria.

The filtrate from I. gave a copious precipitate with ammonia, while that from II. gave only a slight one; both of these were washed on one filter, re-dissolved in dilute hydrochloric acid, and again precipitated by ammonia. An excess of ammonium carbonate entirely dissolved the precipitate. Potassium hydroxide gave a precipitate not soluble in an excess of the precipitant, indicating zirconia, the weight of which was 0·5580 grm. An attempt to purify it from occluded alkali, by again precipitating with ammonia, failed through an accident, in which part of the material was lost. Calculating by difference, the weight of zirconia ought to have been 0·5428 grm. Both precipitates were pure white.

Therefore, this analysis afforded the following composition of the mantles:—Thoria, 17·15 per cent; zirconia, 82·85 per cent.

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

0·0487 grm. was weighed, dissolved, and mixed with the solution of cerium metals from a previous experiment. The solution was nearly neutralised with ammonia, heated to boiling, a hot solution of ammonium oxalate added, and the mixture allowed to cool. The precipitate was caught on a filter and washed with cold water, extracted in boiling ammonium oxalate solution, caught on a filter, and washed hot; the filtrate was allowed to cool (precipitate 1). The residue was macerated in a hot solution of ammonium acetate, filtered (residue A), and filtrate examined for thoria, as follows:—Hydrochloric acid was added to separate thoria as oxalate, which fell in part only, and the remainder was obtained by sodium hydroxide (precipitate 2). Both these precipitates afforded but a part of the thoria originally weighed, the greater part being held yet with the cerium metals. The method had failed.

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

The precipitates, thus obtained in three fractions, were ignited and found to weigh 0·0774 grm., showing that the thoria was very impure. The greyish mass was fused with acid potassium sulphate, and unfortunately a small fraction of the fused mass was lost. However, from the saved portion a pure thoria, weighing 0·0402 grm., was obtained.

In the next experiment, 0·0343 grm. of thoria and 0·1004 grm. of impure cerium oxide were dissolved as sulphates, and treated with ammonium oxalate and acetate, as for precipitate 3, next above. By precipitating the filtrate with ammonia there was obtained 0·0360 grm. of impure thoria, which after purification weighed 0·0344 grm. Cerium oxide recovered weighed 0·0935 grm.

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

(To be continued).

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending February 28th, 1897.

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

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

London, March 10th, 1897.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Feb. 1st to Feb. 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

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

The rainfall at Oxford during February was 2·41 inches. The average for thirty years being 1·76 inches, we have had an excess of 0·65 inch; 1·48 inches fell on the first five days of the month.

Our bacteriological examination of the London waters give the following results —

	Microbes per c.c.
Thames water, unfiltered (average of 20 samples)	9580
Thames water, from the clear water wells of five Thames-derived supplies (average of 99 samples)	22
Ditto ditto highest	89
Ditto ditto lowest	3
New River, unfiltered (average of 19 samples)	1589
New River, from the Company's clear water well (average of 20 samples)	20
River Lea, unfiltered (average of 19 samples)	1177
River Lea, from the East London Water Company's clear water well (average of 19 samples)	40

The quality of the London waters during February has been uniformly good, with one exception. Since the beginning of this year we have much enlarged the scope of our enquiries, and have examined bacteriologically the clear water well at the Hampton Works of the Grand Junction Water Company, as well as that at the Kew Works of the same Company. On some occasions during the month the Hampton water has given high results; these were at once communicated to the Engineer of the Company, and the matter is receiving serious attention.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

A REVISION OF THE ATOMIC WEIGHT OF MAGNESIUM.*

By THEODORE WILLIAM RICHARDS
and
HARRY GEORGE PARKER.

Although numerous determinations of the atomic weight of magnesium have been made, the results obtained show such very wide variations among themselves that the value in use at present cannot be accepted with any certainty. It will not be necessary to review in detail all the work published, as most of it was done more than forty years ago, before quantitative methods had attained their present exactness; but the following table of methods used and results obtained will assist in a clear comprehension of the situation.

Previous Work on the Atomic Weight of Magnesium.†

Synthesis of sulphate by the action of sulphuric acid on the oxide.	
Berzelius, 1826. "Lehrbuch," 5th edition, iii., 1227.	25·3
Svanberg and Nordenfeldt, 1848. Erdmann's *Journ. Prakt. Chem.*, 1848, xlv., 473.	24·7
Bahr, 1852. Erdmann's *Journ. Prakt. Chem.*, 1852, lvi., 310.	24·8
Marignac, 1884. *Ann. Chim. Phys.*, 1884, (5), i., 289, 321.	24·37
Conversion of sulphate into oxide.	
Jacquelain, 1851. *Ann. Chim. Phys.*, (3), xxxii., 195.	24·5
Determination of sulphuric acid in sulphate.	
Gay-Lussac, 1820. *Ann. Chim. Phys.*, xiii., 308.	24·6
Scheerer, 1846, *Pogg. Ann.*, 1846, lxix., 535.	24·5
Scheerer, 1847, Later Correction. *Pogg. Ann.*, 1847, lxx, 407.	24·5 ?
Jacquelain, 1851. *Ann. Chim. Phys.*, 1851, (3), xxxii., 195.	24·2
Conversion of oxalate into oxide.	
Svanberg and Nordenfeldt, 1848. Erdmann's *Journ. Prakt. Chem.*, 1848, xlv., 473.	24·7
Determination of chlorine in magnesic chloride.	
Dumas, 1859. *Ann. Chim. Phys.*, 1859, (3), lv., 129, 187.	24·6
Conversion of carbonate into the oxide.	
Marchand and Scheerer, 1850. Erdmann's *Journ, Prakt. Chem.*, 1850, l., 385.	24·0
Scheerer, 1859, Later Correction. *Liebig's Ann.*, 1859, cx., 236.	24·0
Conversion of metal into oxide.	
Burton and Vorce, 1890. *Am. Chem. Journ.*, 1890, xii., 219.	24·29

It will be seen that, with the exception of the results obtained by the precipitation of the sulphuric acid with barium chloride and the precipitation of the chlorine with argentic nitrate, all the methods employed involve the use of magnesic oxide. The fact that all such results are untrustworthy was shown by T. W. Richards and E. F. Rogers (*Proc. Amer. Acad.*, xxviii., 200) in their work upon the occlusion of gases by the oxides of certain metals when obtained by the ignition of various salts. The error from this source is so large that it seems hopeless to apply a correction to previous work upon the atomic weight of magnesium, as the amount of gas occluded depends in a large degree upon the method and thoroughness of ignition.

Concerning the results obtained by the precipitation of the sulphuric acid in magnesic sulphate, it is only necessary to point out the error due to the occlusion of various soluble substances present in the solution from which the precipitation was made. This error was recognised by Scheerer, after publishing his results, and an approximate correction was made; but such a correction does not merit much confidence, as will be seen.

In the work of Dumas it is evident that some magnesic oxychloride was formed, and he does not appear at all confident of the accuracy of his results. From the experience of the writers it does not seem likely that the method which he used would give magnesic chloride free from the oxide.

Preliminary Experiments.

Because considerable experience had been gained in a previous research (*Proc. Amer. Acad. Arts Sci.*, xxxi., p. 67) upon the occlusion by baric sulphate of salts present in a solution from which this insoluble salt was precipitated, it was thought that Gay-Lussac's and Scheerer's method of precipitating magnesic sulphate with baric chloride might now be used with advantage, applying subsequently the necessary corrections for occluded substances. It had previously been found that the concentration of the solution and the method of pouring had a great deal to do with the amount of occlusion; and hence it seemed likely that by working in a very dilute solution and pouring the magnesic sulphate into the baric chloride with extreme slowness, the occlusion of baric chloride might be large, but that the precipitate might be free from magnesium. Several experiments were made to ascertain the correctness of this supposition, but in each case it was found that, notwithstanding the precautions adopted, a very notable quantity of magnesium was occluded in the baric sulphate. It had been the custom in working upon this precipitation to fuse the weighed baric sulphate with sodic carbonate, to extract the sodic chloride thus formed, and to determine the chlorine with argentic nitrate and calculate as baric chloride, subtracting this amount from the total weight of baric sulphate found. This method gave very satisfactory results, but of course it could not be applied when the baric sulphate was mixed with magnesic chloride and sulphate as well as baric chloride, for then no one could discover the proportion in which each salt was present with sufficient accuracy for work upon atomic weights.

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* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxii., No. 2.

† We are indebted to Mr. F. W. Clarke for most of the above references.

The possibility of obtaining satisfactory results by the determination of the chlorine in magnesic chloride was now considered. The great disadvantage of this method, as is well known, is the extreme difficulty of obtaining pure anhydrous magnesic chloride. The usual method of igniting the double chloride of ammonium and magnesium was tried a number of times, but it was found that a quantity of the oxychloride was always formed. As indicators do not give a sharp reaction in the presence of magnesic salts, the hydrochloric acid driven off cannot be added afterwards by titrating back to the neutral point with a weak acid solution, and it is therefore necessary to obtain in the first place magnesic chloride containing its full complement of acid.

The method was then modified by conducting the ignition of the double salt in a tightly covered platinum crucible in a stream of hydrochloric acid instead of air. That a considerable quantity of oxychloride was usually formed, even under these conditions, was easily ascertained by dissolving the resulting product in water, when the oxychloride remained as an insoluble residue. In two or three cases, however, the amount of oxychloride formed was comparatively small; hence it was hoped that, if the right conditions could be found, the chloride might be obtained in a pure state. Another series of experiments with a modified apparatus was therefore undertaken. The expulsion of the ammonic chloride was conducted in a combustion-tube and the number of drying-tubes was increased, so that the hydrochloric acid gas might be as free as possible from water. The heat was applied very gradually, in order that the double chloride might be almost anhydrous before the sublimation of the ammonic chloride began. This method gave better results. It was observed that in two or three experiments, where the conditions had been unusually favourable, the resulting chloride gave a clear solution; and it seemed therefore probable that, if an apparatus could be devised to deliver a rapid stream of hydrochloric acid gas entirely free from aqueous vapour, the method might be successful.

Assuming that these conditions might be fulfilled, another difficulty remained to be overcome; for even if the magnesic chloride could be obtained in the combustion tube free from water and oxychloride, the problem still remained to weigh the salt without foreign admixture. If the boat were allowed to remain in the tube until cool, and then removed to a weighing-bottle, the salt must absorb a very notable quantity of moisture from the air in the operation, however quickly this operation might be performed. The boat cannot be transferred to another tube and re-heated, as the moisture present reacts upon the chloride, forming some oxychloride and liberating hydrochloric acid. If it is taken from the combustion-tube while hot and allowed to cool in a weighing bottle, the same effect is produced. Dumas had met with the same difficulties in his work with this method, and he endeavoured to compromise matters by removing the boat from the combustion-tube when it had only partly cooled. As his subsequent results proved, however, the moisture from the air reacted upon the chloride, forming some oxychloride, which interfered seriously with the accuracy of his work. To obviate this difficulty the form of apparatus used by one of us (Richards, *Proc. Amer. Acad.*, xxx., 383) in drying strontic bromide was altered so that the boat could be transferred directly from the ignition-tube to the weighing-bottle without an instant's exposure to the outside air. In order to accomplish this result the hard glass tube was ground with a long tapering joint directly into the wider desiccating or cooling tube used to contain the weighing bottle. This desiccating-tube had a sort of bulb or "pocket" blown upon one side of it, to receive the stopper of the weighing-bottle, thus allowing the boat to be pushed past the stopper directly from the ignition-tube into the bottle. Afterwards the stopper could be rolled into place with a rod provided for the purpose. The arrangement was used with great success in a recent determination of the atomic weight of zinc (Richards and Rogers, *Proc. Amer. Acad.*, xxxi., 158, 174), to which it was equally applicable. A reference to the annexed sketch (Fig. 1) will make the apparatus more comprehensible.

The desiccating apparatus for the hydrochloric acid gas consisted of two towers, composed of a number of glass bulbs filled with beads, upon which strong sulphuric acid was allowed to trickle from small reservoirs at the top into suitable receptacles at the bottom. This apparatus was constructed wholly of glass, with glass gridirons for flexibility, and ground or sealed glass connections. Joints were made tight with syrupy phosphoric acid (Morley). The hydrochloric acid, after being evolved by allowing strong sulphuric acid to run into a flask containing a strong solution of hydrochloric acid, was passed through a wash-bottle containing sulphuric acid, thence through the towers just described, afterwards through a tube containing phosphoric pentoxide, and finally into the combustion tube. The apparatus was so arranged that the current of air from an aspirator could be passed through another set of towers, a duplicate of those used for drying the acid gas. By means of stopcocks either dry hydrochloric acid gas or dry air could be passed through the tube containing the weighing tube and boat.

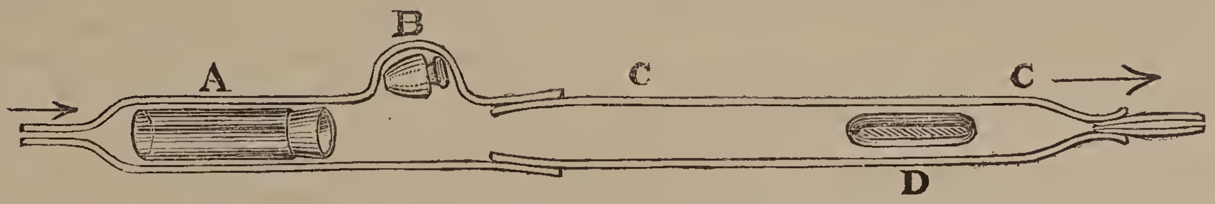


Fig. 1.—Bottling Apparatus, Horizontal Section.

A, weighing-bottle. B, stopper of bottle. C C, hard glass tube. D, platinum boat containing fused magnesic chloride.

With the help of this contrivance it was found possible to drive off the ammonic chloride in a current of dry hydrochloric acid, to drive off the excess of acid from the fused magnesic chloride by means of a current of perfectly dry air, and to shut up the pure salt in a weighing-bottle without the least possible means of access of a trace of aqueous vapour. The details of the method will be described later; magnesic chloride prepared after this fashion gives a perfectly clear solution in water. Since this problem was solved, attention was now turned to the preparation of materials for the atomic weight determinations.

(To be continued).

Industrial Transformation of Oleïc Acid into Stearolactone and Monooxystearic Acid.—M. David.—The author can form at will stereolactone and oxystearic acid, or, if the liquid is exposed to cold, all the oxystearic acid may be converted into stearolactone.—*Comptes Rend.*, cxxiv., No. 9.

Procedure for the Determination or Extraction of Gold from Auriferous Ores.—E. Serrent.—The author introduces into the mass of ground ore, in proportions calculated according to the supposed percentage of gold, a mixture of sodium chloride and nitrate with sulphuric acid. When the reaction is completed the gold chloride is dissolved out by the addition of water and the gold is precipitated by ferrous sulphate.—*Comptes Rend.*, cxxiv., No. 9.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 18th, 1897.

Mr. A. G. Vernon Harcourt, President, in the Chair.

(Concluded from p. 140).

*19. "*On the Production of Pyridine Derivatives from Ethylic β-amido-crotonate.*" By J. Norman Collie, Ph.D., F.R.S.

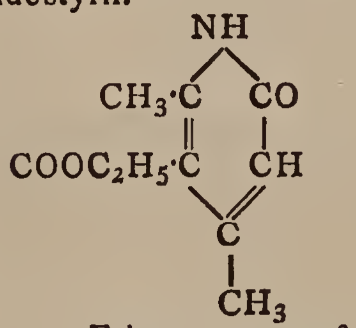
Amongst compounds from which pyridine derivatives can be obtained, ethylic acetoacetate stands out prominently. The author has already called attention to the fact that, when ethylic β-amido-crotonate is distilled, various pyridine compounds are formed. When the hydrochloride of ethylic β-amido crotonate is heated to a temperature of about 120°, it at once condenses according to the equation—

$$2C_6H_{11}NO_2HCl = C_{10}H_{13}NO_3 + NH_4Cl + C_2H_5OH + HCl.$$

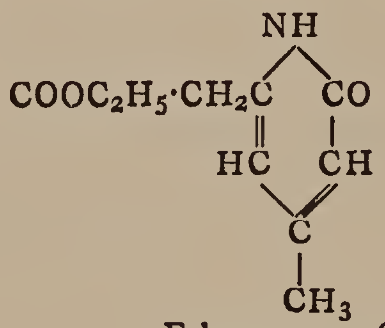
This compound, $C_{10}H_{13}NO_3$, is the ethylic ether of an oxylutidine; it melts at 138—139°. If in its production the hydrochloride of ethylic β-amidocrotonate be heated with one molecular quantity of ethylic β-amidocrotonate,—

$$C_6H_{11}NO_2HCl + C_6H_{11}NO_2 = C_{10}H_{13}NO_3 + NH_4Cl + C_2H_5OH,$$

an isomeric ether is obtained, m. p. 166—167°. The acids obtained from these two ethers melt respectively at 300—304° and 190—191°, and both acids decompose at their melting-point, lose carbon dioxide, and give pseudolutidostyril.



Ether, m. p. 139°.
Acid, m. p. 300°.
A.



Ether, m. p. 167°,
Acid, m. p. 190°.
B.

Ether A, when boiled with soda, only hydrolyses with considerable difficulty. It does not react with acetyl chloride, hydroxylamine, or nitrous acids; strong sulphuric acid dissolves it on warming, but the substance is precipitated unchanged when the mixture is poured into water. With bromine, a mono-substituted derivative is produced, $C_{10}H_{12}NO_3Br$, m. p. 158—159°. With phosphorus pentachloride a chloro-lutidine derivative results, $C_{10}H_{12}NO_2Cl$, which is an oil, b.-p. 288—290°. After prolonged treatment with tin and hydrochloric acid, the chlorine is removed and replaced by hydrogen, and an α γ-dimethyl-β-ethylic carboxylate of pyridine, b.-p. 246—248°, is obtained.

The acid obtained by the hydrolysis of ether A is very insoluble in water, but can best be re-crystallised from that solvent; various attempts were made to convert this acid into the isomeric acid obtained from ether B, but without result.

Ether B, which is isomeric with ether A, is hydrolysed at once when added to soda solution and warmed. It gives a compound with phenylhydrazine, and when boiled with strong hydrochloric acid is decomposed; it is much less stable than ether A.

With bromine it gives a di-substituted product at once, $C_{10}H_{11}NO_3Br_2$. This compound, when treated with soda, gives the sodium salt of a dibromo-acid, which acid melts at 227—228° with complete decomposition. Ether B gives on hydrolysis an acid, m. p. 190—191°, which can easily be crystallised from hot water; when melted it decomposes quantitatively into carbon dioxide and pseudolutidostyril in exactly the same manner as the isomeric acid, m. p. 300—304°. Pseudolutidostyril,—

$$C_5H_3(CH_3)_2NO,$$

which is a dimethylpyridine derivative, was first obtained by Hantzsch (*Ber.*, 1884, xvii., 2904), by the action of heat on a trimethylpyridine derivative. It was found on heating pseudolutidostyril with zinc dust, that, although some dimethylpyridine (lutidine) was formed, the chief product of the reaction was a trimethylpyridine (collidine).

Pseudolutidostyril, when acted on by phosphorus pentachloride, gives α-γ-dimethyl-α-chloropyridine, b.-p. 212—214°, and this compound when passed over heated zinc dust yields dimethylpyridine alone.

Discussion.

Dr. Forster drew attention to the apparent similarity between the reactions of the pyridine derivatives described by Dr. Collie and certain of the nitrogen derivatives of camphor when Tiemann's formula was employed,

Dr. Kipping was of opinion that there was no essential difference between Tiemann's for camphor and that proposed by Bredt. He thought that the possibility of the occurrence of tautomerism or stereoisomerism in the compounds described by Dr. Collie should be kept in view.

Dr. Collie, in reply, said he had not gone completely into the details of the various reactions he had made use of in preparing these substances, and he thought that when the full paper was read it would be seen that the substances were actually different in constitution, and not merely tautomeric or stereoisomeric.

*20. "*Sodamide and some of its Substitution Derivatives.*" By A. W. Titherley, M.Sc., Ph.D.

Sodamide in its reactions with organic haloid compounds invariably gives rise to complex decompositions without appreciable replacement of the halogen by NH_2. The hydrogen of the sodamide, and not the sodium, reacts, giving hydrochloric acid, which with the amide yields ammonia, whilst the group $NaN=$ remains more or less intact, being found afterwards as sodium cyanide and sodium cyanamide. Charring invariably occurs, even when the reaction is conducted with care.

Sodamide on treatment with organic substances possessing a weak acid tendency, such as oximes and hydrazines, readily reacts, giving ammonia and sodium derivatives. In benzene solution these are obtained usually as fine crystalline precipitates, which may sometimes be crystallised from boiling benzene. Sodium acetoxime, sodium hydrazobenzene, sodium phenylhydrazine, and others, have been thus obtained.

A series of substitution derivatives of sodamide formed by the replacement of one or both hydrogen atoms in $NaNH_2$ have also been prepared by the interaction of sodamide with (1) Aromatic amines; (2) Amides, according to the general equations:—

(*a*) $NaNH_2 + R{\cdot}NH_2 = NaNH{\cdot}R + NH_3$;
(*b*) $NaNH_2 + R{\cdot}CONH_2 = NaNH{\cdot}CO{\cdot}R + NH_3$.

In the former case the reaction is conducted with the substances in the free state in an atmosphere of coal-gas, and in the latter in benzene solution.

Potassium ethylamide, $KNHC_2H_5$, is formed by the careful action of ethylamine gas upon gently heated potassium. On heating, it readily decomposes into potassium cyanide, charcoal, and hydrogen. Sodium phenylamide, $NaNH{\cdot}C_6H_5$, sodium diphenylamide $NaN(C_6H_5)_2$, sodium *p*-tolylamide, sodium β-naphthylamide, &c., are all very readily prepared by the above general reaction. They form white, greenish-yellow, or brown, amorphous solids with conchoidal fracture, or light yellowish powders, which are blackened and decomposed quickly in the air, darkening especially when moistened with benzene.

When sodamide reacts with organic amides (best in boiling benzene solution) ammonia is rapidly evolved, and the substituted sodamides are obtained as fine, white, crystalline solids, those of larger molecular weight being appreciably soluble in benzene.

Sodium formamide, $NaNH{\cdot}CO{\cdot}H$, sodium acetamide, $NaNH{\cdot}COCH_3$, sodium propionamide, and sodium benzamide have been thus prepared—the latter apparently identical with the compound obtained by Curtius from the action of sodium upon benzamide by long-continued boiling in xylol solution.

The latter class of substituted sodamides are soluble without decomposition in alcohol, and their solutions, on treatment with alcoholic silver nitrate, throw down bright orange-red precipitates of the silver compounds, which are very unstable. From the colour of these silver derivatives, and the difficulty with which they and the sodium compounds appear to react with alkyl iodides, &c., the author concludes that the silver and sodium atoms, respectively, are directly attached to nitrogen, and that therefore the above derivatives are to be represented as possessing the ordinary amide and not the imido-hydroxy formula; the amides themselves are most probably tautomeric substances.

*21. "*Rubidamide.*" By A. W. Titherley, M.Sc., Ph.D.

Metallic rubidium behaves like the other alkali metals towards ammonia, displacing one atom of hydrogen and forming rubidamide, $RbNH_2$. Though not so energetic as in the case of lithium, the action is very rapid and commences in the cold. On heating in a silver boat to between 200—300°, oily drops of the amide quickly form and flow to a liquid in which the metal floats and partly dissolves to a deep blue solution, at once decolourised and converted into rubidamide by the action of ammonia. Rubidamide crystallises in plates melting at 285—287°, higher than sodamide and potassamide, but lower than lithamide. At 400° it distils undecomposed in a current of ammonia. With water it is violently decomposed, giving ammonia and rubidium hydrate. Alcohol also decomposes it, and its behaviour with organic substances is very similar to that of sodamide or potassamide.

*22. "*On the Spectrographic Analysis of some Commercial Samples of Metals, of Chemical Preparations, and of Minerals from Stassfurt Potash Beds.*" By W. N. Hartley, F.R.S., and Hugh Ramage.

In continuation of the work already published (*Roy. Soc. Proc.*, 1896, lx., 393, and *Proc.*, 1897, xiii., 11), samples were examined of steel made at Middlesbrough from the blast-furnace metal smelted from Cleveland clay ironstone, and rolled into rails; of alumina and "red mud" separated from bauxite at the British Aluminium Co.'s Works at Larne, and of the aluminium prepared from the alumina at Foyers and of various commercial alums.

It is shown that of the constituents of the blast-furnace metal, the alkali metals, calcium, copper, silver, gallium, manganese, and lead are present also in the steel, but the chromium and nickel have been removed.

Of the constituents of bauxite, traces of sodium, potassium, calcium, copper, silver, gallium, iron, manganese, and lead are found in the metallic aluminium. These elements are also present in larger quantities in the "red mud," and in addition nickel and chromium are present.

The Alums.—Examined directly, by heating 0·5 grm. of the dried sample in the oxyhydrogen flame, sodium, potassium, rubidium, calcium, and thallium are found as common constituents, and copper, gallium, iron, and nickel as occasional constituents. More interesting results were obtained by examining the precipitates produced by potassium ferrocyanide in solutions, containing 50 grms. of the alum strongly acidified with hydrochloric acid. These precipitates contained the elements sodium, potassium, rubidium, cæsium, copper, silver, calcium, gallium, thallium, nickel, manganese, besides iron, which was also present in the acid radical. The rubidium, cæsium, gallium, and thallium lines are strong in some of the spectra, and the results indicate that these elements are almost wholly precipitated by this process. A sample of "aluminoferric" from Messrs. Spence and Sons, Manchester, contained all the elements found in the alums, but in much larger quantities. Of these elements the pyrites furnishes the thallium and also a trace of indium found in a by-product of the manufacture of alum, whilst the other elements were traced to the aluminous minerals, bauxite and shale. The shale was richer in alkalis and gallium than the bauxite, but a sample of French bauxite was richer in silver and lithium than either Irish bauxite or shale.

Samples of Stassfurt minerals were examined in the course of the investigation, and were found to yield spectra containing no lines of rubidium, cæsium, gallium, or thallium. These salts gave only weak lines of a few elements besides the lines of the principal elements composing them.

It is pointed out in the paper that the elements found by their spectra actually exist in the specimens, as there is no possibility of them being accidentally introduced, and, furthermore, substances have been examined which have given no trace even of such widely distributed elements as potassium and calcium, and in which the D lines are very weak.

The systematic examination of railway metal by such an analytical method as is here employed might lead to results of practical importance. The method reveals the presence of small quantities of metals such as copper, silver, gallium, and lead, which have not been considered in dealing with commercial irons, and the influences of which upon the physical properties of these have not been studied.

Discussion.

Dr. Rideal suggested that the calcium present in aluminium and its compounds might be derived from the vessels employed in the manufacture as well as from the bauxite. He thought it probable that calcium might be present as metal in commercial specimens of aluminium.

23. "*Dissociation Pressure of Alkylammonium Hydrosulphides.*" By James Walker, D.Sc., Ph.D., and John S. Lumsden, B.Sc., Ph.D.

The dissociation pressures of ammonium, ethylammonium, and dimethylammonium hydrosulphides have been determined, as well as the dissociation pressures of mixtures of these substances in pairs. The values obtained for the mixtures fell in every case considerably below the values calculated from the dissociation pressures of the components by the law of mass action. The ratios of the dissociation pressures of these substances, whether simple or mixed, are independent of the temperature, a fact which proves their heats of dissociation to be equal.

24. "*Supposed Condensation of Benzil with Ethyl Alcohol. A Correction.*" By Francis Robert Japp, F.R.S,

The author finds that the compound, described by him in a paper published jointly with Miss Owens (*Trans.*, 1885, xlvii., 90), as formed by the condensation of benzil with ethyl alcohol, is in reality identical with Japp and Miller's *anhydracetonedibenzil*, $C_{31}H_{24}O_4$ (m. p. 194—195°), and that its formation was due to the presence of acetone in the "methylated spirit" (alcohol "denatured" with 10 per cent of crude wood-spirit), which was used instead of duty-paid alcohol, in the preparation of the compound. The formula, $C_{30}H_{24}O_4$, ascribed to the condensation compound, requires analytical figures differing only very slightly from those required by anhydracetonedibenzil.

At the time the paper was published, the authors believed the compound to be identical with Limpricht and Schwanert's *ethyldibenzoïn*, $C_{30}H_{26}O_4$, which Jena stated that he had prepared by the action of alcoholic potash on benzil—the reaction employed by the authors. On the strength of this belief, they proposed to alter Limpricht and Schwanert's formula to $C_{30}H_{24}O_4$, and they further cast doubt on the existence of an acetyl derivative which these investigators had prepared.

The author regrets the publication of these perfectly baseless criticisms on Limpricht and Schwanert's work.

The author is indebted to Prof. Alexander Smith for privately informing him that he had not succeeded in preparing the compound from benzil and alcohol, and thus calling his attention to the matter.

25. "*The Viscosity of Mixtures of Miscible Liquids.*" By T. E. Thorpe, F.R.S., and J. W. Rodger.

The authors having measured the viscosity of a large number of liquids, mostly carbon compounds and of very different types, at various temperatures up to the boiling-points under a standard atmosphere (*Phil. Trans.*, 1894, clxxxv.A, 379; 1897. clxxxix.A), have made observations on mixtures of chemically indifferent and miscible liquids, with the view of throwing light on the relation of the viscosity of a mixture to the viscosity of its constituents. A sufficiently comprehensive study of this question would afford answers to many questions of interest. Thus it would settle whether viscosity was related to the number of molecules per unit volume or per unit surface, and would indicate, therefore, how viscosity observations—and indeed all observations which depend upon surface effects—should be treated. It would also indicate whether, in the case of a mixture of a simple and a complex liquid, the values of viscosity gave any indication of the decomposition of molecular aggregates, and how such decomposition was related to dilution and temperature.

On the present occasion the authors communicate the results of a series of measurements made at different temperatures on mixtures of carbon tetrachloride and benzene, methyl iodide and carbon disulphide, and ether and chloroform, the last pair of which they studied on account of the relatively considerable evolution of heat which accompanies their admixture. The methods of observation and of reduction were the same as those previously employed, and the apparatus was identical with that already described (*loc. cit.*).

In no case could the density of the mixture be calculated by the ordinary admixture rule. Carbon tetrachloride and benzene contract on mixing, as already found by F. D. Brown (*Trans.*, 1881, xxxix., 207), whereas methyl iodide and carbon disulphide expand. Ether and chloroform contract considerably.

As regards viscosity, the observations afford additional evidence of the fact indicated by Wijkander and supported by Linebarger, that the viscosity of a mixture of miscible and chemically indifferent liquids is rarely, if ever, under all conditions, a linear function of the composition. It seldom happens that a liquid in a mixture preserves the particular viscosity it possesses in the unmixed condition. To judge from the instances hitherto studied, the viscosity of the mixture is, as a rule, uniformly *lower* than the value calculated on the assumption that each constituent exercises an influence proportional to its amount, although many examples are known to the contrary. No simple relation can as yet be traced between the viscosity of a mixture and that of its constituents.

In the case of a mixture of ether and chloroform, the viscosity at low temperatures is *greater* than the admixture rule would indicate; but as the temperature is raised, or as the mixture giving the maximum contraction is diluted, the viscosity eventually becomes *less* than the calculated value, when the general course of the curve showing the relation of viscosity to composition resembles that of such mixtures as carbon tetrachloride and benzene, or of methyl iodide and carbon disulphide. The phenomena in the case of a mixture of ether and chloroform would seem, to begin with, to be analogous to those of a mixture of ethyl alcohol and water, but the condition which determines the contraction and the maximum viscosity, whether it be a feeble chemical combination or a molecular aggregation of a purely physical character, is destroyed by heat or dilution.

26. "*Magnesium Nitride as a Reagent.*" By H. Lloyd Snape, D.Sc., Ph.D.

The object of the experiments detailed in this paper was to investigate whether magnesium nitride could be utilised to introduce nitrogen in the place of oxygen, chlorine, and other negative elements which combine with magnesium. The author investigated the behaviour of magnesium nitride towards chloroform, carbon trichloride, and benzaldehyde respectively, in the hope that the reactions represented by the following equations would occur:—

(1) $2CHCl_3 + Mg_3N_2 = 3MgCl_2 + 2HCN$;

(2) $C_2Cl_6 + Mg_3N_2 = 3MgCl_2 + C_2N_2$;

(3) $3C_6H_5 \cdot CO \cdot H + Mg_3N_2 = 3MgO + (C_6H_5 \cdot CH)_3N_2$.

The substances to be treated with magnesium nitride were sometimes passed in the form of vapour over the latter compound, and sometimes directly mixed with it, the mixture being heated in a sealed tube.

In no case was the desired nitrogenous compound obtained. The chloroform was not attacked at temperatures at which hydrocyanic acid could exist without decomposition, but at higher temperatures an energetic reaction took place, and the observed results were consonant with the reaction—

$$2CHCl_3 + Mg_3N_2 = 3MgCl_2 + C_2 + N_2 + H_2.$$

Carbon trichloride and benzaldehyde were likewise unaffected at temperatures below those at which the anticipated products could be formed. On heating with benzaldehyde to about 240°, a crystalline product, identical with that described by Laurent as amarone, was obtained. Both were subsequently discovered to be identical with the substance named tetraphenylazine by Japp and Burton. (See also the following paper).

27. "*The Identity of Laurent's Amarone with Tetraphenylazine.*" By H. Lloyd Snape, D.Sc., Ph.D., and Arthur Brooke, Ph.D.

Amarone being required to compare with the substance obtained, as described in the preceding paper, by the action of magnesium nitride upon benzaldehyde, the authors repeated Laurent's experiments.

It was necessary, in the first instance, to prepare benzoylazotide. This, it was found, could be more readily prepared than by the methods previously given, by the action of ammonium cyanide upon benzaldehyde. Laurent had stated that benzhydramide was produced by the long-continued action of ammonium cyanide upon benzaldehyde, but this was probably due to his having employed an excess of the former reagent. The formula given by Laurent to benzhydramide would accord with its formation by treating benzoylazotide with benzaldehyde, $C_6H_5 \cdot CO \cdot H + C_{15}H_{12}N_2 = C_{22}H_{18}N_2O$. The authors propose to try whether such a reaction can actually be carried out. The vapours of ammonium cyanide were conducted into a mixture of benzaldehyde and alcohol. Crude benzoylazotide slowly separated out, and was washed with alcohol and re-crystallised from benzene. The crystals softened at 198°, and completely melted, with attendant decomposition, at 202°. They were readily soluble in benzene and chloroform; difficultly soluble in alcohol and carbon disulphide, scarcely at all soluble in ether, and insoluble in water. An estimation of nitrogen established their identity with the benzoylazotide previously obtained by other methods.

To prepare amarone, benzoylazotide was next subjected to dry distillation under a pressure of 21 m.m. The residue left, after hydrocyanic acid and other comparatively volatile vapours had been removed, was crystallised from alcohol containing a small quantity of hydrochloric acid, and washed with some more of the same solution to extract any residual lophine. The crystals which were left melted at 243 to 244°, dissolved in concentrated sulphuric acid giving the characteristic red solution, and behaved towards other solvents precisely in the same manner as the crystalline substance previously prepared from magnesium nitride and benzaldehyde.

By analysis it was found that the empirical formula of amarone was $C_{14}H_{10}N$, not $C_{16}H_{11}N$, as had been stated by Laurent. The amarone which he obtained was evidently not pure, its melting-point being only 233°, or about 10° lower than that of the purified material.

Moreover, a comparison of the properties of pure amarone showed it to be identical with the substance named by Japp and Burton tetraphenylazine, $C_{28}H_{20}N_2$. The authors were kindly supplied by Professor Japp with some of the latter compound, prepared by him from benzoin, for the purpose of instituting this comparison. It was thus established that amarone, as described by Laurent, was actually tetraphenylazine.

It seems probable to the authors that the substance obtained by Curtius and Blumer having the same empirical formula, $C_{14}H_{10}N$, to which they have not assigned a structural formula, will likewise prove to be tetraphenylazine. The properties of this compound, so far as they have been described, agree with this supposition.

28. "*Studies on the Interaction of Highly-purified Gases in presence of Catalytic Agents.*" Part I. By Wm. French, M.A.

In absence of light, spongy platinum does not appear to bring about combination between oxygen and hydrogen if they have been previously carefully dried; and, so far, experiments seem to show that, after the gases have been in contact with the platinum, added moisture does not cause an explosion.

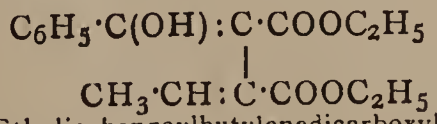
29. "*Contributions to the Knowledge of the β-Ketonic Acids.*" Part III. By S. Ruhemann, Ph.D., M.A.

The author arrives at the conclusion, from the further study of the action of ethylic chlorofumarate and ethylic α-chlorocrotonate on ethereal salts of β-ketonic acids, that the substances described before (*Trans.*, 1896, lxix., 530, 1383) are to be regarded as ketone-compounds, and he gives the corrections necessitated by the change of view concerning the constitution of the various products there recorded. He further shows that the substance formed from ethylic chlorofumarate and ethylic acetomethylacetate is to be looked upon as ethylic acetoallylenedicarboxylate,—

$$CH_3{\cdot}CO{\cdot}C(COOC_2H_5){:}C{:}CH{\cdot}COOC_2H_5.$$

Aniline acts on this ethereal salt with formation of an anile-compound which crystallises in yellow plates (m. p. 180°).

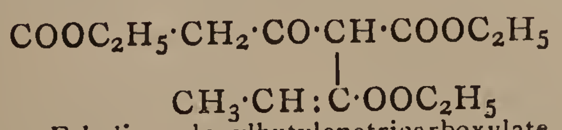
Ethylic benzoylacetate and ethylicacetonedicarboxylate form, with ethylic α-chlorocrotonate, compounds which are to be represented by the formulæ—



$$\begin{array}{l} C_6H_5{\cdot}C(OH){:}C{\cdot}COOC_2H_5 \\ \qquad\qquad\qquad\ \ | \\ \qquad CH_3{\cdot}CH{:}C{\cdot}COOC_2H_5 \end{array}$$

Ethylic benzoylbutylenedicarboxylate.

and—



$$\begin{array}{l} COOC_2H_5{\cdot}CH_2{\cdot}CO{\cdot}CH{\cdot}COOC_2H_5 \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad CH_3{\cdot}CH{:}C{\cdot}OOC_2H_5 \end{array}$$

Ethylic malonylbutylenetricarboxylate.

The latter substance, under the influence of ammonia, yields two isomeric diamides of the ethereal salt, having the formula $C_{11}H_{16}N_2O_5$, besides a diamide of the corresponding acid.

30. "*Contributions to the Knowledge of the β-Ketonic Acids.*" Part IV. By S. Ruhemann, Ph.D., M.A., and A. S. Hemmy, B.A., M.Sc.

Ethylic acetosuccinate was found to give a colour reaction with ferric chloride, in opposition to the statement of Conrad (*Annalen*, 1877, clxxxviii., 218). The authors give an account of various substances formed from this ethereal salt under the influence of ammonia and of phenylhydrazine. In the latter case, ethylic methylphenylpyrazolone acetate is formed, which, on hydrolysis, yields the corresponding acid. The bromo-derivative of ethylic acetosuccinate was prepared, and on distillation in a vacuum gave ethylic carbotetrinate (*cf.* Moscheles and Cornelius, *Ber.*, 1888, xxi., 2603).

Ethylic benzoylsuccinate, obtained according to Perkin's directions (*Trans.*, 1885, xlvii., 272) was found to distil without decomposition at 192—193° at 10 m.m., and to be decomposed by ammonia with formation of succinamide.

31. "*Oxidation of Phenylstyrenyloxytriazole.*" By George Young, Ph.D.

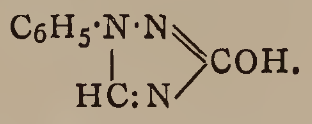
The oxidation by alkaline potassium permanganate of phenylstyrenyloxytriazole,—

$$C_6H_5.CH{:}CH(C_6H_5){\cdot}C_2N_3{\cdot}OH,$$

yields phenyloxytriazole carboxylic acid—

$$C_6H_5{\cdot}C_2N_3(OH)CO_2H.$$

This acid, immediately on liberation, loses carbon dioxide and forms phenyloxytriazole,—



$$\begin{array}{l} C_6H_5{\cdot}N{\cdot}N\diagdown \\ \qquad\ \ | \qquad\ \ \rangle COH. \\ \quad\ HC{:}N\diagup \end{array}$$

The following derivatives of the carboxylic acid have been prepared:—Ethylic phenylethoxytriazole carboxylate, $Ph{\cdot}C_2N_3(OEt)CO_2Et$, white needles, m. p. 82—83°. Amide, $C_6H_5{\cdot}C_2N_3(OC_2H_5)CONH_2$, white needles m. p. 149—150°. Silver salt,—

$$C_6H_5{\cdot}C_2N_3(OC_2H_5)CO_2Ag+2H_2O.$$

Phenylethoxytriazole carboxylic acid, when liberated, loses carbon dioxide and forms phenylethoxytriazole, $C_6H_5{\cdot}C_2N_3H{\cdot}OC_2H_5$, needles, m. p. 60°. This compound has also been formed by the action of ethyl iodide on the silver derivative of phenyloxytriazole.

32. "*Apiin and Apigenin.*" (Preliminary notice). By A. G. Perkin.

Apiin, a constituent of parsley (*Apium petroselinum*), was first isolated by Braconnot (*Ann.*, 1843, xlviii., 349), and subsequently examined by Planta and Wallace (*Ann.*, 1850, lxxiv., 262), who found it consisted of a glucoside. Gerichten (*Ber.*, 1876, ix., 1124, in a more detailed investigation, assigned it the formula $C_{27}H_{32}O_{16}$, and considered its decomposition by dilute acids to be most probably represented by the equation—

$$C_{27}H_{32}O_{16}+H_2O=C_{15}H_{10}O_5+2C_6H_{12}O_6,$$

which is based upon the yield of apigenin thus obtained. He described no derivatives of apigenin, but states that by the action of alkali there is produced phloroglucol and an acid, which by prolonged treatment is decomposed with formation of protocatechuic acid, *p*-hydroxybenzoic acid, formic and oxalic acids.

Having suspected, from a description of its properties, that apigenin was a yellow colouring-matter, and this having been proved to be the case, the present investigation was instituted. It is wished to reserve the further study of the reactions of this interesting substance.

The glucoside apiin is somewhat difficult to fully decompose by dilute acids, the apigenin produced after three hours' digestion with hydrochloric acid of sp. gr. 1·04 yielding $C=64{\cdot}3$; $H=3{\cdot}90$; after ten hours, $C=65{\cdot}81$, $65{\cdot}74$; $H=3{\cdot}45$, $4{\cdot}01$; and only when so treated for twenty-five hours are numbers obtained indicating the formula $C_{15}H_{10}O_5$, evidently the correct one. Calc., $C=66{\cdot}66$; $H=3{\cdot}70$; Found, $C=66{\cdot}34$, $66{\cdot}37$; $H=3{\cdot}87$, $3{\cdot}81$. Apigenin contains no methoxy groups, and does not combine with mineral acids; it, however, forms a sulphonic acid not yet thoroughly examined. Dibromapigenin crystallises in almost colourless needles, melting above 290°. $C_{15}H_8O_5Br_2$ requires C=42·05; H=1·87; Found, C=42·09; H=2·23; and a tribenzoyl compound, $C_{15}H_7O_5(C_7H_5O)_3$, needles, m. p. 210—212°, has also been obtained. Calc., C=74·23; H=3·78. Found, C=74·41; H=4·17. Apigenin reacts with diazobenzene, forming $C_{15}H_8O_5(C_6H_5N_2)_2$, orange-red needles, m. p. 290—292°. Calc., C=67·78; H=3·74; N=11·71. Found, C=67·22; H=3·75; N=11·54, 11·56; which yields a monacetyl derivative $C_{15}H_7O_5(C_2H_3O)(C_6H_5N_2)_2$; orange-red leaflets, m. p. 259—260°. Calc., C=66·92; H=3·84. Found, C=66·66; H=4·05. Experiments on the further acetylisation of this substance are in progress. By treatment with strong alkali there is obtained from apigenin, phloroglucol, an acid, m. p. 208—209°, probably *p*-hydroxybenzoic acid, a trace of acetic acid, and a substance crystallising in colourless needles, m. p. 107°, which bears some resemblance to *p*-hydroxyacetophenone. Fuming nitric acid decomposes apigenin, the principal product being an acid; yellow needles; m. p. 244—245°. The dyeing properties of apigenin will be described in the full communication. The investigation of these substances will be continued, and the study of the ethylation and methylation of apigenin is also in progress.

33. "*Note on the Constitution of the so-called 'Nitrogen Iodide.'*" By J. W. Mallet, F.R.S.

Mr. Chattaway concludes his paper by saying that "at present the formula NH_3I_2 seems best to accord with the reactions of the compound as a whole, and best to group all the known facts regarding it." Reference to a short paper by my sometime student, Mr. W. H. Seamon, published in the Chemical News, 1881, xliv., 188, will show that a very different substance—liquid, and non-explosive—gives results on analysis agreeing well with this formula. It was obtained by the action of dry gaseous ammonia on solid iodine, and appears to be identical with the substance prepared in a different way by Guthrie, of which brief mention is made by Mr. Chattaway in a footnote.

I cannot agree with him that in the explosive compound the ratio of N : I is always 1 : 2. Some analytical results of my own (published in the paper on this subject in the *American Chemical Journal*, 1879, i., 4) were quite incompatible with this ratio, and agreed nearly with the ratio 1 : 3. In view of the fact that the preparation which gave these results had been freely washed with alcohol and afterwards with ether, I cannot think it probable that any considerable formation and retention of iodoform raised the proportion of iodine.

In any discussion of the composition of the explosive substance in question, some attention ought surely to be given to the probable analogy with nitrogen trichloride, for which Gattermann seems to have fairly well established the formula.

NOTICES OF BOOKS.

Our Secret Friends and Foes. By Percy Faraday Frankland, Ph.D., B.Sc., F.R.S., F.C.S., &c., Professor of Chemistry in Mason College, Birmingham. Third Edition, Revised and Enlarged. London and Brighton: Society for Promoting Christian Knowledge. New York: E. and J. B. Young and Co. 1897. Post 8vo. Pp. 238.

The study and application of bacteriology during the past few years has made such rapid strides, in so many directions, that we are always glad to see new and enlarged editions of such well-known works as those given to us by Prof. Percy Frankland.

This latest addition to bacteriological literature sets orth in a clear, and not too technical manner, the fundamental ideas which govern the study of the science. The early chapters deal with the micro-organisms in air and in water. Chapters IV. and V. are devoted respectively to useful and malignant micro-organisms, and it is important for it to be as widely known as possible that many microbes are absolutely essential to our existence. There is a widely-spread belief among the general public that *all* microbes are harmful; and great expense, and a good deal of trouble, is incurred in reducing the number of bacteria in water used not only for drinking purposes, but even for watering roads, putting out fires, &c. It should be borne in mind that many of these microbes act in a certain sense as policemen; the microbes of anthrax, typhoid, and such like, cannot live in water "contaminated" with a certain number of harmless microbes. What risk then is run, if perchance a few of these malignant organisms find their way into an almost sterile water-supply where there are not enough "police" microbes to hold them in check!

The new chapter, number VIII., is one of great interest and importance, entitled "Recent Applications of Bacteriology," several recent discoveries of prevention and cure of disease, snake-bite poisoning, &c., being herein described. Is it necessary to add that, owing to the action of our legislators, most of this excellent and valuable work is being done abroad?

Some curious results of experiments on the "manuring" of land by appropriate microbes are described, and an excellent cut is added showing the difference between two similar vetches, *Vicia villosa*, one inoculated with pure cultivations of *Pisum sativum*, nodule-bacteria, and the other uninoculated; the difference is very striking.

At the end of the book is a table giving the number of microbes per c.c. in London waters during the years 1886, 1887, and 1888, wherein we see that, so short a time ago as ten years, the colonies were counted by hundreds, and even thousands, whereas the average number during last year, 1896, was twenty-five.

CORRESPONDENCE.

THE CHEMICAL SOCIETY ELECTION.

To the Editor of the Chemical News.

Sir,—In view of the insidious attempt that is being made to reverse the recommendations of the Council—an attempt absolutely without precedent in the annals of the Society—I would ask you to allow me to bring under the notice of the Fellows generally what I believe to be the true situation.

Although at the outset it was an attack on the distinguished gentleman who has been nominated President by the unanimous vote of a very large and entirely representative Council, I am satisfied that the rancorous opposition of his fellow countrymen is now put quite in the background, and that the majority of those whose names have been given in as nominating another have been led to promise their votes from an entirely different point of view, and not with any personal motives.

Mr. Muir and his immediate following are no doubt determined haters: those who took the trouble to read the letters which disfigured the columns of *Nature* some couple of years ago will be aware of the virulently personal, most ill-advised, and entirely unprofessional attacks which were made on Prof. Dewar, and will be able to rate the opposition of such men at its true value.

Some, no doubt, have been influenced by the suggestion that the work done within recent times by Prof. Ramsay entitles him to the preference, and have joined the movement out of sheer good nature. To these it may be pointed out that, although of a less sensational character, the work done by Prof. Dewar on the physical properties of metals and other substances at very low temperatures is of altogether extraordinary importance and value in the eyes of those who can appreciate it, and not inferior in interest to any work accomplished during the past few years. Moreover, it has not been initiated by any casual observation, but is the final outcome of preparations made with unwearied perseverance and most remarkable skill during a long series of years, and of work carried out with great courage and at most serious personal risk.

When I ask those about me what motives have inspired their conduct, no two give the same or a straightforward answer. But as I extend my inquiries, I find that wrongheadedness and narrowness, combined with a certain amount of personal vanity, are really at root the cause of the movement.

Dr. Collie, Dr. Kipping and their friends are, in fact, of opinion that undue preference has been shown to senior members of the Society. How the juniors have suffered at the expense of the seniors I am totally unable to discover—the more so when I find that during the past ten years the Society has borne the expense of publishing papers by Dr. Kipping, for example, covering some 500 pages of the Society's *Transactions*. A gentleman who has received such treatment at the hands of the Publishing Committee and the Council can scarcely have any grievous cause of complaint against his seniors—but if he have, let him state it fairly and openly.

I assert, on the basis of considerably over twenty years' experience, that no Council has been more loyal or careful of the interests of all sections of the Society; each year the new members have been selected on the ground of service rendered to Chemical Science and for no other reason, and men such as Collie and Kipping have been given a voice in the management at the earliest possible opportunity.

One of my late students, whose name figures on the list of objectors, to whom I wrote asking his reasons, replies as follows:—

"I allowed my name to be added to the list of Ramsay's nominators on the ground that this is the only means the rank and file of the Society have of influencing the election of Officers, and as a protest against the present mode of election. The present system amounts to the Council electing President and also electing itself.

"I imagine that the fact that Dewar is unpopular has been seized as the means of making the protest."

It is clearly a case in which, as the poet has well put it:—

"The dog to serve some private ends
Went mad and bit the man."

But surely, Sir, Englishmen have a reputation for fairness. It would be outrageous to attempt to damage the public reputation of a man who is deemed good enough by the managers of the Royal Institution to occupy the post of Resident Manager,—a post once held by Faraday,—and with whom Lord Rayleigh is prepared to work as a colleague in conducting the Davy-Faraday laboratory. Young gentlemen like Dr. Lapworth, but six months ago a student in my laboratory, Mr. Marshall, Mr. Mills, Mr. Evans,—all recently students under me,—my junior Demonstrator Mr. Pope, Mr. Ling, and many others on the list personally known to me, can neither know anything against Professor Dewar nor have any grievance against the Society which justifies them in their action, and straightlaced representatives of the analytical profession like Mr. Cassal must have other motives than mere personal ones for joining in such a crusade.

Dr. Collie is reported to have stated at the last meeting of the Society that the nomination of Prof. Ramsay had been made without his knowledge or permission. I venture to challenge the accuracy of this statement; if I am not altogether misinformed, Prof. Ramsay has known what is going on from the beginning, and is pledged to "reform" the Society, I believe, by abolishing the "old buffers" and ensconcing the young radicals in their places.

I will yield to no one in the desire in every way to promote the interests of the Chemical Society as representative of the interests of chemical science in this country. We have accomplished much during the past twenty years, and may do much more in the future; but it behoves us to work together fairly and honestly if we are to continue to exert an influence for good. I trust, therefore, that all right-minded Fellows of the Society will unite in resisting the ill-considered attempt that is being made both to prejudice the position of a man who has the interests of the Society most warmly at heart, and to introduce changes which, whether desirable or not, have not been for one moment previously brought under our notice.—I am, &c.,

Henry E. Armstrong.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 9, March 9, 1897.

Researches on the Uranic Rays.—Henri Becquerel.—Will be inserted in full.

Discharge of the Röntgen Rays: Part Played by the Surfaces Struck.—Jean Perrin.—Already inserted.

Existence of Anodic Rays Analogous to the Kathodic Rays of Lénard and Crookes.—P. de Haen.—This paper requires the accompanying diagram.

Determination of Atmospheric Ozone on Mont Blanc.—Maurice de Thierry.—Will be inserted in full.

Action of Dilute Nitric Acid upon Nitrates in Presence of Ether.—M. Tanret.—Already inserted.

Action of Aluminium Chloride upon Camphoric Acid.—G. Blanc.—Will be inserted in full.

MEETINGS FOR THE WEEK.

Monday, 29th.—Society of Arts, 4.30. (Cantor Lectures). "Alloys," by Prof. W. Chandler Roberts-Austen, F.R.S.
Tuesday, 30th.—Royal Institution, 3. "Animal Electricity," by Prof. A. D. Waller, F.R.S.
—— Society of Arts, 8. "Lead-Work," by W. R. Lethaby.
Wednesday, 31st.—Society of Arts, 8. "Cycling—Historical and Practical," by George Lacy Hillier.
—— Chemical, 3. (Annual General Meeting). Ballot for Election of Officers and Council. At 7 p.m., Anniversary Dinner at the Criterion Restaurant.
Thursday, April 1st.—Chemical, 8. "Oxidation of α-γ-dimethyl α′-chloro-pyridine," by E. Aston and J. Norman Collie, Ph.D.. F.R.S. "Composition of Cooked Fish," by K. I. Williams.
—— Royal Institution, 3. "The Relation of Geology to History," By Prof. W. Boyd Dawkins, M.A., F.R.S., F.G.S.
—— Society of Arts, 4.30. "A Visit to Russian Central Asia," by M. F. O'Dwyer.
Friday, 2nd.—Royal Institution, 9. "Metallic Alloys and the Theory of Solution," by C. T. Heycock, F.R.S.
Saturday, 3rd.—Royal Institution, 3. "Electricity and Electrical Vibrations," by Right Hon. Lord Rayleigh, M.A., F,R.S.

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THE CHEMICAL NEWS.

Vol. LXXV., No. 1949.

ON THE DETECTION OF THE COLOURING-MATTERS OF COAL IN WHITE WINES, AND ON DISTINGUISHING THESE PIGMENTS FROM THE COLOURS OF CARAMEL.

By ALB. D'AGUIAR and W. DA SILVA.

The recognition of the coal-tar colours, and their distinction from caramel in liqueurs, has already been undertaken by Rocques, Saglor, Rœser, and other chemists. Quite recently Cruz Nagelhâes has sought to demonstrate that the methods in common use for the detection of coal-tar colours in old white wines may prove defective, and lead us to confound caramel with the yellow or orange-yellow colours of coal.

We request permission to present on this question our experiments conducted in the Municipal Laboratory of Oporto.

We shall confine ourselves to reporting the results obtained by the use of amylic alcohol on wines rendered alkaline by the addition of ammonia, with dyeing experiments on silk by immersion in amylic alcohol.

We have experimented with the following colours:—1, binitro-naphthol; 2, chrysoidine; 3, Bismarck brown; 4, orange II.; 5, tropeoline; 6, Biebrich red; 7, azo-flavine; 8, helianthine; 9, methyl-orange; 10, amido-azo-benzene; 11, naphthol yellow S; 12, caramel. These colours were respectively dissolved each in alcohol of sp. gr. 20°, and the solutions were mixed with 400 c.c. of white wine from Ermida, grown in the north of Portugal. The caramel was added to the wine in the proportion of 5 c.c. to 400 c.c., and was obtained with 500 grms. of pure sugar, heated to 215°, and lastly dissolved in 800 c.c. of water. The intensities of colour were compared with Ermida wine, seen in a stratum at the depth of 12 c.m.

We made three series of experiments.

The colours of caramel give, by the usual treatment with amylic alcohol, results very doubtful and sometimes negative. On the contrary, the coal-tar yellows present a group of very distinct colours, which are very characteristic if they are used in the fraudulent wine-trade.—*Chemiker Zeitumg.*

ESTIMATION OF THORIA.
CHEMICAL ANALYSIS OF MONAZITE SAND.*

By CHARLES GLASER.

(Concluded from p. 147).

Systematic Method of Analysis.

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

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

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

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

When completely settled, the liquid is filtered and the filtrate boiled to expel hydrogen sulphide. Any free acid may be nearly neutralised with ammonia; to the boiling liquid is added an excess of a boiling solution of ammonium oxalate, as much as 100 c.c. of the cold saturated solution for 2 grms. of monazite sand. The excess necessarily must be large. The mixture is then permitted to cool, best for an entire night. The solution will contain phosphoric acid, the oxides of iron, manganese, aluminum, glucinum, yttrium, zirconium, and calcium. In the precipitate will be found thoria and the oxides of the cerium group.

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

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

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

If the carbonate solution be boiled for one hour the earths are completely precipitated. They may be caught on a filter and dissolved in hydrochloric acid; or the carbonate solution may be treated directly with that acid, carbon dioxide expelled by boiling, the solution cooled

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* From the *Journal of the American Chemical Society*, vol. xviii., No. 9.

and treated with an excess of sodium hydroxide. Zirconium and yttria are completely precipitated, while glucina remains dissolved; to precipitate this, boil the solution one hour.

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

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

Separation of the precipitated oxalates of thoria and of the cerium group is accomplished as follows:—The oxalates are reduced to oxides by ignition, then converted into sulphates, the greater part of the free acid 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 few c.c. of solution of ammonium acetate are added. When cold, the entire cerium group is precipitated as oxalates, while thoria remains in solution. After prolonged standing, best over night, the insoluble oxalates are removed by filtration; in the filtrate, precipitate thoria with ammonia in excess, filter, ignite, and weigh.

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

Separation of lanthanum from didymium was not attempted.

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

Titanic acid	4·67
Silica	6·40
Phosphorus pentoxide	18·38
Lead	trace
Alumina	1·62
Lime	1·20
Cerium oxide (CeO)	32·93
Lanthanum and didymium oxides	7·93
Thoria	1·43
Ferric oxide	7·83
Zirconia and yttria	13·98
Glucina	1 25
Tantalic acid	0·66
Not determined	1·72
	100·00

Titanic acid and silica was determined in a separate portion.

The determination of tantalic acid was only approximate, since a part of it is dissolved by fusion with acid potassium sulphate, and thus escapes weighing. As several such fusions were made, it is probable that the greater part of the matter "not determined" ought to be reckoned as tantalic acid. The quantity stated was an average of three determinations (minus or plus 0·05) from the residue of repeated fusions.

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

Analysis of of a Coarse Monazite Sand from Shelby, North Carolina.

Silica	3·20
Titanic acid	0·61
Cerium metals as CeO	63·80
Phosphorus pentoxide	28·16
Thoria	2·32
Zirconia, glucina, yttria	1·52
Manganese	trace
No iron, alumina, or lime	0·00
	99·61

The colour of this sand was honey-yellow.

Analysis of a Fine Monazite Sand from Bellewood, North Carolina.

Silica	1·45
Titanic acid	1·40
Cerium metals as CeO	59·09
Phosphorus pentoxide	26·05
Thoria	1·19
Zirconia, glucina, yttria	2·68
Tantalic acid	6·39
Iron and manganese oxides	0·65
Alumina	0·15
	99·05

The colour of this sand was honey-yellow.

A REVISION OF THE ATOMIC WEIGHT OF MAGNESIUM.*

By THEODORE WILLIAM RICHARDS
and
HARRY GEORGE PARKER.

(Continued from p. 149).

Preparation of Materials.

The sample of ammonic magnesic chloride which will be hereafter referred to as sample No. 1, was prepared as follows:—About 500 grms. of ordinary "C. P." magnesic chloride were saturated with hydrogen sulphide, a small amount of ammonia was added, and the whole was allowed to stand in a warm place for several days. To the supernatant liquid after decantation a small quantity of very pure ammonic oxalate was added. The magnesic chloride thus almost wholly freed from calcium was again decanted; and after more ammonic oxalate had been added, the whole was allowed to stand, and the clear liquid was yet once more decanted. The solution was then evaporated to dryness, and the resulting cake dried in an oven and ignited in a platinum dish. The mixture of magnesic oxide and oxychloride thus formed was washed with the aid of a filter pump for about sixty hours. At the end of this time, although the wash water contained no sodium, the insoluble precipitate was not free from that metal. The precipitate was therefore dissolved in hydrochloric acid, previously distilled in platinum for the purpose, and the solution was filtered. In order to eliminate the sodium, a portion of the magnesium was precipitated by passing into the solution a current of ammonia gas. The precipitate formed by this very wasteful process was washed for several days, at the end of which time it was found to be free from any appreciable traces of sodium and potassium, when tested with the spectroscope.

Ammonic chloride was now prepared by mixing streams of ammonia and hydrochloric acid gas. This gave am-

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* Contributions from the Chemical Laboratory of Harvard College, From the *Proceedings of the American Academy of Arts and Sciences.* vol. xxxii., No. 2.

monic chloride mixed probably to a certain extent with various amines, but free from inorganic salts. As the amines must be driven off later, it was not thought worth while to take the trouble of removing them at this stage of the work.

The solution of ammonic chloride thus prepared was added to the solution of magnesic chloride obtained by dissolving the oxychloride in hydrochloric acid in proportions corresponding to formula $Mg.Cl_2(NH_4)Cl$, and the mixture was carefully evaporated to dryness and gently heated in an oven. It is, of course, unnecessary to say that all the latter part of this purification was done as far as possible in platinum. The solid cake was powdered in an agate mortar, and placed in a glass-stoppered bottle which was kept in a closed jar. The double chloride thus prepared was then tested with the spectroscope, but no impurities could be discovered; and its solution in water was perfectly clear. Tests were made with ammonic oxalate and baric chloride, but in neither case was a precipitate formed on long standing.

The second sample of magnesic chloride was treated in a similar way up to the point where it was necessary to get rid of sodium and potassium. The solution was evaporated to dryness in a platinum dish with the aid of an alcohol lamp, and the resulting cake was gently ignited and then washed for a long time, nothing but platinum being allowed to come in contact with the material from this time forth, and all the heating being done by means of alcohol lamps to avoid the danger of contamination of sulphur from illuminating gas. The oxychloride thus formed was then dissolved in pure hydrochloric acid and filtered. By evaporating down again the magnesium was again rendered insoluble. This process was repeated again and again, until there was no trace of sodium or potassium remaining.

The ammonic chloride necessary for the preparation of the double salt from this second sample of magnesic chloride was prepared by digesting ammonic chloride with nitric acid to destroy the amines (Krüss, *Liebig's Annal.*, ccxxxviii., 51). It was then dried, sublimed several times, re-crystallised five or six times from its aqueous solution, and again sublimed in a current of air which had been passed through wash bottles containing respectively a concentrated solution of potash and sulphuric acid. After having been sublimed in this manner about ten or twelve times, it was dissolved in re-distilled water and added to the sample of magnesic chloride. The whole was then filtered, evaporated to dryness, partly dehydrated, broken up and placed in a glass stoppered bottle. The usual tests were made as to its purity, but no traces of foreign matter were discovered.

The third sample of magnesic chloride, which was used for the final experiment in the last series, was at first treated in about the same way as the others. The precautions taken were somewhat greater, and the fractional precipitation with ammonic oxalate was continued long after the last traces of calcium discoverable by the spectroscope had disappeared from the precipitates of magnesic oxalate. The ammonic magnesic chloride, already very pure, prepared from this sample, was then crystallised eight or ten times, the last six or eight re-crystallisations being conducted in platinum. From over a kilogrm. of magnesic chloride used in the beginning, the portion finally separated out consisted only of a few grms. This sample showed no traces of the sodium line when tested with the spectroscope; indeed, several other samples, obtained from the mother liquors of the purest sample, gave equally satisfactory negative spectroscopic results. Since the magnesic chloride had contained in the first place a very noticeable amount of sodic chloride, the fact of the complete elimination of the impurity seemed a satisfactory indication of the elimination of other foreign materials. The double chloride was dried over an alcohol lamp, and treated in the same manner as the other samples.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 4th, 1897.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Certificates were read for the first time in favour of Messrs. Alaric Vincent Colpoys Fenby, B.Sc., Hutton Grammar School, Preston; R. Glode Guyer, 20, Queen's Road, St. John's Wood, N.W.; Tom Mitchell, Cemetery House, Shaw, near Oldham; Robert Howson Pickard, B.Sc., Southfield, Priory Road, Edgbaston, Birmingham.

Mr. Cassal asked whether the officers had withdrawn the certificate of a candidate from the list to be balloted for that evening.

Professor Thomson stated that the certificate of one of the candidates had been postponed pending further information.

Dr. Armstrong remarked that such action had been taken by the officers on former occasions, and was within their discretion.

The following were duly elected Fellows of the Society:—Messrs. John Owen Alexander; Thomas Hannibal Aquino; William Arbuckle; John B. Ashworth; John Barclay, B.Sc.; Frank Bastow; Jyoti Bhushan Bhaduri, M.A.; James Herbert Brown; F. Hewlett Burton-Brown, M.A.; Alfred Cartmell; Masumi Chikashigé, B.Sc.; Alfred Foster Cholerton; Clarence Hamilton Creasey; James Crowther, B.Sc.; William Alfred Davis; William Diamond; John Wallis Dodgson, B.Sc.; Lawrence Dufty; William Buckland Edwards; Joseph Lake Gibbons; Alexander W. Gilbody, M.Sc., Ph.D.; Harold Walter Gough, B.A.; Ernest Goulding; Edward Graham Guest, M.A.; Vaughan Harley, M.D; Ernald G. Justinian Hartley, B.A.; Thomas Hartley; Charles Heppenstall; John Holmes; Fred Ibbotson, B.Sc.; William Rose Innes, B.Sc., Ph.D.; David Smiles Jerdan, M.A., B.Sc.; Harold Johnson; Otis C. Johnson; Herbert King; William Robert Lang, B.Sc.; Theophilus Henry Lee; Charles Henry Martin; Barker North; Charles Henry Parker; Samuel Pollitt, B.Sc.; Herbert Spindler Pullar; William Ralston, B.Sc.; John Stewart Remington; Edward Rosling; Alfred Rutter; Frank Southerden; William James Stainer, B.A.; Henry Potter Stevens, B.A.; Leonard Sumner, B.Sc.; Harry Thompson; Andrew Turnbull, Ph.D; Basil William Turner; Rustomji Navroji Umwalla; Samuel Matthew Walford; J. Wallace Walker, M.A., Ph.D.; and Meyer Wilderman, Ph.D.

In accordance with the Bye-law, the lists of the names of the Fellows recommended for election as official and ordinary Members of Council were read from the Chair.

Of the following papers those marked * were read:—

*34. "*Some Hydrocarbons from American Petroleum. I. Normal and Iso-pentane.*" By Sydney Young, D.Sc., F.R.S., and G. L. Thomas, B.Sc.

The two pentanes were separated by fractional distillation from the "pentane" supplied by Merck of Darmstadt. This substance, which is obtained by the distillation of American petroleum, is a complex mixture of butanes, pentanes, and hexanes, with some benzene and a little hexanaphthene. A combination of a dephlegmator with a constant (or rather "regulated") temperature still-head was employed; the apparatus is fully described in the paper.

Some of the constants of isopentane were determined so as to compare them with those of the two specimens prepared synthetically; the agreement was found to be very satisfactory. The boiling-points under normal pressure are:—Isopentane, 27·95; normal pentane, 36·3. The specific gravities at 0° are:—Isopentane, 0·63930; normal pentane, 0·64539.

*35. "*The Vapour Pressures, Specific Volumes, and Critical Constants of Normal Pentane; with a Note on the Critical Point.*" By Sydney Young, D.Sc., F.R.S.

The critical temperature of normal pentane is 197·2, the critical pressure is 25,100 m.m., and the critical volume of a grm. 4·303 c.c. The vapour pressures and specific volumes were determined from low temperatures to the critical point, and the observations were taken as near to the critical point as possible (197·15), in order to obtain more complete experimental evidence regarding the condition of a substance at and very near that point.

The ratios of the absolute temperatures (boiling-points) and volumes to the critical constants, also the ratio of the actual to the theoretical density at the critical point (3·765), lead to the conclusion that, at the critical temperature and in the liquid state, the molecules are simple, like those of the gas.

Discussion.

The President said that for many years he had been interested in the isopentane derived from American petroleum, having proposed that its flame should be used, under specified conditions, as a standard of light. He had purified it by shaking with sulphuric acid, and afterwards with soda. He had no doubt it was an improvement to use nitric acid, as Dr. Young had done. He had used a dephlegmator very similar to that described, but had never succeeded by fractional distillation in obtaining a substance of such a constant boiling-point as that obtained by Dr. Young. He was much interested to hear this proof by Dr. Young of the identity of isopentane with that which is obtained from amyl iodide, as experiments on the illuminating power did not quite settle this question.

Dr. Armstrong thought that it was not quite certain that the isopentane used by Dr. Young was a single thing, and it was probably very difficult to obtain satisfactory proof of purity. In the case of the specimen derived from amyl alcohol, he considered it likely that this was a mixture of two hydrocarbons, as it did not appear that the amyl alcohol of fusel oil had first been separated into its two constituents.

Dr. Craw said that Dr. Young seemed to have shown that the critical temperature could be determined accurately for the class of compounds on which he had worked; but he asked whether the critical temperature is capable of being determined with the same accuracy for all classes of compounds.

Mr. Groves agreed with Dr. Armstrong as to the necessity of taking special precautions in purifying materials and of not trusting to those supplied by manufacturers.

Dr. Thorpe said he had had some experience in the preparation of isopentane. He had obtained it from amyl alcohols of very different origin. The question was whether the isopentane derived from fusel oils of very different origin would give the same hydrocarbon. He had found that all the specimens of isopentane gave practically the same boiling-point and density numbers as those obtained by Dr. Young. Nevertheless, Mr. Rodger and he had found that the viscosities of isopentane derived from different sources varied considerably, and it was significant that their specific volumes and specific gravities agreed closely with those recorded by Dr. Young. In the case of other liquids differently prepared and purified, the same viscosity numbers were obtained: for example, Prof. Dunstan had provided him with a sample of pure ether, and Dr. Perkin also provided him with a sample, and the viscosities of the two were in perfect agreement. Similarly, he had compared two samples of benzene of different origin, and here also the two samples gave the same viscosity number. On this account he was inclined to question the homogeneity of isopentane prepared from amyl alcohol.

Dr. Young, in reply said he had spent many months in purifying the materials, and was satisfied that they were pure. He was, indeed, surprised that doubt should be cast upon the matter.

In the fractionation of the pentane and isopentane, he started with considerable quantities of materials, about 1500 grms., and he obtained about 110 grms. of pure substance. The liquid was fractionated about twenty times, and the loss was nearly 20 grms. in each fractionation. There were only, as far as he knew, three isomeric pentanes, and, as they had distinctly different boiling-points, he did not see that there could be any mistake as to their identity. The critical temperatures and pressures are very delicate tests of the purity of the substance. With slightly impure ether, the difference in critical pressure is very considerable.

With regard to the fractionation of pentane and isopentane, the ordinary methods of fractional distillation would not answer. With the ordinary still-head, the loss by evaporation was greater than the gain by distillation, but the regulated still-head he had used gave most satisfactory results. He had no hesitation in saying that, with all substances which do not undergo decomposition when heated, the critical point can be determined within one-tenth of a degree.

*36. "*On the Freezing-point Curves of Alloys containing Zinc.*" By C. T. Heycock, F.R.S., and F. H. Neville.

The paper is divided into two sections, the first dealing with cases where the freezing-point of zinc is depressed by the addition of another metal, the second with the cases where it is raised by such an addition.

In Section I. complete binary alloys of the following pairs of metals, zinc-cadmium, zinc-aluminium, zinc-tin, and zinc-bismuth, are given. In the first three cases the metals appear to be miscible with each other in all proportions; but for zinc-bismuth the freezing-point curve shows the horizontal line of identical freezing-points characteristic of the state when the alloy has separated into two conjugate liquids.

Taking the freezing-point of zinc as 419°, the authors find for the temperatures of freezing and the composition of the eutectic mixtures the following:—

Alloy.	F.-P.	Atomic p.c. of zinc.
Zn—Cd	264·5	74
Zn—Al	281	11
Zn—Sn	198	84
Zn—Bi	254·5	91·8

They do not consider that there is any indication of these metals combining chemically to form definite compounds when they are melted together.

Dilute solutions of the following metals in zinc were also examined:—Lead, thallium, antimony, magnesium.

The authors find that, with the exception of aluminium and cadmium, all the above-mentioned metals, when added in small quantities to molten zinc, cause the same atomic fall; that is, an alloy containing 1 atomic weight in solution in 99 atomic weights of zinc has a freezing-point lower by 5·1° than that of pure zinc. Cadmium causes a somewhat smaller and aluminium a decidedly smaller depression. The atomic depression of 5·1°, when used with van 't Hoff's equation for the latent heat, gives 28·3 calories for the latent heat of fusion of zinc, instead of Person's value of 28·13.

In Section II. dilute solutions of copper and of gold in zinc are considered, and also a complete freezing-point curve for all alloys of zinc and silver.

When small quantities of any one of these three metals are added to molten zinc the effect is the same: the freezing-point is raised, and the whole mass of metal appears to solidify at a temperature above the freezing-point of pure zinc. The rise in the freezing-point, moreover, is proportional to the amount of the second metal present. But when as much as 2 atomic per cents of silver or of copper, or 3·3 of gold, have been added, the phenomenon alters, apparently abruptly. There are now two freezing-points, a higher one which is very fugitive, and which is followed by the precipitation of much solid, and a lower one which is very constant, and which is independent of the amount of the added metal so long as the above-mentioned minimum is present. In the zinc-silver curve singularities are also found near 70 and 60 atomic per cents of zinc, indicating the existence of more or less stable compounds; but the formula of these compounds is uncertain. Near 37·5 atomic per cents of zinc there is another well-marked angle and a series of eutectic second freezing-points, the phenomenon being possibly due to the separations of the alloy into conjugate liquids.

The authors also describe briefly some of the physical properties of the zinc-silver alloys, which appear to change in character at the angles of the curve.

The composition of the silver-zinc alloys at each freezing-point was determined by extracting a portion in the liquid state, and estimating the percentage of silver by a volumetric analysis.

Discussion.

Mr. **Newlands** asked whether the formulæ of the compounds which were supposed to exist at certain points,—viz., AgZn, $AgZn_2$, and $AgZn_3$,—represented atoms of the metals, or only that the metals were present in that proportion.

Mr. **Groves** asked whether there was any connection between the colour of the silver-zinc alloy and any of the points on the curve.

Mr. **Jenkins** asked whether the colour of the alloy was in any way due to the effect of mechanical stress during sudden cooling.

Dr. **Craw** asked whether the atoms in the alloy were in the monatomic state, and whether the alloy might be compared with a solution.

Mr. **Neville**, in reply, said the formulæ were only empirical. They were disposed to think that the dissolved metal was in a monatomic state. The colour of the alloy did not seem to have any connection with the points on the curve, and, although great mechanical stress occurred in its production, this did not seem to afford an explanation of the colour.

*37. "*The Oxides of Cobalt and the Cobaltites.*" By Arthur H. McConnell and Edgar S. Hanes,

The authors describe a method for the preparation of alkali cobaltites, and show that cobalt forms an oxide, CoO_2, and an acid, H_2CoO_3, which have hitherto been looked upon as hypothetical, and a series of alkali salts on the type of potassium cobaltite, K_2OCoO_2. The conclusions the authors arrive at are as follows:—

1. That Durrant (*Proc.*, 1896, xii., 96, 244) has not produced sufficient evidence for the existence of either cobaltic acid or cobalt percarbonate.

2. That cobaltous acid corresponds with cobalt dioxide, and forms alkali salts fairly stable in solution, which solutions have an unmistakable green colour.

3. That cobalt forms a series of compounds with other metals in which the cobalt is part of the acid radicle.

4. That cobaltous acid and cobaltites are strictly analogous to manganous acid and manganites, thus showing that the properties of cobalt are closely allied to those of the other elements associated with it in the periodic classification. Manganese is readily oxidised to the peroxide MnO_2, but cobalt much less readily yields the corresponding peroxide CoO_2.

5. In view of the fact that cobalt dioxide does undoubtedly exist in a number of compounds, the authors suggest that the oxides of cobalt should be re-named, to bring them into line with the corresponding oxides of manganese.

6. It is highly improbable that the formation of this green solution will prove to be of any use for the separation of cobalt from nickel, either quantitatively or qualitatively.

*38. "*A New Synthesis in the Sugar Group.*" By Henry J. Horstman Fenton, M.A.

In previous communications it has been shown that the acid (dihydroxymaleic acid) obtained by oxidation of tartaric acid in presence of iron decomposes, on heating with water, almost quantitatively into glycollic aldehyde and carbon dioxide. Also, that this aldehyde, when heated in a vacuum, undergoes condensation, yielding a sweet-tasting, solid gum, which has the formula $C_6H_{12}O_6$.

The present paper describes an investigation which has been made upon the properties of this condensation product.

It is easily soluble in water, and its solution quickly reduces Fehling's solution and ammoniacal silver nitrate. It gives various colour reactions characteristic of "sugars," and, after purification with alcohol, yields, with phenylhydrazine, a normal hexosazone, $C_{18}H_{22}N_4O_4$, melting at 168—170°. Heated with water to 140°, it yields furfural. It is optically inactive, and appears to be incapable of fermentation by yeast.

The purified "sugar," when further heated in a vacuum to 100—106°, loses water and becomes hard and brittle. After two to four hours' heating it has the composition $C_{12}H_{22}O_{11}$, and after twenty-four hours' heating the composition nearly approximates to $C_6H_{10}O_5$.

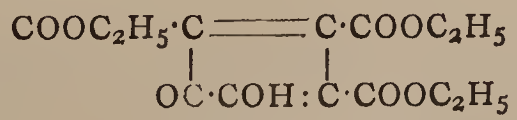
The conditions under which tartaric acid may be converted into dihydroxymaleic acid by atmospheric oxygen exhibit close analogies with some of the essential conditions of vegetable growth; and it is suggested that the direct production of a "sugar" in the manner above indicated may possibly help to throw light upon the natural formation of carbohydrates.

39. "*The Dinitrosamines of Ethylene Aniline, the Ethylene Toluidines and their Derivatives.*" By Francis E. Francis, Ph.D., B.Sc.

The dinitrosamine of ethylene aniline gives *p*-dinitroso-ethylene aniline hydrochloride on treatment with a mixture of glacial acetic and hydrochloric acids, and the resulting tetramine yields quinone on oxidation, showing that it is a *p*-diamine, ethylene-*p*-phenylene diamine. The dinitrosamines of ethylene-*o*-toluidine and ethylene-*m*-toluidine yield di-nitroso compounds, which on reduction pass into corresponding tetramines, whereas the dinitrosamine of ethylene-*p*-toluidine is decomposed. This clearly shows that in the substances investigated the nitroso-group can only pass under the treatment described to the *p*-position in the benzene nucleus.

40. "*Contribution to the Knowledge of the β-Ketonic Acids.*" Part V. By S. Ruhemann, M.A., Ph.D., and A. S. Hemmy, B.A., M.Sc.

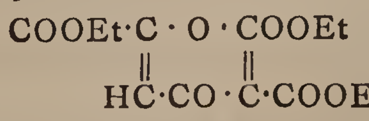
Whilst studying the interaction between the sodium derivative of ethylic oxalacetate and ethylic chlorofumarate, the authors observed the formation of two isomerides of the formula $C_{14}H_{16}O_8$. One of them, melting with decomposition at 200°, forms blue salts with alkalis which, by an excess of the reagent, become colourless. The other, which melts at 123°, does not yield coloured salts, but gives a dark red colouration with ferric chloride. The authors arrive at the view that in the formation of these compounds, ethylic oxalacetate alone takes part, and they represent the constitution of the substance decomposing at 200° by the formula—



$$\begin{array}{lcl} \mathrm{COOC_2H_5{\cdot}C} & = & \mathrm{C{\cdot}COOC_2H_5} \\ \quad\quad\quad\quad | & & | \\ \quad\quad\quad \mathrm{OC{\cdot}COH} & : & \mathrm{C{\cdot}COOC_2H_5} \end{array}$$

Ethylicanhydro-oxalaconitate,

the other by the symbol—



$$\begin{array}{lcl} \mathrm{COOEt{\cdot}C} & \cdot\ \mathrm{O}\ \cdot & \mathrm{COOEt} \\ \quad\quad\quad \| & & \| \\ \quad\quad \mathrm{HC} & \cdot\mathrm{CO}\cdot & \mathrm{C{\cdot}COOEt} \end{array}$$

Ethylicpyronetricarboxylate.

41. "*Enantiomorphic Forms of Ethylpropylpiperidonium Iodide.*" By Clare de Brereton Evans.

It has been found that ethylpropylpiperidonium iodide ($C_5H_{10}EtPrNI$) may be obtained from its solution in absolute alcohol, in right-handed and left-handed crystals. The enantiomorphism, however, is of a purely crystallogenic order, due to the arrangement of the molecules in the crystal, and not to the position of the atoms in space. This is proved by the optical inactivity of the substance in solution, as well as by the fact that either variety may be converted into the other by re crystallisation, the behaviour being like that observed in the case of sodium chlorate and bromate, &c., &c.

42. "*Further Note on Ketopinic Acid — Pinophanic Acid.*" By W. S. Gilles and F. F. Renwick.

The further investigation of the acid obtained by oxidising the solid hydrochloride from pinene with the strongest nitric acid (*Trans.*, 1896, lxix., 1397) has brought to light a variety of interesting points.

Although bromine alone does not attack it, ketopinic acid is readily brominated if a small quantity of phosphorus be present; the product has the formula—

$C_{10}H_{13}O_3Br$. (C=46·18; 46·06; H=4·96, 5·00; Br=30·70. Calc. C=45·98; H=4·98; Br=30·66).

Monobromoketopinic acid melts at 181°; it is readily soluble in ether, acetone, acetic acid, and ethylic acetate, but sparingly so in benzene, chloroform, and hot water. When heated with aniline or quinoline, it is re-converted into ketopinic acid.

The hydroxime of ketopinic acid is merely hydrolysed when boiled with 50 per cent sulphuric acid, being reconverted into ketopinic acid.

When cautiously fused with caustic soda, or even when boiled with an alcoholic solution of sodium ethylate, ketopinic acid is converted into a dibasic acid, *pinophanic acid*, of the formula—

$C_{10}H_{16}O_4$ (C=60·14, 60·13; H=7·86, 8·02; Ag in silver salt =51·87, 52·03. Calc. C=60·00; H=8·00; Ag=52·17).

Pinophanic acid melts at 203°; it is insoluble in benzene, light petroleum, and chloroform, moderately soluble in hot water and hot ethylic acetate, and readily soluble in alcohol, acetone, and ether. Like ketopinic acid, it does not combine with bromine.

Although but slowly attacked, ketopinic acid is oxidised by prolonged digestion with neutral potassium permanganate solution. The product appears to be identical in composition with Kipping's camphotricarboxylic acid and Marsh and Gardner's camphoic acid, but more closely resembles the latter.

These acids are now being fully investigated.

43. "*A Synthesis of Citric Acid.*" By W. T. Laurence, B.A., Ph.D.

Ethylic citrate was obtained synthetically by the condensation of ethylic bromacetate with ethylic oxalylacetate in the presence of zinc, as indicated by the following equations:—

(1) $COOEt{\cdot}CH_2Br + COOEt : CH_2{\cdot}CO{\cdot}COOEt + Zn = = COOEt{\cdot}CH_2{\cdot}C(OZnBr)(CH_2{\cdot}COOEt){\cdot}COOEt.$

(2) $COOEt{\cdot}CH_2{\cdot}C(OZnBr)(CH_2{\cdot}COOEt){\cdot}COOEt + H_2O = = COOEt{\cdot}CH_2{\cdot}C(OH)(CH_2{\cdot}COOEt){\cdot}COOEt + Zno + + HBR.$

The yield of ethylic citrate is very poor, owing to other reactions proceeding simultaneously. To further confirm the formation of ethylic citrate, it was converted into the calcium salt of citric acid, and a substance obtained showing the characteristic properties of calcium citrate. The same salt was also obtained by heating the zinc compound formed in equation No. 1 with alcoholic potash and precipitating the calcium citrate from the hot solution.

The results were all confirmed by analysis. The above synthesis of citric acid seems to be of interest as being more direct and simple than the synthesis from sym-dichloracetone or from ethyl-γ-cyanacetoacetate.

Ordinary Meeting, March 18th, 1897.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Messrs. H. P. Stevens, J. W. Walker, W. Arbuckle, N. T. N. Wilsmore, M. Wildermann, W. J. Pope, A. W. Crossley, H. R. Le Sueur, J. H. Miller, R. D. Littlefield, F. H. Neville, W. M. Heller, G. McGowan, C. M. Crossman, J. Holmes, and F. Southerden were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Alfred Hunter Boylau, Ellerslie, Richmond Road, Ealing, W.; Henry Norris Davidge, 37, Duke Street, Grosvenor Square, W.; Charles Henry Field, The Elms, Green Street Green, Orpington; Thomas Girtin, B.A., 125A, Highbury New Park, N.; James Jones, 117, Old Christchurch Road, Bournemouth; Charles MacCulloch, 395, Collins Street, Melbourne; George Fowlie Merson, 65, Northumberland Street, Newcastle; Thomas Tickle, 4, Packenham street, W.C.

In accordance with the By-laws, the following communication was read from the Chair:—

We, the undersigned, beg to propose Prof. William Ramsay, Ph.D., F.R.S., as President of the Chemical Society in succession to Mr. A. Vernon Harcourt, M.A., M.D., D.C.L., F.R.S.:—

Baly, E. C. C.; Baker, C. F.; Burgess, Herbert E.; Blount, Bertram; Blundstone, Edward, R.; Berncastle, Richard; Cassal, Charles E.; Chattaway, F. D.; Chapman, Alfred C.; Collie, J. Norman; Chorley, John C.; Coste, J. H.; Crossley, Arthur; Dufton, S. T.; Ekins, Arthur E.; Edwards, W. Buckland; Evans, R. C. T; Elborne, William; Earle, Alfred; Elford, P.; Forster, M. O.; Graham, Edward; Grimwood, R.; Harley, Vaughan; Harvey, Sydney; Baker, Julian L.; Floris, R. B.; Jackman, E. J.; Jones, Cecil; Johnson, David; Kipping, Stanley F.; Kellas, Alex. M.; Kingzett, C. T.; Ling, A.; Lapworth, A.; Livingston, W. T.; Littlefield, R. D.; Routledge, R.; Lamb, Edmund; Moody, Gerald T.; Bodmer, R.; Moor, C. G.; Millar, J. H.; McCrae, J.; Macdonald, G.; Mills, Charles; McGowan, Geo.; Pope, W. J.; Parry, Ernest J.; Picton, Harold; Plimpton, R. T.; Richmond, H. Droop; Simpson, Arthur M.; Stevens, H. P.; Travers, M. W.; Le Sueur, H. R.; Wade, John; Wagner, W. G.; Wilsmore, N. T. M.; Walker, J. Wallace; Sworn, Sydney A.; Cornish, Vaughan; Sykes, Walter J.; Waterhouse, Robert; Chattaway, William; Priest, Martin; Marsh, J. E; Muspratt, Edmund K.; Mitchell, C. A.; Muspratt, Sydney K.; Adams, Arthur; Marshall, Arthur; Wilson, John; Bone, W. A.; Fisher, E. H.; Chapman, Arthur J.; Wheelwright, E. W.; Lewis, W. H.; Sudborough, J. J.; Veley, V. H.; Walker, James; Colman, Harold G.; Christopher, George; Macnair, D. S.; Bell, Chichester A.; Wertheimer, J.; Hodgkin, John; Archbutt, Leonard; Muir, M. M. Pattison; Shaw, G. E.; Taylor, R. L.; Colwell, J. Kear; Cribb, Cecil H.; Butterfield, W. J. Atkinson; Hanes, Edgar S.; Sutherland, D. A.; Teed, Frank L.; Fulcher, L. W.; Heller, W. M.; Sandford, P. Gerald; Snape, H. Lloyd; Knight, J. B.; Cooper, A. J.; Adams, P. T.; Adams, M. A.; Eiloart, A.; Corfield, W. H.; Muter, J.; Muter, A. H. M.; Dodd, W. H.; Koningh, L. de; Mawer, W. F.; Lascelles, P. B.; Bruce, James; Turpin, G. S.

Professor Collie stated that the nomination of Professor Ramsay had been made without his knowledge or his permission.

Of the following papers those marked * were read:—

*44. "*On the Atomic Weight of Carbon.*" By ALEXANDER SCOTT, M.A., D.Sc.

The object of this paper is to call attention to the unsatisfactory nature of the experimental evidence on which the determinations of the atomic weight of carbon rest. The two methods on which reliance is chiefly placed are shown to be only in agreement because a source of error which affects both acts in opposite directions. This is due to an erroneous determination of Dumas and Stas, in 1840, of the expansion produced in potash solutions by the absorption of carbon dioxide. All later workers at this problem seem to have accepted their conclusions without further verification. The seriousness of this source of error is apparent when we consider that over 40 m.grms. is the correction for the weight *in vacuo* of the carbon dioxide in one experiment alone. The correction per grm. of carbon dioxide is shown to be 0·56 to 0·57 c.c., instead of 0·15 c.c. as taken by Dumas and Stas. The probable effect of the gases "occluded" in the copper oxide is next considered, and, as far as possible, allowed for. It is shown by many determinations that the experiments of Richards give the quantity as much too great, the mean result of his best experiments being 0·088 per cent by weight of nitrogen in copper oxide made from the nitrate, whilst the experiments here described give as a mean only about 0·007 per cent.

Other sources of error and the best methods of making more accurate determinations are next considered. The re-calculated values are 12·008 from the combustion of the various forms of carbon, and 12·050 from the conversion of the monoxide into the dioxide.

DISCUSSION.

In reply to questions from Mr. GROVES, Mr. BLOUNT, Mr. HEYCOCK, and the PRESIDENT, Mr. SCOTT stated that 150 grms. of the oxalate furnished about 4 grms. of carbon. In the case of the potash solution, it was the expansion of the liquid which had to be corrected for. The rate of absorption of carbon dioxide by potash solution at any given time was affected by the amount of carbon dioxide which had been already absorbed. Carbon monoxide was completely absorbed by potash after some time.

*45. "*On a New Series of Mixed Sulphates of the Vitriol Group.*" By ALEXANDER SCOTT, M.A., D.Sc.

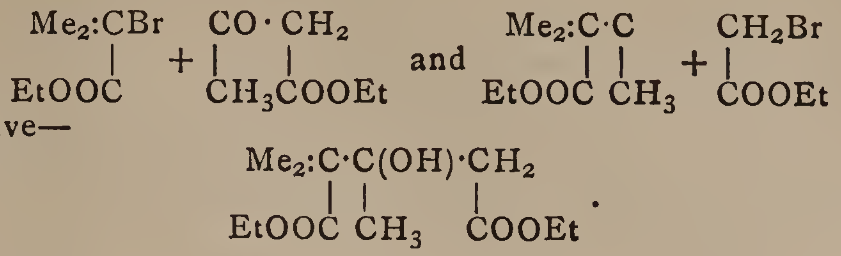
This paper describes a new series of mixed sulphates of the form $(M,N)''SO_4\,H_2O$. The most interesting is the ferrous cupric sulphate, the colour of which is reddish brown; it dissolves in water, giving a blue green solution. The composition of this salt on analysis corresponds to the formula $(CuFe)SO_4,H_2O$, or $(Fe_5Cu_2)(SO_4)_7,7H_2O$. These salts are made by adding about an equal bulk of strong sulphuric acid to solutions of the mixed sulphates.

DISCUSSION.

Mr. SPILLER, referring to investigations he had conducted on some double sulphates of this group, crystallised from water, the results of which were communicated to the British Association ten years ago, said that he was led to the conclusion that the amount of water of crystallisation in such mixed sulphates was the mean of that present in their constituent salts.

*46. "*A Synthesis of Camphoronic Acid.*" By WILLIAM HENRY PERKIN, jun., F.R.S., and JOCELYN FIELD THORPE, Ph.D.

In a previous communication (*Proc.*, 1896, xii., 155) experiments were described dealing with the action of metallic zinc on mixtures of bromo-ethylic salts and ketones or ketonic acids; notably on mixtures of ethylic aceto-acetate and ethylic α-brom-iso-butyrate, and of ethylic dimethylacetoacetate and ethylic bromoacetate, and it was shown that the same hydroxy-ethylic salt, namely, ethylic-β-hydroxy-α-α-β-trimethyl glutarate was in each case produced thus:—



$$\begin{array}{c}\mathrm{Me_2{:}CBr}\\ |\\ \mathrm{EtOOC}\end{array} + \begin{array}{cc}\mathrm{CO\cdot} & \mathrm{CH_2}\\ | & |\\ \mathrm{CH_3} & \mathrm{COOEt}\end{array} \text{ and } \begin{array}{cc}\mathrm{Me_2{:}C\cdot} & \mathrm{C}\\ | & |\\ \mathrm{EtOOC} & \mathrm{CH_3}\end{array} + \begin{array}{c}\mathrm{CH_2Br}\\ |\\ \mathrm{COOEt}\end{array}$$

give—

$$\begin{array}{ccc}\mathrm{Me_2{:}C\cdot} & \mathrm{C(OH)\cdot} & \mathrm{CH_2}\\ | & | & |\\ \mathrm{EtOOC} & \mathrm{CH_3} & \mathrm{COOEt}\end{array}.$$

This *ethylic-β-hydroxy-α-α-β trimethylglutarate* (b. p. 165°, 30 m.m.), as previously stated, splits up, on hydrolysis with alcoholic potash, into acetic and isobutyric acids. When, however, it is boiled with dilute hydrochloric acid, it does not behave in this way, but yields considerable quantities of the corresponding *β-hydroxy-α-α-β-trimethylglutaric acid*,—

$$COOH{\cdot}C(CH_3)_2{\cdot}C(OH){\cdot}(CH_3){\cdot}CH_2{\cdot}COOH,$$

which is a crystalline body, separating from a mixture of light petroleum and ethylic acetate in glistening prisms melting at 128°.

In the previous communication, an acid melting at 148°, obtained by the action of alcoholic potassium cyanide on ethylic-β-brom-α-α-β-trimethyl glutarate, was described as a trimethylglutaric acid: we now wish to correct this statement. Alcoholic potassium cyanide is apparently without action upon the bromethylic salt at the temperature of the boiling water-bath, and, on hydrolysing the product with alcoholic potassium hydroxide, the unsaturated acid, *α-α-β-trimethylglutaconic acid*,—

$$COOH{\cdot}CH{:}C(CH_3){\cdot}C(CH_3)_2COOH,$$

melting at 148°, is produced, and not the trimethylglutaric acid as was at first supposed. This acid is remarkably stable, and is not affected by boiling with sodium amalgam. When, however, its boiling solution in alcohol is treated with sodium, the unsaturated acid is gradually reduced to *α-α-β-trimethylglutaric acid*, $COOH{\cdot}CH_2{\cdot}CH(CH_3){\cdot}C(CH_3)_2{\cdot}COOH$, which crystallises from dilute hydrochloric acid in prismatic needles melting at 109°; the anhydride of this acid melts at 38°, and yields, on treatment with aniline, an *anilic acid* forming lustrous plates from dilute alcohol melting at 155°. Although the melting-points of the acid and of the anil are very similar to those of the trimethylglutaric acid which Balbiano obtained from camphoric acid, it does not appear that the acids are identical, and it is probable that Balbiano's acid is the isomeric α-β-β-trimethylglutaric acid,—

$$COOH{\cdot}CH(CH_3){\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}COOH,$$

as this chemist suggests.

On treating ethylic β-hydroxy-α α-β-trimethylglutarate with phosphorus pentachloride, the chlorethylic salt, namely, *β-chlor-αα β-trimethyl glutarate*,—

$$COOC_2H_5C(CH_3)_2{\cdot}C(Cl){\cdot}(CH_3){\cdot}CH_2{\cdot}COOC_2H_5,$$

is obtained as a colourless mobile liquid which boils at 139° (20 m.m.). When this substance or the corresponding bromo-derivative is heated with alcoholic potassium cyanide in a closed tube at 160° *ethylic-β cyano-α-α-trimethyl glutarate*,—

$$COOEt{\cdot}C(Me_2){\cdot}C{\cdot}(CN){\cdot}(Me){\cdot}CH_2{\cdot}COOEt,$$

is obtained after twelve hours as an oily liquid boiling at 180—185° (25 m.m.). It is difficult to isolate in the pure condition owing to the presence of varying quantities of the ethylic salt of trimethylglutaconic acid, a substance which boils at about the same temperature as the nitrile (175°, 30 m.m).

This nitrile was hydrolysed by boiling with dilute hydrochloric acid, and after filtering from the trimethylglutaconic acid, which separated on cooling, the filtrate yielded on neutralisation with ammonia and addition of barium chloride no precipitate, but on boiling, a quantity of a sparingly soluble barium salt separated. This salt was collected, well washed, and decomposed by boiling with the calculated quantity of sulphuric acid; the filtrate from the barium sulphate was then evaporated to a small bulk, when on cooling a crystalline acid separated, which melted at 157° with decomposition, and on analysis gave the following numbers:—

0·1258 grm. gave 0·2276 grm. CO_2 and 0·0746 grm. H_2O. Calc. for $(C_9H_{14}O_6)$: H=6·40; C=49·50. Found: H=6·58; C=49·34. *α-α-β-Trimethyltricarballylic acid*, $COOH{\cdot}CH_2C(COOH)(Me)C(Me_2)COOH$.

That this acid is identical with camphoronic acid is, in our opinion, proved by the following considerations:—

(1). The synthetical acid gives the same results on analysis, and melts at the same temperature as camphoronic acid.

(2) When equal quantities of the synthetical acid and camphoronic acid are intimately mixed, the mixture melts at exactly the same temperature, *i.e.*, 157°, with decomposition.

(3) It gives, when dissolved in a slight excess of ammonia, no precipitate with barium chloride until the liquid is warmed, and then the insoluble barium salt separates exactly as in the case of camphoronic acid.

(4) When heated with acetyl chloride, both the acids are converted into an anhydro-acid, which melts in both cases at 135—136°.

The anhydrocamphoronic acid from the synthetical acid gave on analysis the following results:—Found, C=54·03; H=6·11. $C_9H_{12}O_5$ Calc. C=54·00; H=6·00 per cent.

In a previous communication (*Proc.*, 1896, xii., 192),* one of us had occasion to express the opinion that Tiemann's formula for camphoronic acid,—

$$COOH{\cdot}CH(CH_3){\cdot}C(CH_3)_2{\cdot}CH{\cdot}(COOH)_2,$$

which contains the group $-CH(COOH)_2$ must be incorrect, on account of the fact that camphoronic acid, when heated with water at 230°, is not decomposed with elimination of CO_2. The experiments which we have briefly described in this communication appear to us to prove that camphoronic acid has the constitution first proposed by Bredt (*Ber.*, 1893, xxvi., 3048), namely, that of an $\alpha\alpha\beta$-trimethyltricarballylic acid,—

$$COOH{\cdot}C(CH_3)_2{\cdot}CCH_3(COOH){\cdot}CH_2{\cdot}COOH.$$

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, March 26th, 1897.

Mr. Shelford Bidwell, President, in the Chair.

At the invitation of Dr. S. P. Thompson, the meeting was held at the Technical College, Leonard Street, Finsbury.

Mr. Rollo Appleyard read a paper on "*Liquid Coherers and Mobile Conductors*," and showed the following experiments:—

(1.) A glass tube, containing mercury and paraffin oil, is shaken up until the mercury divides into small spheroids. The resistance of the chain of spheroids under these conditions is several megohms. Coherence can be brought about by a direct current, a spark, or by a Hertz oscillator. The coherence is visible, the spheroids forming into large globules. At the same time, the resistance falls to a fraction of an ohm. (2.) An unstable emulsion is formed by shaking water and paraffin oil together, in a glass tube, called by the author a "rain" tube. The oil may be coloured with alkanet root. By electrification, the water suspended in the oil is suddenly precipitated in a shower through the oil, precisely as rain is precipitated in the air, after thunder. (3.) A mixture of paraffin oil and water is poured into a photographic dish, just covering the bottom, and a little mercury is poured in. Any two separate globules of mercury in the dish are then connected by wires to a battery of about 200 volts, through a reversing-key. A momentary tap of the key causes instantaneous deformation of the mercury, especially of the globule connected to the negative pole. If the current is kept on, the negative globule sends forth a long tentacle of mercury across the dish to the positive globule. The tentacle may break into spheroids. Intermediate globules send forth "fingers" towards the positive terminal-globule, and, by continued application of the current, the "fingers" link intermediate globules,—illustrating the nature of liquid coherence. By using the current-reverser as a telegraphic transmitting-key, the motions, to right or left, of the "finger" of any stray globule, may be interpreted to form the letters of the Morse code. By a succession of taps of the key in one direction or the other, a globule can be made to "caterpillar" along the dish.

Prof. Ramsay said he had once attempted to facilitate churning by the application of 8 or 9 volts to some milk. He thought the cream came a little faster, but it turned sour very quickly.

Prof. Fitzgerald thought that the effects observed in experiment 3 were the result of current, and not of electrostatic changes; and he would like to know the value of the actual current used. There was no doubt that the motions were due to variations in capillarity.

Mr. Shelford Bidwell asked how the mercury was formed into spheroids in the tube in experiment 1.

Mr. Appleyard, in replying to Prof. Fitzgerald, said it was not easy to define the circuit, as the terminal-globules were rather capricious, but he would try and measure the current in some particular case. The mercury-tube in experiment 1 was shaken in a horizontal plane; the operation took about ten minutes. Equal volumes of mercury and oil was a good proportion. One quarter of the length of the tube should be left as an air-space.

Prof. Dalby then exhibited five pieces of apparatus:—(1.) A Kinematic Slide. (2.) An Inertia Apparatus with trifilar suspension. (3.) A Wilberforce Spring. (4.) An Ewing's Reading-telescope. (5.) A Kinematic Hook-gauge. Models 1, 2, 4 and 5 illustrated the various degrees of freedom of bodies restrained at different numbers of points. It was shown with 3 that in extending a spiral spring there results a certain amount of twisting. If a mass is hung at the lower end of the spiral in such a way that, when suddenly released after extension of the spring, the time of oscillation of the mass in the horizontal plane (rotation) is the same as the time of vertical oscillation, then the tendency to twist results in a change of energy which alternates between the rotary and linear forms.

Mr. Boys drew attention to the conditions of restraint, and suggested a criterion for determining whether a piece of mechanism was designed for minimum strain on the structure: a thin wedge slipped under any one point of contact should not disturb the other points of restraint.

Prof. Fitzgerald pointed out the effect of symmetry upon the motion of the spring of 5. The spiral happened to be an unsymmetrical form; the change of phase from vertical to rotary oscillation was therefore rapid. In the case of the vibration of a symmetrical stretched cord the change of phase would be very slow.

Dr. Thompson exhibited two Kinematic Models depending upon the principle that any simple harmonic motion may be considered as the resultant of two oppositely directed motions. The first illustrates the synthesis of two opposite circular motions of equal period and magnitude to form a straight line motion; the second shows the combination of two simple harmonic motions of equal period and amplitude in any difference of phase, to form a circular motion. In each case the motion is communicated to a stylus by a link-gear, operated by two wheels rotating in opposite directions. In the first appa-

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* The formula given here from Bredt's constitution of camphoronic acid is a misprint, it should be—

$$COOH{\cdot}C(CH_8)_2{-}C(CH_8)(COOH){-}CH_2{\cdot}COOH.$$

ratus the wheels are pivoted about their centres, and the link-gear is pinned to one point on the flat surface of each wheel, near the circumference; in the second apparatus the wheels rotate as eccentrics at 180° to one another, and the motion to the link-gear is communicated by thrust-rods, held by springs against the peripheries of the corresponding wheels.

Dr. **Thompson** further exhibited a device for projecting, by lantern, the rotating magnet and copper disc of Arago. The curious rotations and lateral movements of iron-filings, in a revolving magnetic field, were similarly projected on a screen. He also showed some experiments with a heat-indicating paint, made from a double iodide of copper and mercury, discovered twenty years ago by a German physicist. At ordinary temperatures the paint is red, but at 97° it turns black. If paper is covered with this substance, and then warmed at a stove, the change is effected in a few seconds. Various designs can be wrought upon the back of the paper in dead-black or gold, so that when warmed they appear in red or black on the front, according to their respective absorptive powers. Or local cooling by the hand will yield a silhouette. If the paper is allowed to cool, the silhouette vanishes, but it appears again when the paper is re-heated. It has thus a kind of thermal "memory." A yellow double iodide of silver and mercury is even more sensitive. It changes from yellow to dark red at 45° C.

Lastly, Dr. **Thompson** exhibited a Kinematic Model of Hertz-wave Transmission. A row of lead bullets is suspended from strings, so that the bullets hang clear of one another by about an inch, in a right line. The strings are meshed, and herein the model differs from the well-known wave-models used in acoustics. If the attempt is made to send an acoustic form of wave through the system, by giving an impulse to the first bullet in the plane of the other pendulums, it fails immediately, owing to the slackening of parts of the meshes. Thus only *transverse* vibrations can be transmitted. To illustrate the propagation of a Hertz-wave, a heavy pendulum, oscillating in a plane at right angles to the line of bullets, at one end, represents the Hertz "oscillator." A metal ring, mounted horizontally on a trifilar suspension, and properly "tuned," represents, at the distant end, the Hertz "resonator." Waves, formed by the transverse vibrations of successive bullets, are then propagated from end to end.

Prof. **Fitzgerald** said the model was specially interesting as illustrating the difference in velocities of propagation of a given wave, and of the energy corresponding to it. The model did not accurately compare with ether, because in ether the rate at which the energy is propagated is the same as that of the wave. The difference of the two rates, for any medium, depended upon the "dispersion" of the medium. By slight alteration of the pendular-suspensions this dispersion might be made different at different parts of the model, and would then correspond to certain known cases of "anomalous" dispersion. Or again, it might be made to illustrate the theory of Helmholtz with regard to the vibrations of the molecules of glass; according to which, the vibration of the molecules alters the vibrations of the waves, so that dispersion occurs, and the energy is not propagated at the same rate as the waves themselves. It was shown by Michaelson that it was possible to have a medium in which the energy is propagated in one direction and the wave in another. This was attained, in a magnetic model, by Ewing. The mesh apparatus indicated how a model could be made which should give our "harmonics" and "over-tones" very different from one another; where different wave-lengths would be propagated with different velocities, and the over-tones would correspond to the differences. Further, it indicated a mechanism for producing any desired spectrum, such, for instance, as that of hydrogen. A somewhat similar model had been designed by Glazebrook for illustrating the absorption-bands of a medium when the rate of vibration was the same as the free period of the vibrations of each of the molecules, which is the theory of Helmholtz, but it was not such a simple model. The experiment of red paper changing to black was interesting as illustrating a red spectrum varying with temperature.

Mr. **Shelford Bidwell** proposed a vote of thanks to all the exhibitors, and the Society adjourned until April 9th.

NOTICES OF BOOKS.

Principles and Practice of Agricultural Analysis: a Manual for the Examination of Soils, Fertilisers, and Agricultural Products. For the Use of Analysts, Teachers, and Students of Agricultural Chemistry. Vol. III. — *Agricultural Products.* By **Harry W. Wiley**, Chemist to the U.S. Department of Agriculture. Easton, Pennsylvania: Chemical Publishing Co. 1897. Pp. 644.

This volume opens with a carefully compiled dissertation on sampling, drying, incineration, and extraction—subjects in which it is possible, even for experienced practitioners, to go astray, with grievous inconvenience and injury to their professional reputation.

As regards the scope of the work, we note that whilst hops are included, opium with of course morphia are left outside the pale. Nor are organic matters, odoriferous and tinctorial, admitted, except as regards the pigments of wines. The importance and the delicacy of the procedures for desiccation and incineration are certainly not exaggerated. The apparatus for dyeing samples *in vacuo* or in currents of inert gases, though somewhat complicated, will be found of great utility.

Part II. is devoted to sugars and starches. In considering the areometric method for the determination of sugars, we regret to find the total omission of Twaddle's instrument and scale in favour of Baumé.

Part III. treats of the separation and determination of carbohydrates in agricultural products, crude and manufactured; and Part IV. deals with fats and oils. Here the usual analytical methods are expounded. It is truthfully admitted that the spectroscope is of little practical utility in oil analysis.

In the fifth, sixth, and seventh parts, we find an account respectively of the separation and determination of nitrogenous bodies, of dairy produce, and of miscellaneous agricultural products. Here the defects of ensilage are admitted. The writer condemns as fraudulent the sale of horse-flesh as beef and pork, but he rightly holds that it is unobjectionable if sold under its own name.

The author's orthography is apt to set the teeth of us Britishers on edge, and raises the question why, if Americans have gone so far in the "fonetic" direction, they do not fully adopt the code of the spelling reformers?

Concerning the value of Mr. Wiley's work as a whole, there can be no difference of opinion.

Chapters on the Aims and Practice of Teaching. Edited by **Frederick Spencer**, M.A., Ph.D., Professor of the French Language of Literature at the University College of North Wales; formerly Chief Master on the Modern Side at the Leys Schools, Cambridge. Cambridge: University Press. 1897. 8vo., pp. 284.

Much of this book deals with subjects on which our opinion is little more valuable than that of the "man in the street." At the same time, whilst admitting the wealth of thought which is here put forth, we must presume to express our regret at the predominating "verbalism" of some of the writers. Too often they seem to forget the glaring facts that so long as boys are compared by the figure which they make in classical subjects the gravest mistakes are committed. Every one knows that Justus Liebig and Charles Darwin were in their school-days set down as hopeless dunces. But when released from verbalism they became, each in his department, great creative spirits, of more value to the world than generations of grammarians. Yet one of the writers here before us "has no hesitation in saying that, on the average, boys trained on the classical side of our public schools make better men of science and medicine than the boys who come to the University from the modern side; for the classics develop the power of sustained and orderly thinking!" Our conclusion is, that the power of sustained and close observation, as required by the chemist and the biologist, is checked by classical studies. The writer seems to detect objections to the study of physiology which strike us as singular. The "honest boy" discussed on p. 275 must be a morbid, and we believe a rare, phenomenon.

The objections urged against zoology, as tending "to become uncleanly," cannot apply to its widest, most interesting, and at the same time most utilitarian department—entomology.

The writers of these "Chapters" merit full recognition as being unfriendly to the modern educational idol, examinationism. Hence we must conscientiously and warmly recommend it to the heads of colleges.

The University of Nebraska. Calendar, 1896-1897.

The University of Nebraska is in some respects exceptional in its constitution. Unlike the German universities, but like those of Britain, it has what we may venture to call a faculty of music. Unlike all the European seats of learning, it includes painting, sculpture and architecture, and elocution and oratory in its scope. In other words, according to Section 5211 of its Rules, it comprises a college of literature, science, and art; secondly, an industrial college, embracing agriculture, practical science, civil engineering, and the mechanical arts; third, a college of law; fourthly, a college of medicine; fifthly, a college of the fine arts.

Section 5221 enacts that no person shall—because of age, sex, colour, or nationality—be excluded from the privileges of this institution. This sweeping proviso might, we submit, be amended by fixing a junior limit of age for matriculation. For "colour" we would, had we the right to interfere, substitute "race."

There is here, as it appears to us, too great a tendency to commit different duties to one and the same person. Thus we find a professor of entomology, ornithology, and *taxidermy*. Taxidermy is generally the duty of the curator or "custos." We perceive that there are at the Nebraska University a chemical laboratory, a philosophical laboratory, and a physical laboratory, as well as a botanical and an electrical. It must be at times difficult to define the scopes and duties of the different laboratories.

The "sugar school" confines its attention to practical study of the beet sugars.

A branch of study, concerning which we feel in some doubt, is known as "civics," and, considered in conjunction with political economy, "electives" may mean optional courses of study.

There is also a department for military studies, doubtless for tactics and strategy.

New Process of Sterilisation by Heat under Pressure.—W. Kühn.—The author's experiments show that when the conditions of heating prevent all loss of gas and of aromatic and volatile principles the liquid is unchanged in its argonoleptic properties.—*Compt. Rend.*, cxxiv., No. 9.

CORRESPONDENCE.

THE CHEMICAL SOCIETY ELECTION.

To the Editor of the Chemical News.

Sir,—At the Chemical Society meeting, March 18, 1897, I made the statement that the nomination of Professor W. Ramsay as a candidate for the Presidentship of the Chemical Society was made without his knowledge or consent. To the best of my belief, and so far as I have any means of judging, that was an accurate statement. I have seen a letter in the Chemical News from Prof. Armstrong in which he "ventures to doubt the accuracy of that statement." I wish to state distinctly that he has no ground whatever for his doubt. When I made my statement I was sure of my facts and I am so still.—I am, &c.,

J. Norman Collie.

16, Campden Grove, Kensington, W.,
April 1, 1897.

THE NEW SCIENTIFIC CLUB.

To the Editor of the Chemical News.

Sir,—My attention has been called to the fact that my name appears on a circular, signed "Robert Ingram," relating to the proposed formation of a new Scientific Club. I wish to say that the use of my name in this connection is entirely unauthorised. I have no intention of joining any Club promoted by Mr. Robert Ingram.—I am, &c.,

T. E. Thorpe.

March 25, 1897.

TEACHING OF CHEMISTRY.

To the Editor of the Chemical News.

Sir,—The importance of this subject is the only apology I offer for re-opening the discussion. Its importance to the rising generation of chemists, manufacturers, &c., is obvious.

Mr. Beebe adduces three reasons why the novice, at the outset of his career, should not devote his time to the preparation of gases, salts, and such like. I will take them in order:—

1. *That they are dangerous.*—Mr. Wigley, who, judging from his letter, must have had a lengthened experience as a teacher of chemistry, says "that there is more danger in acid from a test-tube being boiled over a neighbour's face than in making hydrogen." I agree with him; for, as far as my experience goes, I have never seen any one hurt in the preparation of the latter, whereas several instances have come under my notice in which boiling acid or other liquid has been shot out into a fellow student's face.

2. *Failure in connecting the various experiments.*—I think the boot is on the other foot. There is a great similarity between a good many of the experiments leading from one thing to another. Take as an example $KClO_3$,NH_4NO_3,NH_4NO_2,$H_2C_2O_4$, and many other substances which, when heated, split up into simpler bodies, whereas in precipitating a substance a more complex compound is often produced.

3. *Does not awaken and hold students' interests like Qualitative Analysis.*—My answer to this is, if the student is guided aright he very soon acquires sufficient powers of observation to find them interesting, and he gets a thorough grounding in the fundamental truths of chemistry whereby he may become a sterling and intelligent chemist. Such has been my experience of students.

Mr. Beebe remarks that lecture experiments are unnecessarily complex, and students' ideas confused and hazy. Does not this statement controvert his own objection to the students performing his own experiments?

To commence a beginner's course of chemistry with qualitative analysis is tantamount to teaching a boy who is intended to become a musician the art of turning the handle of a barrel organ. A novice is incapable of intelligently understanding what he does in qualitative analysis, or why he does it. I agree with Mr. Beebe that the first lessons should be as simple as possible. But which is the easier for the young student to understand (I take the simplest instance in each case), $AgNO_3 + HCl = AgCl + HNO_3$ or $HgO = Hg + O$? I say most decidedly the latter.

I regret to find that Mr. Beebe thinks a man is a "real chemist" when he can work through an arbitrary analytical table and discover what a simple salt is. I have met with men capable of telling most ordinary substances simply by looking at them, and who had no idea of the reaction that occurs when carbon is burnt. These I presume must be more "real chemists" still.—I am, &c.,

C. Sordes Ellis, A.I.C., F.C.S.,
Late Demonstrator to the Pharm. Soc. of Great Britain.

The Technical School,
Radcliffe, Lancashire,
March 19, 1897.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 10, March 8, 1897.

Researches on the Earths contained in Monazitic Sands. — MM. Schützenberger and Boudouard. — The authors have separated: — 1. A cerium of an atomic weight bordering upon 138 or somewhat lower, the solution of which is not precipitated by copper oxide. 2. A cerium of an atomic weight close upon 148, the sulphate of which is precipitable by copper oxide and also by sodium sulphate. 3. A cerium of an atomic weight close upon 157, its sulphate being precipitable by copper oxide, but not by sodium sulphate. The solutions of this sulphate are characterised by the gummy aspect which they take during concentration. These three earths yield yellow ceric salts decomposable by heat into white cerous salts. Hydrogen peroxide with soda precipitates them with an orange-red colour. Ammonium oxalate precipitates all these, and the precipitates are not soluble in a cold excess of the reagent. No difference between the three earths is detected on spectroscopic examination. The portion soluble in neutral ammonium oxalate, and not precipitable by sodium sulphate, does not display the coloured reactions of cerium. It belongs to the thorium group. The experiments indicate that we have not to do with a homogeneous product.

Apparatus employed for Collecting Air at Great Heights in the Ascent of the Aërophile on February 18, 1897. Analysis of the Air collected.—L. Cailletet. —In 100 vols. of air deprived of carbonic acid, and taken at the height of 15,500 metres, there was found—

Oxygen	20·79 vols.
Nitrogen	78·27 ,,
Argon	0·94 ,,

The ratio of argon to the total of nitrogen plus argon = 0·01185.

Action of Phosphorus upon Gold. — A. Granger. — The author, after referring to the experiments of Schrötter, Hautefeuille, and Perry, states that he has obtained a gold phosphide, Au_3P_4, of a grey colour and very brittle. It is easily destroyed if heated in contact with air, and is readily attacked by chlorine and aqua regia.

Determination of Antimony as Peroxide. — H. Baubigny.—This paper will be inserted in full.

Action of Free Bases upon Salts.—Albert Colson.— The decomposition of ammoniacal salts is a phenomenon of heterogeneous dissociation, comparable to the decomposition of lead chloride by sulphuric acid.

A New Derivative of Phenylisindazol obtained by the Action of Salicylic Aldehyd upon Phenylhydrazin.—H. Causse.—The product of the reaction of salicylic aldehyd upon phenylhydrazin has been hitherto regarded as a hydrazone with the melting-point at 142°. The product which we have obtained has a composition agreeing with the formula $C_{12}H_{10}N_2$. When pure and dry it forms stable, colourless needles, which turn green on exposure to light, and melt without decomposition at 142°. Ferric chloride occasions no change of colour, and Fehling's liquid effects no reduction.

Action of Tannin upon some Alkaloids.—Œchsner de Coninck. — The author takes 0·0834 grm. pure dry tannin and 4·610 grms. pure tannin. On mixing the two substances no precipitation is occasioned, though the tannin becomes moist and is gradually dissolved. The liquid is placed above sulphuric acid, when in about three days it deposits a viscid mass, insoluble in cold water. The author introduces, into a very strong aqueous solution of pyridine, a little pure tannin, when there is no precipitation, but the tannin rapidly forms a viscid mass. A solution of tannin serves for the ready distinction of pyridine and piperidine.

Employment of Cryoscopy in the Analysis of Milk.—MM. Bordas and Ganin.—The authors maintain that it is impossible to admit the constant congelation point of milk.

MISCELLANEOUS.

Chemical Society.—Anniversary Meeting.—At the General Meeting held at the Society's Rooms, Wednesday, March 31st, 1897, Professor Dewar, F.R.S., was elected President. The meeting was the fullest on record, between 300 and 400 Fellows being present.

MEETINGS FOR THE WEEK.

Monday, 5th.—Society of Arts, 4 30. (Cantor Lectures). "Alloys," by Prof. W. Chandler Roberts-Austen, F.R.S.
—— Society of Chemical Industry, 8. Election of Officers and Five Members of Committee. "Chemical Stability of Nitro-compound Explosives," by O. Guttmann, F.I.C.
Tuesday, 6th.—Royal Institution, 3. "Animal Electricity," by Prof. A. D. Waller, F.R.S.
—— Society of Arts, 8. "Recent Travels in Rhodesia and British Bechuanaland," by C E. Fripp.
Wednesday, 7th.—Society of Arts, 8 "Dairy Produce and Milk Supply," by M. J. Dunstan, F.R.S.E.
Thursday. 8th.—Royal Institution, 3. "The Relation of Geology to History," By Prof. W. Boyd Dawkins, M.A., F.R.S., F.G.S.
Friday, 9th.—Royal Institution, 9. "The Limits of Audition," by Lord Rayleigh, F.R.S.
—— Physical, 5. "A Nickel Stress Telephone," by T. A. Garrett, M.A., and W. Lucas, M.A. "On Alternating Currents in Concentric Conductors," by W. A. Price, M.A. "Effect of Capacity on Stationary Electrical Waves in Wires," by W. B. Morton, M.A.
Saturday, 10th.—Royal Institution, 3. "Electricity and Electrical Vibrations," by Right Hon. Lord Rayleigh, M.A., F,R.S.

TO CORRESPONDENTS.

D. W. Birch.—Write to the author of the paper, care of the Secretary of the Academy of Sciences, 55 Quai des Grands-Augustins, Paris.

H. I. Foster.—Consult "The Practical Methods of Organic Chemistry," by L. Gattermann. Published by Macmillan & Co., 1896.

THE CHEMICAL NEWS.

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ON THE GASES ENCLOSED IN CRYSTALLINE ROCKS AND MINERALS.*

By W. A. TILDEN, D.Sc., F.R.S.

It has long been known† that many crystallised minerals contain gas enclosed in cavities in which drops of liquid are also frequently visible. The liquid often consists of water, occasionally of hydrocarbons, and not unfrequently of carbon dioxide, the latter being recognisable by the peculiarities of its behaviour under the application of heat. The liquid supposed to be carbon dioxide has been found in some cases to pass from the liquid to the gaseous state, and therefore to disappear, and to return from gas to liquid at temperatures lower by two or three degrees than the critical point of carbon dioxide. This seems to indicate the presence of some incondensable gas, and as H. Davy found nitrogen in the fluid cavities of quartz, it seemed probable that the alteration of the critical-point was due to that gas.

My attention was drawn to this subject by the observation that Peterhead granite, when heated in a vacuum, gives off several times its volume of gas, consisting, to the extent of three-fourths of its volume, of hydrogen (*Roy. Soc. Proc.*, vol. lix., p. 218).

Since this observation, I find that the presence of hydrogen in crystalline rocks has been recognised by other observers, notably by A. W. Wright (*Amer. J. Sci.*, vol. xii., p. 171). In the course of a study of the gases from meteorites, Wright obtained from a certain "trap" rock, the origin and character of which is not stated, at a low red heat, "about three-fourths of its volume of mixed gases, which were found to contain about 13 per cent of carbon dioxide, the residue being chiefly hydrogen. Another specimen of trap containing small nodules of anorthite was examined at the request of Mr. G. W. Hames, who had observed gas cavities in a thin section of the mineral prepared for microscopic examination. This gave off somewhat more than its own volume of gas, which was found to contain some 24 per cent of carbon dioxide."

Professor Dewar and Mr. Ansdell have also examined one or two rocks in the course of their researches on meteorites (*Roy. Inst. Proc.*, 1886). They found that both gneiss and felspar, containing graphite, yield gas, which, upon analysis, was found to have the composition stated below:—

	Occluded gas in volumes of the rock.	CO_2.	CO.	H_2.	CH_4.	N_2.
Gneiss ..	5·32	82·38	2·38	13·61	0·47	1·20
Felspar ..	1·27	94·72	0·81	2·21	0·61	1·40

Dewar and Ansdell remark that "the small quantity of marsh gas, no doubt, comes from the disseminated graphite, but the presence of the hydrogen is more difficult to explain, and requires further investigation."

I have lately been following up this question, and have obtained results which present some points of considerable interest. For materials I have been indebted chiefly to my colleague, Professor Judd, who has also supplied information as to the probable geological age of the specimens of rocks and minerals tested. All that I have examined yield permanent gas when heated in a vacuum. This gas varies in amount from a volume about equal to that of the rock or mineral to about eighteen times that volume. It usually consists of hydrogen in much larger proportion than that found by the observers just quoted, together with carbon dioxide and smaller quantities of carbon monoxide and hydrocarbons. Every specimen has been examined by the spectroscope for helium, but in no case could D_3 be recognised, or any other line which would lead to a suspicion of the presence of this substance. The gas is very frequently, but not always, accompanied by water in notable quantities.

The gas is apparently wholly enclosed in cavities which are visible in thin sections of the rock when viewed under the microscope, but as they are extremely minute, very little gas is lost when the rock is reduced to coarse powder, and as a result of experiment in one or two cases, I find that practically the same amount of gas is evolved on heating the rock whether it is used in small lumps or in powder. In the first series of experiments undertaken with the object of a rapid survey of the materials, the gases were not completely analysed. They were collected, measured, the carbon dioxide removed by potash, and the residue examined by the spectroscope. When ignited in the air it always burned with a pale flame resembling that of hydrogen.

The accompanying table gives the results of these experiments.

A selection of these was then subjected to more careful and exact analysis. For this purpose fresh masses of the rock were taken, and the gas extracted in the usual way. The following are the results:—

	CO_2.	CO.	CH_4.	N_2.	H_2.
Granite from Skye	23·60	6·45	3·02	5·13	61·68
Gabbro from Lizard	5·50	2·16	2·03	1·90	88·42
Pyroxene gneiss, Ceylon ..	77·72	8·06	0·56	1·16	12·49
Gneiss from Seringapatam.	31·62	5·36	0·51	0·56	61·93
Basalt from Antrim	32·08	20·08	10·00	1·61	36·15

To account for the large proportion of hydrogen and carbonic oxide in these gases, it is only necessary to suppose that the rock enclosing them was crystallised in an atmosphere rich in carbon dioxide and steam which had been, or were at the same time, in contact with some easily oxidisable substance, at a moderately high temperature. Of the substances capable of so acting, carbon, a metal, or a protoxide of a metal, present themselves as the most probable.

The reduction of carbon dioxide or of water vapour by carbon gives rise to the formation of carbon monoxide, and if carbon had been the agent the proportion of this gas in the mixture must have been greater than is found to be the case. It is, of course, well known that carbon dioxide and water vapour are both dissociated at moderately high temperatures, but the greater part of the liberated oxygen re-combines at lower temperatures, though a small portion may remain free in the presence of a large quantity of an indifferent gas or vapour. No free oxygen has been found in any of the gases analysed.

Direct experiments made with ferrous oxide (obtained by gently heating pure chalybite) and with magnetic oxide of iron, show that while the former, at a red-heat, decomposes both steam and carbon dioxide quite freely, liberating hydrogen and carbon monoxide, and becoming itself oxidised into magnetic oxide; the latter has no action at all upon either steam or carbon dioxide. Magnetic oxide of iron is the final product of the action of steam or of carbon dioxide at a high temperature upon metallic iron:—

$$3Fe+4H_2O=Fe_3O_4+4H_2.$$
$$3Fe+4CO_2=Fe_3O_4+4CO.$$

Now, metallic iron has been detected in basalts and some other rocks by Andrews (*Brit. Assoc. Rep.*, 1852,

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* A Paper read before the Royal Society, March, 1897.

† The chief literature of this subject is contained in the following papers:—Brewster, *R. S. Edin. Trans.*, 1824, vol. x., p. 1; *Edin. J. Science*, vol. vi., p. 115; Simmler, *Pogg. Ann.*, vol. cv., p. 460; Sorby and Butler, *Roy. Soc. Proc.*, vol. xvii., p. 291; Vogelsang and Geissler, *Pogg. Ann.*, vol. cxxxvii., pp. 56 and 257; Hartley, *C. S. Trans.*, 1876, vol. i., p. 137, and vol. ii., p. 237.

Name of rock or mineral.	Locality.	Character.	Volume of gas per volume of rock.	Composition in 100 volumes.	
				CO_2.	H_2, &c.
	Rocks of Tertiary Age.				
Granite 1	Skye	Plutonic, acid	1·6	11·5	88·5
„ 2	„	„ „	2·8	31·0	69·0
„	Salen, Mull	„ „	1·3	34·7	65·3
Gabbro	L. Coruisk, Skye	„ basic	3·5	21·6	78·4
Basalt	Antrim	„	8·0	32·0	68·0
	Rocks of Palæozoic Age.				
Quartzite	Durness (Sutherland)	Aqueous, altered	2·2	14·3	85·7
Gabbro	Lizard	Plutonic, basic	6·4	trace	100·0
Granite	Peterhead	„ acid	2·6	24·8	75·2
„	Cornwall	„ „	4·3	8·8	91·2
	Rocks of Unknown Age (mostly Archæan).				
Granite	Near Dublin	Plutonic, acid	5·0	9·4	90·6
„	Ardshiel	„ „	6·9	79·5	20·5
Greisen	Altenburg (Saxony)	„ altered	1·8	13·6	86·4
Granulite	Central India	„ „	2·6	48·7	51·3
Quartz schist	Cas. Wellan (Co. Down)	Metamorphic	2·8	23·0	77·0
Fuchsite schist	Baroda	„	4·2	20·8	79·2
Corundum rock	Pipra, S. Rewah, India	„	3·5	26·0	74·0
Pyroxene gneiss	Dombra (Ceylon)	„	7·3	84·4	15·6
Gneiss with corundum	Seringapatam	„	17·8	18·0	82·0
„ „ garnets and graphite	Doloswella (Ceylon)	„	4·5	11·0	89·0
„	Himalayas (Nanga Parbut)	„	7·2	11·5	88·5
	Recent Lava.				
	Vesuvius, 1760	—	0·65	72·0	28·0
	Minerals.				
Graphite	Ceylon	—	7·5	48·0	52·0
Quartz matrix of same	—	—	1·2	44·5	55·5
Beryl	Irish	—	6·7	6·0	94·0
Tinstone	Straits Settlements	—	1·3	45·4	54·6

Sections, p. 34), and by some other observers (*e.g.*, G. W. Hawes, *Amer. J. Sci.*, 1877, Ser. 3, vol. xiii., p. 33), and I have verified this observation in the case of the gabbro of Loch Coruisk. But it must be remembered that both the reactions indicated in the equations just given are reversible, and therefore the presence of metallic iron along with the magnetic oxide in such rocks cannot be taken by itself as final proof that the oxide and the associated gases, hydrogen and carbonic oxide, are the products of the action of steam and carbon dioxide upon metallic iron. The presence of marsh gas in these rocks and the production of large quantities of hydrocarbonous gases, as well as liquid petroleum, in many parts of the earth's surface, tend to support the view, which is apparently gaining ground, that in the interior of the earth's crust there are large masses, not only of metal but of compounds of metals, such as iron and manganese, with carbon. Assuming the existence of such material, it is easy to conceive how, by the action of water at an elevated temperature, it may give rise to metallic oxides and mixtures of hydrogen with paraffinoid and other hydrocarbons. This view was put forward some years ago by Mendeleeff ("Principles of Chemistry," Translation by Kamensky and Greenaway, vol. i., 364—365), and it has lately received further support from the results of the study of metallic carbides, which we owe especially to Moissan (*Roy. Soc. Proc.*, vol. lx., 1896, pp. 156—160).

Determination of Phosphate in Thomas Slags.—According to Dr. O. Böttcher (*Chemiker Zeitung*), the citrate method cannot be universally accepted for the determination in ground Thomas slags of phosphate soluble in citric acid until further comparative analyses have been carried out.

DETERMINATION OF ATMOSPHERIC OZONE ON MONT BLANC.

By MAURICE DE THIERRY.

Thanks to the kind support of M. Janssen I have been able to commence, in 1894, a series of researches on Mont Blanc, and continue them in 1895 and 1896. The bad weather, which has not ceased to prevail on these heights during last summer, has hindered me from completely executing the programme which I had drawn up; still the interest which the first part of my researches seemed to present encourages me to present them to the Academy.

In September, 1894, I was struck with the rapidity with which slips of amidised ozonoscopic paper (Schœnbein's paper), and red litmus paper saturated with potassium iodide (Houzeau's paper), exposed to the air on the platform of the Observatory on the summit of Mont Blanc, at the altitude of 4812 metres, took respectively deep violet and blue colourations. Paper steeped in thallous oxide was equally and rapidly blackened with formation of thallic oxide (Bœttgen reaction). It was the same with plates of silver which I had prepared by reducing a solution of silver nitrate with lactose.

These first observations were already interesting when —on Tuesday, August 13th, at noon—I, along with my two guides, was attacked by a tempest of snow (altitude of 42,000 metres), accompanied by numerous peals of thunder, and the fall of hailstones perfectly spherical and of the size of large peas.

A violent N.W. wind was blowing; Naudin's air hygrometer marked 115°, and the thermometer, which before the storm was at 0°, fell rapidly to −15. A number of hailstones, collected on a sheet of iodo-amidised ozonoscopic paper, made immediately circular violet spots, larger than the diameter of the hailstones, the centre of the spots occupied by the hailstones being paler than the circumference. The violence of the storm did not allow me to examine closely if these spots were formed by an atmosphere of ozone surrounding the hailstone when it fell, or by hydrogen peroxide (which might give the same action) derived from the melting of the hail. I must add that the snows (recent or old) taken on adjoining heights have never given the characteristic reactions of hydrogen peroxide. The water from melted snow has always given the characteristic reaction of ammonia with Nessler's test.

The author resolved to determine quantitatively the atmospheric ozone on Mont Blanc. He finds that at Chamounix (1050 metres) the atmospheric ozone is 3·5 m.grms., and on the Grand Mulets (3020 metres) 9·4 m.grms. per 1000 cubic metres of air,—that is to say, nearly four times greater than at Paris. The quantity of ozone therefore increases with the altitude.

The author is engaged with the analysis of air which he has brought with him from the Grand Mulets. He is also studying the possible presence of nitrous acid in certain strata of air.—*Comptes Rendus*, cxxiv., No. 9.

EXPERIMENTS ON THE ACTION OF PERMANGANATE OF POTASH AND ACETIC ACID ON THE BACTERIA IN RAW THAMES WATER.

By HENRY CROOKES, A.R.S.M., M.I.E.E.

A few months ago I carried out a series of experiments on the action of certain germicides on the bacteria in raw Thames water, my primary object being to determine the influence of time, and quantity of material employed. After a number of tentative and preliminary experiments, to get an idea of the most suitable quantities and strengths, I at length decided to work with a constant volume of 250 c.c. of raw water, adding to it a standard solution of $KMnO_4$ of 20 grains per gallon. The method of procedure was as follows:—

In the first series of experiments 10 c.c. of the standard $KMnO_4$ were added to three different bottles, each containing 250 c.c. of unfiltered water; these were marked B, C, D, while A was the raw water untreated.

B was allowed to stand for 15 minutes, when 0·5 c.c. was mixed with 10 c.c. of nutrient gelatin peptone, poured into a sterile Pietri dish, and when cool placed in the incubator, and kept at 20° to 20·5° for 48 hours.

C was allowed to stand for 30 minutes, and D for 60 minutes, both these (as well as A) being then treated in exactly the same manner as B. After 48 hours the colonies were counted under the microscope, and the following results obtained:—

Series I.	Colonies per c.c.
A. Unfiltered water untreated	3876
B. 250 c.c. of same water + 10 c.c. standard $KMnO_4$, after 15 minutes	332
C. 250 c.c. of same water + 10 c.c. standard $KMnO_4$, after 30 minutes	240
D. 250 c.c. of same water + 10 c.c. standard $KMnO_4$, after 60 minutes	36

These figures show a very rapid diminution in the number of bacteria, even with so weak a solution of $KMnO_4$ as 20 grains per gallon.

My next experiments were to determine the germicidal power of varying quantities of $KMnO_4$ (always the same standard strength) in a constant time. Four bottles were taken, as before, A being untreated; to B were added 5 c.c., to C 10 c.c., and to D 20 c.c. of $KMnO_4$; these were all allowed to stand for 15 minutes, then treated as before, and incubated for 48 hours. At the end of that time the following number of colonies per c.c. were found:—

Series II.	Colonies per c.c.
A. Unfiltered water untreated	3850
B. 250 c.c. of same water + 5 c.c. standard $KMnO_4$, after 15 minutes	260
C. 250 c.c. of same water + 10 c.c. standard $KMnO_4$, after 15 minutes	190
D. 250 c.c. of same water + 20 c.c. standard $KMnO_4$, after 15 minutes	40

From these figures it would appear that there is very little difference in the action of a small quantity of $KMnO_4$ for a long time, and a much larger quantity for a shorter time.

Another set of experiments conducted in exactly the same manner, save that the standard $KMnO_4$ was made slightly acid with acetic acid, gave the following results:—

Series III.	Colonies per c.c.
A. Unfiltered water, untreated..	2040
B. 250 c.c. of same water + 10 c.c. standard $KMnO_4$, after 15 minutes	116
C. 250 c.c. of same water + 10 c.c. standard $KMnO_4$, after 30 minutes	90
D. 250 c.c. of same water + 10 c.c. standard $KMnO_4$, after 60 minutes	55

Series IV.	Colonies per c.c.
A. Unfiltered water, untreated..	2400
B. 250 c.c. of same water + 5 c.c. standard $KMnO_4$, after 15 minutes	589
C. 250 c.c. of same water + 10 c.c. standard $KMnO_4$, after 15 minutes	141
D. 250 c.c. of same water + 20 c.c. standard $KMnO_4$, after 15 minutes	90

Finally, another set was done, in all respects similar, but that the standard $KMnO_4$ was made alkaline with caustic soda, the results being as follows:—

Series V.	Colonies per c.c.
A. Unfiltered water untreated..	3080
B. 250 c.c. of same water + 10 c.c. of standard $KMnO_4$, after 15 minutes	268
C. 250 c.c. of same water + 10 c.c. of standard $KMnO_4$, after 30 minutes	120
D. 250 c.c. of same water + 10 c.c. of standard $KMnO_4$, after 60 minutes	87

Series VI.	Colonies per c.c.
A. Unfiltered water untreated	12400
B. 250 c.c. of same water + 5 c.c. of standard $KMnO_4$, after 15 minutes	3720
C. 250 c.c. of same water + 10 c.c. of standard $KMnO_4$, after 15 minutes	2170
D. 250 c.c. of same water + 20 c.c. of standard $KMnO_4$, after 15 minutes	434

These six series of experiments, when calculated as percentages of microbes present at each stage, appear as follows, and can be easily compared:—

	Neutral.		Acid.		Alkaline.	
Series	I.	II.	III.	IV.	V.	VI.
A.	100·0	100·0	100·0	100·0	100·0	100·0
B.	8·5	6·7	5·7	24·5	8·7	30·0
C.	6·1	4·9	4·4	6·0	3·9	17·5
D.	0·9	1·0	2·7	3·7	2·8	3·5

We see at once that the strongest and most rapid action takes place when the permanganate solution is neutral, the most noticeable difference being the remarkable loss of power of 5 c.c. of both acid and alkaline permanganate (Series IV. and VI.) when acting for fifteen minutes (B).

I next turned my attention to the action of acetic acid alone on unfiltered water; the methods of procedure and incubation were the same as in the previous experiments, the first being with a varying quantity of a 1 per cent solution standing for 15 minutes. After 48 hours in the incubator the following results were obtained:—

Series VII.	Colonies per c.c.
A. Unfiltered water untreated	5890
B. 250 c.c. of same water + 1 c.c. of 1 per cent acid, after 15 minutes	3684
C. 250 c.c. of same water + 5 c.c. of 1 per cent acid, after 15 minutes	3262
D. 250 c.c. of same water + 10 c.c. of 1 per cent acid, after 15 minutes	2846

These figures show a slight and regular diminution in the number of bacteria; but the acid was evidently too weak, so a stronger solution—viz., 10 per cent—was prepared and the experiments repeated with the following results:—

Series VIII.	Colonies per c.c.
A. Unfiltered water untreated	824
B. 250 c.c. of same water + 1 c.c. of 10 per cent acid, after 15 minutes	600
C. 250 c.c. of same water + 5 c.c. of 10 per cent acid, after 15 minutes	456
D. 250 c.c. of same water + 10 c.c. of 10 per cent acid, after 15 minutes	238

These showed a stronger action, but nothing striking, so a further lot was done with a 50 per cent solution of acetic acid, with the following remarkable results:—

Series IX.	Colonies per c.c.
A. Unfiltered water untreated	1976
B. 250 c.c. of same water + 1 c.c. of 50 per cent acid, after 15 minutes	750
C. 250 c.c. of same water + 5 c.c. of 50 per cent acid, after 15 minutes	30
D. 250 c.c. of same water + 10 c.c. of 50 per cent acid, after 15 minutes	0

A 50 per cent solution of acetic acid proving unnecessarily strong, two more trials were made with the 10 per cent solution, keeping the quantities constant, viz., 5 c.c. and 10 c.c., and varying the time 10, 30, and 60 minutes.

Series X.	Colonies per c.c.
A. Unfiltered water, untreated	9792
B. 250 c.c. of same water + 5 c.c. of 10 per cent acid, after 10 minutes	4096
C. 250 c.c. of same water + 5 c.c. of 10 per cent acid, after 30 minutes	2176
D. 250 c.c. of same water + 5 c.c. of 10 per cent acid, after 60 minutes	1280

Series XI.	Colonies per c.c.
A. Unfiltered water, untreated	2090
B. 250 c.c. of same water + 10 c.c. of 10 per cent acid, after 10 minutes	508
C. 250 c.c. of same water + 10 c.c. of 10 per cent acid, after 30 minutes	380
D. 250 c.c. of same water + 10 c.c. of 10 per cent acid, after 60 minutes	280

By converting the results of Series IX., X., and XI. into percentages as before, we get the following table:—

	Series IX.	Series X.	Series XI.
A.	100·0	100·0	100·0
B.	37·9	41·8	24·3
C.	1·5	22·2	18·1
D.	0·0	13·0	13·4

From these figures we see that time is a stronger factor in the decrease in the number of microbes than an increase in the quantity of the acid used. Thus, in Series X. and XI., while after ten minutes standing (B) the difference is very marked, after sixty minutes (D) there is practically nothing to choose between them.

Further experiments are being carried on, and I hope to be able to publish the results in due course.

A REVISION OF THE ATOMIC WEIGHT OF MAGNESIUM.*

By THEODORE WILLIAM RICHARDS
and
HARRY GEORGE PARKER.

(Continued from p. 159).

Purification of Silver.

No very great labour was expended upon the purification of the first quantity of silver, as the chlorine in magnesic chloride was to be precipitated with an undetermined excess of silver nitrate. Residues were therefore worked up by dissolving silver (obtained by reduction with zinc) in nitric acid, precipitating the metal as chloride, and converting the chloride into metallic silver by means of invert sugar. The reduced silver, after having been fused into buttons, was thoroughly washed and dissolved in nitric acid. The solution of argentic nitrate thus obtained was diluted very much with water, allowed to stand, and filtered just previous to using.

With the second sample, on the other hand, much greater care was taken, as it was designed in this case to ascertain the direct ratio between silver and magnesic chloride. The material came partly from some refined silver, purchased in the market, and partly from some pure silver residues remaining from previous work. The silver was precipitated from a solution of the nitrate with pure hydrochloric acid, and reduced by means of invert sugar and pure sodic hydrate, the sodic hydrate having been previously freed from heavy metals by electrolysis. Both the chloride and reduced silver were very thoroughly washed, the silver was dissolved in pure nitric acid, and the process was repeated. After this cycle of operations had been performed four or five times, the reduced silver was fused on a cupel of sugar charcoal before the blowpipe. The resulting button was scrubbed with sand, and made the anode of a weak galvanic circuit in a solution of argentic nitrate prepared from the same silver. The cathode was a piece of pure silver wire, upon which the whole of the silver was deposited in a crystalline mass. The silver crystals were then removed from the solution and fused in a vacuum upon a boat of pure lime (*Proc. Amer. Acad. Arts Sci.*, xxx., 379; xxxi., 173), which was contained in a porcelain tube. Such a boat may be made by lining a porcelain boat with a mixture of three parts of pure lime and one part of pure anhydrous calcic nitrate, and igniting the mixture. The porcelain boat is thus covered with a firm coherent layer of pure calcic oxide. In order to prevent the possibility of a trace of organic matter distilling off from the rubber stoppers usually used to close such a tube, a set of hollow brass stoppers were made, through which a current of cold water circulated. This latter device is due to a suggestion of Professor Hempel. The construction of this piece of apparatus is evident from the diagram (Fig. 2).

Of course, the button after fusion showed no trace of spirting from contained oxygen. It was scrubbed with distilled water and clean sand, and divided into small pieces by means of a clean steel chisel. The fragments were alternately boiled in strong hydrochloric acid and digested in ammonia water, this process being repeated ten or fifteen times. The silver was finally washed with

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* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxii., No. 2.

distilled water and afterwards kept in a desiccator, which was opened only when necessary to weigh out silver for a determination.

A portion of the second sample was treated in the same way, except that in the end it was fused on sugar charcoal before the blowpipe and cooled in the reducing flame. Particular pains were taken to prevent the absorption of oxygen, and the button did not show the slightest trace of having contained this gas. From this portion wire was prepared of various thicknesses, by means of a draw plate; and the weights of given lengths of these wires were determined, so that small weights could be made with considerable accuracy. Of course, the wire was treated in the same fashion as the rest of the silver, in order to remove any iron which might be present on the surface.

The third and fourth samples of silver were prepared in the same manner as the second, the starting-point being the pure residues left from the analyses made with previous samples. No qualitative nor quantitative difference could be observed between any of these preparations of silver. Fused upon sugar charcoal, they melted to a clear globule free from any film,—a fact which in itself, according to Stas, is an excellent test of the purity of silver,—and all gave practically the same results in later determinations.

All water used was re-distilled with potassic permanganate, some of it being condensed in a platinum condenser, and some of it by means of a tube of pure block tin, which was carefully tested in order to prove the absence of an impurity of lead. Considerable quantities upon evaporation in platinum left a scarcely appreciable residue, there being apparently no difference between the water condensed in tin and that in platinum (see *Proc. Amer. Acad. Arts Sci.*, xxvi., 249; xxx., 380). The water was prepared as short a time as possible before being used, and was carefully kept in a suitable bottle fitted with a syphon, air being admitted to the bottle through a filter of cotton-wool. It was carefully tested for chlorine by means of the nephelometer from time to time.

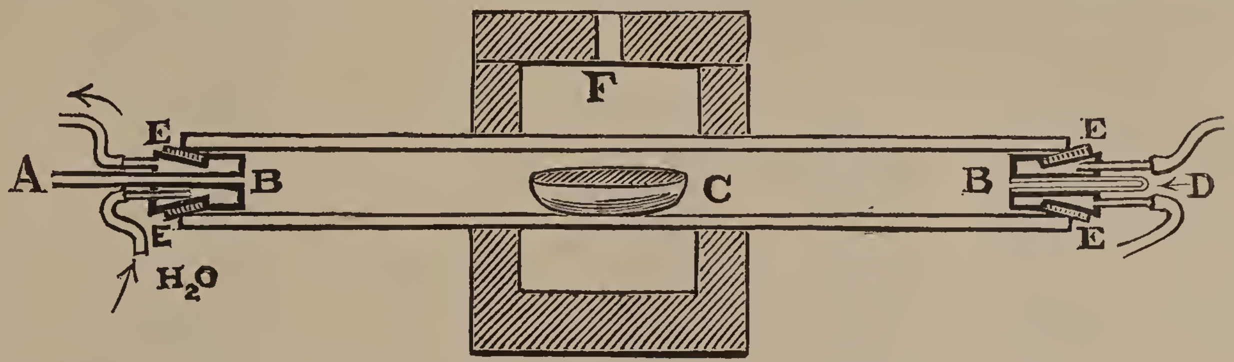


Fig. 2.—Apparatus for Fusing Silver, Vertical Section.

A is connected with a Sprengel pump. B B, hollow brass stoppers in porcelain tube. C, boat of lime containing silver. D, "window" for observation. E E E E, rubber packing of stopper. F, Fletcher furnace.

The sulphuric acid used for the preliminary drying of the gases was the usual "chemically pure" acid of the laboratory, of a specific gravity of about 1·83. For the final drying this acid was boiled down in platinum.

Weighing.

The balance used was a long-armed Becker, sensitive to about one-thirtieth of a milligrm. with the largest load that it was required to carry during the investigation, while the weights were a good set of gold plated ones, which were kept in the balance case under a glass cover. These weights were very carefully compared with one another, and all weighings were, of course, reduced to the vacuum standard. The specific gravity of magnesic chloride used for this computation was the value 2·177 determined by Playfair and Joule. Weighing was done by substitution, the object to be weighed being placed on the right-hand pan and balanced by tare weights on the left. In general, the precautions used in the recent work done in this laboratory upon copper, barium, strontium, and zinc were adhered to with great care (Richards, *Proc. Amer. Acad. Arts Sci.*, xxvi., 240; xxviii., 1; xxix., 55; xxx., 369; xxxi., 158). We are indebted to the Cyrus M. Warren Fund of Harvard University for some of the platinum ware used in the following work.

The atomic weights used in this investigation were as follows:—

O	16·000	Ag	107·930
Cl	35·456		

Method of Work.

The method of operating may be inferred from the description of the apparatus. The platinum boat, after having been weighed within its weighing bottle, was filled with the double chloride of ammonium and magnesium and placed in position in the ignition-tube, resting upon a sort of carriage of platinum foil. The weighing bottle was placed with its stopper in appropriate position in the "bottling tube," as previously described. A current of dry hydrochloric acid gas was then passed through the apparatus and the ignition tube was heated by a suitable arrangement of burners. At first the residual moisture was driven off by the heat and carried away by the stream of gas. When as much water as possible was expelled in this manner, the heat was slowly increased, so that the ammonic chloride commences to vaporise. It was found that the sublimation commenced before the salt was freed from the last traces of moisture, but an effort was always made, by the very gradual increase of heat, to make this proportion of water as small as possible; and it is probable that the salt was practically anhydrous some time before the last of the ammonic chloride was sublimed. When no further evolution of ammonic chloride could be observed, the heat was increased until the tube and boat were heated to redness, and the magnesic chloride had fused into a clear, colourless limpid liquid. It requires a very excellent piece of combustion tubing to stand the heat necessary to fuse magnesic chloride, and a number of tubes were spoiled during the course of the work. In the first series of determinations the boat was allowed to cool while the current of hydrochloric acid gas was still passing. The tubes containing the boat and weighing bottle were then thoroughly washed out with a current of air dried in an apparatus similar to that used for drying the hydrochloric acid gas, as previously described. After it was certain that all of the acid gas had been displaced, and while the current of air was passing rapidly to prevent any diffusion of moist air back into the apparatus, the bulbs were removed from the farther end of the ignition-tube, and the boat was pushed into the bottle in the manner already described. The boat itself remained constant in weight during these operations, showing that the magnesic chloride had not acted upon it.

After weighing, the boat and its contents were placed in a large glass-stoppered Erlenmeyer flask, and the magnesic chloride was dissolved in pure water. The chlorine was precipitated with a dilute solution of argentic nitrate (this solution contained never more than 1 per cent of silver); and after a thorough shaking the whole was allowed to stand in the dark over night. The argentic chloride was washed by decantation a number of times, with vigorous shaking, and was finally collected upon a Gooch crucible in the usual manner. The precipitate was dried from five to ten hours in an oven, carefully protected from dust and dirt, and weighed. After weighing, the cake of precipitate, together with some adherent asbestos, was removed to a tared porcelain crucible and heated until it began to fuse. The crucible was again weighed, and the loss of weight, if any, noted, and subtracted from the weight of the Gooch crucible and contents. The filtrate, containing a little dissolved argentic chloride, was evaporated down to small bulk and filtered through a very small filter; and the weight of the precipitate was added to the weight of the first portion. In some cases the small amount of argentic chloride present was determined with the nephelometer (see *Proc. Amer. Acad. Arts Sci.*, xxx., 385).

The wash water from the precipitate collected on the Gooch crucible was also run through a small filter to make sure that no asbestos had been carried away from the crucible in the process of washing; and this correction, when appreciable, was applied in the appropriate place.

The washing and filtration were both performed in dim orange light, which had been suitably tested as to its non-actinic properties. Even after fusing the argentic chloride was almost colourless, showing that only unessential traces had deen decomposed by the light.

The result of the first series of five experiments is given below. These determinations were consecutive, except that one determination met with an accident and was not completed.

SERIES I.

No. of expt.	Sample of $MgCl_2$ used.	Sample of Ag used.	Weight of $MgCl_2$.	Weight of AgCl.	Ratio. $MgCl_2 : 2AgCl$ = 100 : *n*.	Atomic weight of Mg.
1	1	1	1·33550	4·01952	300·975	24·368
2	1	1	1·51601	4·56369	301·033	24·350
3	1	1	1·32413	3·98528	300·974	24·369
4	1	1	1·40664	4·23297	300·928	24·384
5	1	1	1·25487	3·77670	300·963	24·373
					Average.. ..	24·369

A careful consideration of the possible constant errors involved in the foregoing results lead to the belief that the figures found are too high rather than too low, as the presence either of a small amount of water or of oxychloride in the magnesic chloride would tend in this direction.

Second Series of Determinations.

In order to drive all the subliming ammonic chloride to the further end of the combustion-tube during the ignition, it had been found necessary that the current of gas should be very considerable; and hence it was desirable to construct a piece of apparatus which should deliver the various gases rapidly, but nevertheless as dry as it is possible to obtain them. It was also desirable to work with larger quantities of materials than could be handled in the former apparatus. For these reasons another piece of apparatus was constructed to dry the hydrochloric acid gas; this apparatus contained several flasks of sulphuric acid, three very efficient towers containing the same acid, which was constantly renewed, and a long tube containing re-sublimed phosphoric pentoxide. One of the towers is shown (Fig. 3). The whole apparatus was fused or ground together, thus wholly avoiding rubber or cork connections.

In the following determinations the boat was allowed to cool in an atmosphere of dry nitrogen, as a further precaution against a possible partial decomposition of the sensitive magnesic chloride. As soon as the salt had been fused, a current of dry nitrogen was passed into the combustion-tube and the hydrochloric acid generator was disconnected. The nitrogen was prepared by passing mixed air and ammonia over rolls of copper gauze heated to redness, the excess of ammonia being removed by passing the gases through wash bottles containing dilute sulphuric acid and the nitrogen was dried in a set of towers similar to those used for drying the current of air. When the tube was cool, the current of dry air was turned on, and the tube and its contents washed out as in previous experiments.

As there were no especial objections against the use of rubber connections and stoppers in the part of the apparatus used for drying the air, several large towers were employed, each filled with crushed pumice-stone and saturated with sulphuric acid previous to using. Both air and nitrogen were finally dried by re-sublimed phosphoric pentoxide. The bottling and combustion-tubes were of the same construction as in the former apparatus, except that they were larger.

In the second series the method of igniting the double salt to obtain the magnesic chloride was the same as in the first; but the method of estimating the amount of chlorine present was different. From the approximate atomic weight of magnesium already found, a calculation was made as to the amount of silver necessary exactly to precipitate the chlorine present in the sample of magnesic chloride taken. This amount of silver was weighed out as nearly as possible, dissolved in nitric acid in an Erlenmeyer flask, provided with a set of bulbs to catch the spray from the evolution of gas, and added to the solution of magnesic chloride contained in a large flask. The flask was thoroughly agitated in the dark, and allowed to stand over night. Fifty c.c. were then withdrawn by means of a pipette, and tested by means of a nephelometer, or apparatus for determining the amount of precipitate from the intensity of the opalescence produced by it. This piece of apparatus was constructed for the purpose, and consisted of two rectangular glass cells, with a mirror enclosed in a dark case, so arranged that the column of liquid contained in the lower part of the cells could be viewed horizontally without disturbance from

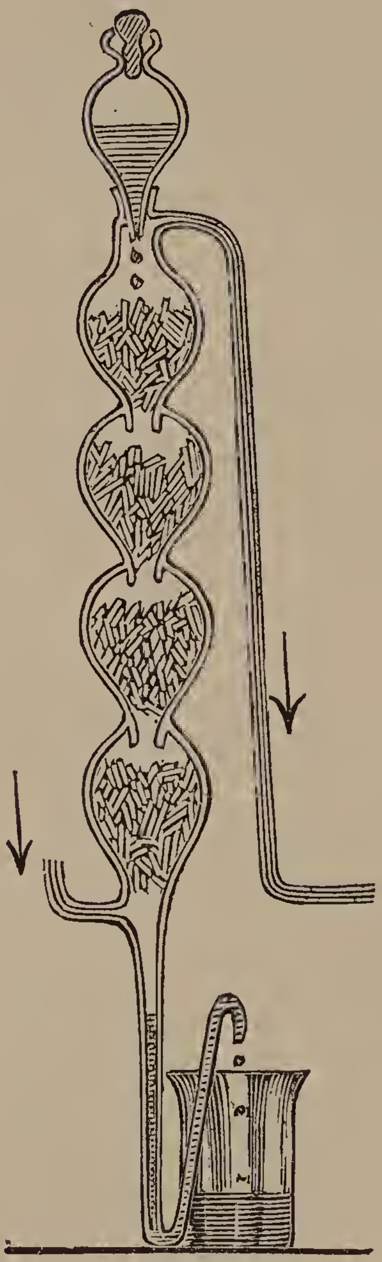


FIG. 3.—ONE OF THE TOWERS USED FOR DRYING HYDROCHLORIC ACID (70 c.m. high).

surface reflections. A dark screen was placed at the further end of the cells, and the whole so arranged that light could come to the eye only by reflection from solid particles which might be suspended in the column of liquid inspected. If the liquid was perfectly clear, the field of vision remained black, but an extremely small amount of precipitate produced a very marked change, and the intensity of opalescence was approximately proportional to the amount of precipitate. It was found perfectly easy and certain, by this method, to distinguish the difference between 0·002 and 0·003 of a milligrm. of argentic chloride or between 0·004 and 0·005 of a milligrm., and larger amounts in proportion. This instrument gave such satisfaction in this research that the method will be worked out for various other reactions, and published later.

The method of using this apparatus was as follows:—25 c.c. of the clear supernatant liquid from the flask containing the well-shaken argentic chloride and magnesic nitrate were placed in each cell, 5 c.c. of a very dilute solution of argentic nitrate being added to one, and 5 c.c. of a correspondingly dilute solution of ammonic chloride to the other. The silver solution contained 1 m.grm. of silver to the c.c. An unequal depth of cloudiness indicated an excess of either silver or chlorine in the original solution, and accordingly the amount necessary for neutralisation was run into the large flask containing precipitate and solution from a burette. The solution was again allowed to stand in the dark with occasional shaking, and after the precipitate had entirely subsided was again tested as before, and this cycle of operations was repeated until the opalescences matched one another.* It will be observed that, if water is added to the cell giving the more dense opalescence until the effect becomes equal on both sides, the amount of dilution will give a means of ascertaining the amount of precipitate in each cell. The appropriate corrections were then applied to the amount of silver taken. Due allowance was made for the slightly diminishing volume of the solution in the flask. The addition of 1-10th of a m.grm. of silver to a litre of solution produced a distinct change in the depth of colour observed. After the matching was completed, repeated trials were made with fresh portions of the solution to confirm the result; and as the depth of opalescence as seen in the nephelometer was perfectly flat, without disturbing eflections, the end point could be determined with great precision.

Several results obtained in this manner are given in Series II.

SERIES II.

No. of exp.	Sample of $MgCl_2$ used.	Sample of Ag used.	Weight of $MgCl_2$.	Weight of Ag.	Ratio. $MgCl_2 : 2Ag = 100 : n$.	Atomic weight of Mg.
6	1	1	2·78284	6·30284	226·490	24·395
	1	1	2·29360	5·19560	226·526	24·379
8	1	2	2·36579	5·35989	226·558	24·366
					Average.. ..	24·380

These results, however, do not merit great confidence' for the apparatus, which had become somewhat complicated, did not work smoothly at first, on account of some minor imperfections which were remedied later. Besides this, careful consideration led to the suspicion that the towers used for drying the air and nitrogen were not efficient enough to remove the last traces of water. Of necessity the towers had to be charged with sulphuric acid an hour or two before their final use, and during that time a large part of the acid drained out of the pumice stone. This surmise was fully confirmed by later experiments; and since this was the case, the second series must be rejected in the final estimate of the atomic weight.

(To be continued).

For details of this method see Stas, *Mem. Acad. Belg.*, xliii., Part II., and Richards, *Proc. Amer. Acad.*, xxix., 86; xxx., 385.

THE ATOMIC WEIGHT OF JAPANESE TELLURIUM.

By MASUMI CHIKASHIGE, Rigakushi,
College of Science, Imperial University.

THE atomic weight of tellurium has been determined by Berzelius (1833), von Hauer (1857), Wills (1879), Brauner (1883, 1889), and Staudenmaier (1895), Berzelius gave it as 128·3 (O = 16). Staudenmaier has only reduced it to 127·6. Brauner had also obtained this number, that is, 127·64, by determining the quantity of bromine in the tetrabromide; but in other ways, which he could not admit to be inaccurate, he obtained widely varying numbers for the atomic weight. To explain these variations, he assumed that what passes for the element tellurium is a mixture or compound. The number 125, which since 1884 has been generally accepted as the atomic weight of tellurium, was suggested by Mendeleeff, but was adopted on the grounds of Brauner's determinations (partly by faulty methods, as he has since ascertained) published in 1883 in Russia. A paper by him, on the atomic weight of tellurium, which appeared last year in the *Journal of the* (London) *Chemical Society*, supplies no new data. It throws no light upon the causes of the varying results he had previously obtained by different methods, but apparently contains the admission from him at last that, so far as can be determined by known methods, the atomic weight of tellurium is 127·64 (127·7 *in vacuo*).

The object of the research described in the present communication has been, not to add one more to the above-mentioned determinations of the atomic weight of tellurium, by some modification of a method already employed or by some new method, but to apply Brauner's tetrabromide method to tellurium of utterly different origin from that of what he worked upon. European and American tellurium occurs in association with heavy metals, and might, therefore, when separated from those which are known, still retain unknown elements, in accordance with Brauner's conception. But in Japan tellurium is found in native sulphur, as was discovered by Divers, Shimose, and Shimidzu, in 1883 (CHEM. NEWS; *J. Chem. Soc.*). There occurs, in fact, in this country, a massive, crystalline, red sulphur, a variety of the *selensulphur* (Stromeyer) found in the Lipari Isles, in Naples (Phipson), and in the Hawaian Islands (Dana). It is semi-transparent, and indistinguishable in appearance from native sulphur, except by its beautiful orange colour, and occurs interspersed with simple sulphur in the same blocks. I take from the CHEMICAL NEWS the composition of a sample analysed by Divers and Shimidzu:—Tellurium, 0·17; selenium, 0·06; arsenic, 0·01 per cent; traces only of molybdenum and earthy matter, and sulphur, by difference, 99·75 per cent. It is accordingly much more a tellurosulphur than a selenosulphur.

Concerning this tellurium, it need not be contended that it is more truly an element than that found combined with bismuth, gold, lead, and silver; it is sufficient to assert the high improbability that it should contain the same unknown elements as the latter. That being the case, then if it gives the same result by Brauner's tetrabromide method as that obtained with Hungarian tellurium, the likelihood that tellurium with atomic weight 127·6 is an element is greatly increased, if not raised to a certainty. Such was the view taken of the matter by my honoured teacher, Dr. Edward Divers, F.R.S., who placed in my hands about 14 grms. of tellurium, which had been prepared by him and Mr. Shimose years ago. They had obtained this tellurium from the sediment removed from the lead-chambers of a sulphuric acid factory, by a method the particulars of which they communicated to the CHEMICAL NEWS in 1883. The tellurium, which I thus received, had already been carefully freed from selenium and distilled in hydrogen.

Before I had made very much progress in preparing for the determination of the atomic weight, a preparation which has taken a very long time, Staudenmaier's memoir came to hand, but its contents did not deter me from finishing my investigation, though they can leave no reasonable doubt, I think, that the atomic weight of the element is really 127·6.

Long as the work has occupied me, there is now no occasion to describe it in detail, since it was purposely the closest copy I could make of Brauner's operations, so far as these seemed to be material to the point. The tellurium, already so pure, was tested for impurities, and was again distilled in hydrogen.

Excellent commercial bromine was distilled from potassium bromide, zinc oxide, and water (Stas). It was dehydrated first by means of anhydrous calcium bromide left in it for some days, and then by baryta, from which it was filtered through asbestos in vessels closed from the air. It was then distilled into a receiver sealed on to the distilling flask.

The silver was first precipitated by Stas's well-known sulphite method, fused under borax and nitre, then kept for a time in fusing potassium-sodium carbonate, washed with water, hydrochloric acid, and ammonia, melted again in a lime crucible, and granulated in distilled water.

The distilled water of the laboratory was fractionally re-distilled, and the nitric acid was treated in the same way.

The balance used is one by Sartorius (his first quality), which has been hitherto only sparingly used for special cases. The weights are of quartz and platinum, from Gerhardt, and were found by me to have been closely adjusted.

The tellurium bromide was prepared by adding the tellurium to the bromine, in a tube, exactly as described by Brauner. In such a tube he directly sublimed it, but I had to transfer it to another longer tube. The procedure was to slide into this tube, nearly to the bottom, an open tube loosely fitting it, down this to drop the powdery crude tetrabromide, and then withdraw it, leaving the walls of the sublimation tube unsoiled. This tube, at once closed by a cork, was then contracted about 25 c.m. from its closed end, and again about 12 c.m. further off, where it was cut off from the corked end, and the narrowed mouth attached by caoutchouc tubing to the drying tube connected with a Sprengel pump. The tube was placed in the furnace with its first contraction just outside; the bromide before sublimation occupied the hinder third of the tube within the furnace. Sublimation was in all other respects effected just as described by Brauner, a little dibromide being sublimed off at 200° into the outer part of the tube, and the tetrabromide sublimed at a temperature kept closely at 300° into the anterior part of the tube within the furnace. Practically nothing remained unsublimed, which showed that the transference of the undistilled bromide from tube to tube had been effected with impunity, this compound not being noticeably hygroscopic, and the air, at the time, being cold and very dry. The sublimation furnace was an exact copy of Brauner's.

The tellurium bromide was weighed off and dissolved in tartaric acid in one vessel, added to the silver nitrate, shaken for hours in the bottle, with a conical, polished, pointed stopper projecting into it, and then finished off volumetrically, all just as described by Brauner (except that the final titration was not effected in a dark room, but in feeble daylight).

I made only the three determinations here given, neglecting a trial for practice, with good result, in which high accuracy was not sought for. The following are the results:—

Expt.	Tellm. brom.	Silver.	At. wt.
I.	4·1812	4·0348	127·57
II.	4·3059	4·1547	127·61
III.	4·5929	4·4319	127·58

The details of Exp. II. are:—Silver weighed off, 4·1548 grms.; time of continuous shaking by water-motor, 4 hours; precipitate, thoroughly pulverulent; silver solution added, 0·4 c.c., which produced no turbidity; potassium bromide solution required, 0·8 c.c. = 0·54 c.c. silver solution. Since there had been taken silver in excess, equivalent to 0·14 c.c. silver solution, and therefore 0·00014 grm. silver, the actual quantity of silver required by the 4·3059 grms. bromide had been 4·1547 grms. Then—

$$\frac{79{\cdot}963 \times 4{\cdot}1547 \times 100}{107{\cdot}938 \times 4{\cdot}3059} = 71{\cdot}48 \text{ per cent bromine,}$$

and—

$$4\left(\frac{107{\cdot}938 \times 4{\cdot}3059}{4{\cdot}1547} - 79{\cdot}963\right) = 127{\cdot}61 \text{ at. wt. tellm.}$$

In Exp. I. the silver weighed out was not so closely apportioned, and several c.c. of the volumetric solution had to be used; otherwise it agreed with II., as did also III. in its details.

When it is considered that Brauner and I have obtained by the same method identical results, although he worked with tellurium that had presented itself in combination with metals, while I have worked with that occurring in native sulphur of high purity, except for the presence of this tellurium and of selenium, so far as can be ascertained by tests for known elements; and when it is further considered that Staudenmaier's results are the same as Brauner's, though obtained by a wholly different method, no reasonable doubt can remain that the atomic weight of tellurium is 127·6.

The occurrence of tellurium in Japan in association with selenium in native sulphur is also a fact of great significance in settling the place of this substance in a natural classification of the elements, showing, as this does, so close a habitude to exist between it and sulphur and selenium.—*Journal of the College of Science, Imperial University, Japan*, vol. ix., Part II., p. 123.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 18th, 1897.

Mr. A. G. Vernon Harcourt, President, in the Chair.

(Concluded from p. 164).

47. "*Note on a Method for Determining Melting-points.*" By Ernest H. Cook, D.Sc.

So many methods have been introduced for the determination of melting-points that an apology is perhaps necessary for describing another; but the following method has been found to work so well in this laboratory, and to be so easy of manipulation, that the author ventures to place it on record.

Notwithstanding, however, the theoretical simplicity of taking a melting-point, it is surprising that in commercial work considerable differences frequently occur between analysts when reporting upon such a substance, for example, as paraffin scale. Probably most, if not all, of these differences are caused by the different methods employed. Thus it is well known that "the English test," which consists in allowing the wax to solidify in a test-tube in which the thermometer is placed, gives results from 2½ to 3° Fahr. lower than the "American test," in which the wax was melted in an open dish. Both these methods again differ slightly from the capillary-tube plan, and in this process a different result is obtained when an open tube is used than when it is closed. There are, in fact, many precautions which are necessary to be observed if concordant results are to be obtained, and it is much to be desired that some distinct and definite regulations should be made with reference to the matter.

The apparatus employed is a beaker filled to the brim with water; inside this, and separated from it on all sides, is a smaller one. The smaller beaker is partly filled with mercury in which is placed a thermometer. A stirrer is used to keep the water in the large beaker of uniform temperature. A cardboard or other disc covers the smaller beaker when the operation is in progress. The whole is heated from below by means of a sand-bath. When the melting-point to be determined is under 30° it is better to replace the sand-bath by an evaporating dish containing water.

The process is conducted as follows:—The material whose melting-point is to be taken is placed on three or four small pieces of thin ferro-type plate, or other thin metallic sheet, or on the cover glasses which are used for microscope slides. If ferro-type or other metallic slips are used, care must be taken to remove the varnish or other coating, in order that good metallic contact can be had with the mercury. The slips, with the substance on them, are now placed on the surface of the mercury, and the heat applied until the substance melts. The solidifying-point is obtained by raising the temperature above the melting-point, and allowing the beaker to cool, noting the thermometer when the first solidification takes place.

For temperatures between 100 and 200°, the larger beaker is filled with paraffin wax.

The following precautions have been found to be necessary:—(1) The temperature must be made to rise very slowly. (2) The liquid in the outer beaker must be frequently stirred. (3) Not less than 2·5 c.m. in depth of mercury must cover the inner beaker. (4) Sufficient volume of water must be allowed between the two beakers. The minimum distances to give good results are 1 inch between them laterally and 1½ inches at the bottom. (5) The inner beaker must be immersed a sufficient depth in the water. This point is of great importance, the least distance between the top of the mercury and the top of the water being 3 inches. A greater distance is, however, to be preferred. (6) The whole apparatus should be protected from draughts. (7) The disc should be kept on the smaller beaker during the determination.

The following examples will show the degree of accuracy to be obtained in ordinary working, some of the results being obtained by students who have never taken a melting-point determination before:—Paraffin wax (1), 49·8, 49·7, 49·5, 49·8. Paraffin wax (2), 46·2, 46·0, 46·0, 46·0. Paraffin wax (3), 46·5, 46·3, 46·5. Ortho-mono-nitro-phenol, 44·5, 44·7. Urea, 131·0, 131·5, 131·2.

48. "*Velocity of Urea Formation in Aqueous Alcohol.*" By James Walker, D.Sc., and Sydney A. Kay, B.Sc.

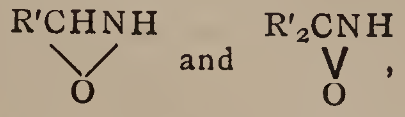
The authors have investigated the rate of formation of urea from ammonium cyanate in pure water, and in mixtures of water and alcohol, containing 10, 30, 50, 70, and 90 per cent by volume of the latter. The alcohol acts in two ways: first, it diminishes the degree of dissociation of the cyanate, and thus retards the action by diminishing the number of active molecules; secondly, it increases the rate at which the ions produced by the dissociation interact. The second mode of action outweighs the first, so that there is on the whole a marked acceleration as the water of the solvent is replaced by alcohol. If the reverse transformation of urea into cyanate, and the degree of dissociation of the latter at the various stages of the process, are taken into consideration, the requirements of the law of mass-action are strictly fulfilled.

Methylic alcohol, acetone, glycol, glycerol, and cane-sugar exert a similar accelerating effect when part of the water used as solvent is replaced by them.

From the displacement of the point of equilibrium between cyanate and urea by change of temperature, it is calculated that the transformation of ammonium ions and cyanic ions into urea is accompanied by a heat evolution of about 5000 cals. per grm.-molecule.

49. "*Action of Alkyl Haloids on Aldoximes and Ketoximes.*" By Wyndham R. Dunstan, F.R.S., and Ernest Goulding.

The authors find that, when formaldoxime, acetaldoxime, and acetoxime are heated in alcoholic solution with an alkyl iodide or bromide, they are converted into compounds of alkyloximes in which the alkyl group is united to nitrogen $R'CHN(R')O$ and $R'_2CNCH(R')O$. These derivatives are isomerides of the little-known ethers of the oximes $R'CH:NOR'$ and R'_2CNOR', and are to be regarded as derivatives of the tautomeric or isoximido-forms of the ordinary aldoxime or ketoxime—



$$\underset{O}{R'CHNH} \quad \text{and} \quad \underset{O}{R'_2CNH},$$

in which the alkyl replaces the hydrogen of the amido-group. Their constitution has been proved by their hydrolysis into β-substituted hydroxylamines, $NH(R')OH$, and the corrresponding aldehyde or ketone.

Formaldoxime, when mixed with methyliodide, either in alcoholic or ethereal solution, is converted into a crystalline salt of the formula $(CH_2NOH)_3CH_3I$. It has been previously shown (Dunstan and Bossi, *Proc.*, 1894, x., 55) that formaldoxime forms salts with monobasic acids which contain 3 mols. of the oxime $(CH_2NOH)_3HCl$, &c. On hydrolysis, followed by reduction, 1 molecule of methylamine hydrochloride and 2 mols. of ammonium chloride are produced, and on heating near its melting-point (102°) only 2 molecules of formaldoxime distil from it. The formula of the compound may therefore be written $(CH_2NOH)_2,CH_2N(CH_3)O.HI$. The base corresponding with this salt could not be separated. Methyl bromide heated with formaldoxime furnishes the corresponding hydrobromide.

Acetaldoxime combines with methyliodide, forming the hydriodide of a base which has so far only been obtained in the liquid state even after a process of fractional precipitation of an alcoholic solution by ether. On hydrolysis this salt furnishes acetaldehyde and β-methyl-hydroxylamine. There can therefore be no doubt that its formula is $CH_3CHN(CH_3)O.HI$. Methyl bromide combines in the same manner, forming the corresponding hydrobromide. Ethyl iodide forms the hydriodide of the ethyl derivative, $CH_3CHN(C_2H_5)O.HI$. Neither of the salts has been crystallised, and the corresponding bases are highly unstable.

Acetoxime.—By heating acetoxime with methyl iodide a red liquid is obtained, which, on concentration, deposits red crystals with a fine green lustre. The mother-liquor furnished the little-known *methylamine hydriodide*—

$$(CH_3NH_2.HI),$$

in glistening, crystalline plates (from alcohol and ether). This is a very stable non-deliquescent salt, melting at 220° with partial decomposition.

The red crystals were proved by analysis to be a methylacetoxime periodide of the formula—

$$[(CH_3)_2CN(CH_3)O.HI]_2I.$$

On hydrolysis it breaks up into acetone and β-methyl-hydroxylamine.

Many attempts were made to isolate the hydriodide from the periodide, and also to prepare other salts from this compound, including the base, but without success, owing to the great instability of these substances.

The hydrobromide appears to be formed when methyl bromide is heated with an alcoholic solution of acetoxime, but this salt could not be crystallised.

THE FRENCH ACADEMY OF SCIENCES.

The following communication from their Correspondent in Paris appeared in *The Times* of April 7th:—

M. Berthelot read this afternoon, at the Academy of Sciences, the following letter addressed to him in French by Mr. H. Wilde, President of the Manchester Literary and Philosophical Society, announcing to the Academy the gift of £5500 to be set apart for an annual prize of

4000 frs. I send you the original letter, without undertaking, considering its special and technical character, to translate it.

“Diverses considérations m'engagent actuellement à me mettre en communication avec l'Académie dans le but de stimuler de nouvelles investigations dans les sciences physico-chimiques, et de faire disparaître quelques-uns des obstacles qui entravent leurs progrès. L'un de ces obstacles qui appelle la sérieuse attention des penseurs philosophes est l'invasion d'une autorité dogmatique dans une science scolastique, pour soutenir des erreurs démontrées et des méthodes erronées d'observation et d'expérience. Il sera suffisant pour l'objet que j'ai actuellement en vue de citer le système périodique des éléments chimiques comme un exemple de l'abus d'autorité dans une branche de la science où vous occupez un rang si distingué. J'ai à vous exprimer mes regrets que vos vues au sujet de la prétendue loi périodique ne soient venues que recemment à ma connaissance; sans cela je m'y serais référé dans mes travaux généraux sur les relations numériques des poids atomiques. Quoique vous ayez clairement indiqué, monsieur, dans vos ‘Origines de l'Alchimie,’ les sophismes et les contradictions inhérents à ce système, et que vous ayez également montré que la prédiction de l'existence et des propriétés des éléments inconnus n'a aucune relation nécessaire avec la prétendue loi périodique, cependant ce système a depuis été imposé aux personnes qui s'occupent de science par les sociétés scientifiques et les corps enseignants comme une vérité naturelle d'une autorité indiscutable.

“Je n'ai pas besoin de vous rappeler que l'état actuel de la chimie théorique en raison de la connaissance formelle de ce dogme est réellement déplorable. Les savants qui aspirent à se distinguer dans la chimie et dans la physique estiment qu'il est nécessaire de donner des preuves de leur croyance personnelle, en tâchant de montrer la correlation de leurs propres travaux sur des points particuliers avec le système périodique, et ils évitent toute référence aux proportions multiples des poids atomiques, comme à une dangereuse hérésie. Beaucoup de ces néophytes, de même que certains auteurs de manuels, ne peuvent se faire une idée, ou ignorent la signification de l'idée de la périodicité telle qu'elle est définie par De Chancourtois, Newlands et Mendeleief dans leurs mémoires respectifs. Ils appliquent l'expression impropre de loi périodique à la progression de propriétés antérieurement connues observables dans les familles naturelles des éléments, à la correlation avec les poids atomiques de propriétés physiques et chimiques établies depuis longtemps, à la progression bien connue des propriétés physiques dans les séries homologues des composés organiques. Par suite, le danger pour les progrès future de la chimie théorique est que, lorsque l'idée illusoire d'une spiro-périodicitè des propriétés analogues des éléments sera universellement abandonnée, le nom impropre de loi périodique est exposé à prendre dans la science un caractère parasite de la même facon que cette autre expression impropre, ‘esprit lunatique,’ avec ses dérivés, subsiste encore dans la civilisation moderne comme une survivance de la physiologie mentale barbare des âges passés.

“Heureusement pour l'avenir de la philosophie chimique que l'esprit de Dumas vit encore dans les esprits de la plupart des chimistes français, qui ne reconnaissent aucune autre autorité que la vérité de la nature telle qu'elle se présente à l'entendement, et qu'ils sont par là exempts de l'illusion de la prétendue loi périodique En renonnaissance des nombreux profits que j'ai retirés de la science française, tant pure qu'appliquée, j'ai l'honneur d'offrir à l'Académie la somme de £5500 (137.500 f.) pour être placée en rente française, et l'intérêt provenant de sette somme devra être appliqué à la fondation d'une prix de 4000 f. à décerner tous les ans à l'auteur d'une découverte ou d'un ouvrage quelconque en astronomie, physique, chimie, minéralogie, géologie, et mécanique, qui, au jugement de l'Académie, sera jugé le plus méritant. L'attribution de ce prix sera internationale et pourra être retrospective.

“Alderley Edge, Cheshire, 15 Mars, 1897.”

The gift has given great satisfaction at the Academy, and is as much to the honour of the donor as to that of the distinguished secretary of that Academy, whose work is referred to in such terms of gratitude.

CORRESPONDENCE.

THE CHEMICAL SOCIETY ELECTION.

To the Editor of the Chemical News.

Sir,—In view of the misleading reference recently made in the press to an unfortunate incident in the celebrated Edison-Swan patent action, and as this incident has, I believe, been twisted into an argument against voting for Professor Dewar in the ill-considered contest to which he has just been exposed, I would request, Sir, that you will give publication to the answers I have received from several very eminent gentlemen who were engaged in the case, whose opinion on the incident I ventured to solicit in the interests of truth and fairness. I would beg that you will also give publication to a letter on the same subject which Mr. Crookes has received from the Right Hon. Lord Davey. I need scarcely add that the full authority of the writers has been secured for the publication of the correspondence.—I am, &c.,

Henry E. Armstrong.

86, Brook Street, W.,
March 31, 1897.

Dear Professor Crookes,

I was away from home yesterday, and am truly sorry that I did not get your letter in time to reply to it last night. I am afraid this letter will be of no use to you.

The incident in question occurred during my cross-examination of Professor Dewar. My recollection of it is sufficiently clear to enable me to say that I did not think that Professor Dewar intended to mislead either his Court or myself. I feel sure that the misunderstanding was due to imperfect appreciation, by the learned Judge and by myself, of the nature and object of the experiment which Professor Dewar was explaining. You may show this letter to Professor Dewar himself or anybody else.

Yours very truly,
Davey.

Wm. Crookes, Esq., &c., &c.

57, Onslow Square, S.W.,
March 27th, 1897.

Dear Professor Armstrong,

You have my full authority for saying that the remark made by Mr. Justice Kay about Professor Dewar's evidence in the Edison case was quite without cause. It arose, I think, from a misunderstanding on the part of the Judge as to the meaning of the evidence.

The further evidence fully substantiated the position taken by Dewar in the matter, and the Court of Appeal reversed Kay's decision.

Yours very sincerely,
J. Fletcher Moulton.

2, Pump Court, Temple, E.C.,
31 March, 1897.

Dear Professor Armstrong,

I am in receipt of your letter of the 29th with enclosures.

The attack upon Professor Dewar is most unfair and unjustifiable. I am intimately acquainted with everything that happened in the case before Mr. Justice Kay which is referred to. No experiment of any kind was performed which could be in any way characterised as an attempt to mislead. The late Lord Justice, then Mr. Justice Kay, was mistaken, and did not understand the nature of the experiment to which he was referring. His decision was reversed in the Court of Appeal, and I say, without the slightest hesitation, that everything which Professor Dewar did upon that occasion was perfectly straightforward and justifiable. Make any use you like of this letter.

Yours faithfully,
Richard Webster.

Holmwood, Wimbledon Common, S.W.,
31 March.

My Dear Armstrong,

With regard to the incident in the Edison and Swan case some years ago, I thought strongly at the time, and I still think, that Dewar's answers did not tend to mislead the Court, and that he certainly did not mean to mislead.

I followed Dewar in the box, but I do not remember that I confirmed the particular experiment in question. I considered the experiment as of little consequence in the case.

Yours very truly,
J. Hopkinson.

Athenæum Club,
April 2nd, 1897.

Dear Armstrong,

In reply to your enquiry *re* Edison and Swan *v.* Holland we have to say that, being on the opposite side to Prof. Dewar, no one could have been more likely than ourselves to take an adverse view of the experiment which formed the subject of Mr. Justice Kay's remarks.

We, however, were both of opinion that the experiment brought forward by Prof. Dewar was perfectly *bonâ fide*, and that there was nothing in his description of it to justify the adverse remarks of the Judge, and certainly nothing to justify the conclusion that the Judge seemed to draw from it.

We need scarcely add that there was nothing whatever in the incident which reflected upon the honesty and truthfulness of the conclusion which Prof. Dewar drew from his experiment. The garbled version which appeared in one or two journals has no doubt misled the public, both scientific and otherwise, as to the severe comments made by Mr. Justice Kay upon Prof. Dewar's experiment. The misunderstanding was completely cleared up by the evidence of subsequent witnesses and by experiments tried before Prof. Stokes on behalf of the Court.

We are
Yours very truly,
E. Frankland.
William Crookes.

THE CHEMICAL SOCIETY ELECTION.

To the Editor of the Chemical News.

Sir,—As I had written privately to Professor Armstrong, assuring him that Dr. Collie's statement that my nomination to the Presidentship of the Chemical Society was made without my knowledge or consent, I had hoped that his honourable feelings would have led him to retract publicly his statement challenging Dr. Collie's veracity. As my hopes are disappointed, I have no choice but to ask you to publish this letter, and to state that Dr. Collie's remarks at the meeting of the Chemical Society, as reported in the *Proceedings* on the 18th March, were literally true.—I am, &c.,

William Ramsay.

University College, London, W.C.,
April 3, 1897.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 11, March 15, 1897.

New Apparatus for the Application of Spectral Analysis to the Recognition of Gases.—M. Berthelot.—The experiments described throw a clear light on the nature of the nitrogenous principles which are formed under the influence of the effluve acting upon organic compounds. What brightens the interest is analogy of this order of reactions with those exerted between the nitrogen of the atmosphere and the immediate principles of plants.

Action of High Temperatures upon Antimony Peroxide.—H. Baubigny.—Experiment proves that antimonic acid, Sb_2O_5, is stable at 357°; it begins to decompose at 440°, though very slowly, and even at nascent redness the decomposition is very slow. It is not until about 750°—800° that the antimonic acid is quickly transformed into antimony peroxide, Sb_2O_4, which is stable at this temperature. But if it is further heated the hypoantimonic acid is decomposed in turn, perhaps at the temperature of melting silver, but assuredly a little above, and certainly below the fusion-point of gold, at which its decomposition into oxygen and volatile antimonious acid becomes fairly rapid. Antimony peroxide cannot therefore be considered as a fixed body, since it is decomposed by the mere action of heat.

Action of Tannin and other Organic Derivatives upon certain Compound Alkaloids and Ureas.—Oechsner de Coninck.—The author has experimented with pure tannin, a mixture of tannin and piperidine, gallic acid, pyrogallol, pyrocatechine, hydroquinone, and the compound ureas.

Certain Derivatives of Anethol.—Georges Darzens.—The substitution of chlorine for hydrogen in the lateral chain does not modify the odour of anethol. Carbon tetrachloride has the property of dissolving almost all organic bodies.

Fixation of Iodine by Wheat and Rice Starches.—G. Rouvier.

Solubility of the Red Pigment of the Grape and the Sterilisation of the Musts of Fruit.—A. Rosenstiehl.—The exclusion of the air is necessary for preserving the red colour of the grape and of other fruits. Musts preserved from contact with the air retain the agreeable taste of fresh grapes. The red colouring matter of the skins of the grape and of other fruits is soluble in the unfermented juice. The action of the air renders the colouring matter insoluble. It is one of the causes of the boiled taste. We may make preserves of musts, possessing the colour, the flavour, and the aroma of the fresh fruit.

No. 12, March 22, 2897.

Note on an Electric Commutator which can be Managed from a Distance.—C. Gros.

On Autoradioscopy.—Foveau de Courmelle.

Researches on the Monazite Sands.—G. Urbain and E. Badischowsky.—Will be inserted in full.

A Reaction of Carbon Monoxide.—A. Mermet.—Will be inserted in full.

On Isolauronic Acid.—G. Blanc.—The author has in a former paper described certain derivatives of isolauronolic acid, especially the aldehyd $C_9H_{14}O$.

New Method of Staining Acetylene. — Georges Claude and Albert Hass.—The authors describe an experiment which consists in maintaining indefinitely in acetone at a pressure of 3 atmospheres a platinum wire heated to bright redness by the electric current.

MISCELLANEOUS.

Carbohydrates remaining in Beer. — P. Petit. — As regards inversion of acids, the dextrine of beer behaves in a manner quite different from ordinary dextrines, and its manner of inversion approximates rather to that of melitriose.—*Comptes Rendus*, cxxiv., No. 10.

Royal Institution.—The following are the Lecture arrangements after Easter:—Dr. Tempest Anderson, four lectures on "Volcanoes" (the Tyndall Lectures); Dr. Ernest H. Starling, three lectures on "The Heart and its Work"; the Rev. Canon Ainger, four lectures on "Some Leaders in the Poetic Revival of 1760-1820—Cowper, Burns, Wordsworth, Scott"; Professor Dewar, three lectures on "Liquid Air as an Agent of Research"; the Reverend J. P. Mahaffy, three lectures on "The Greek Theatre according to Recent Discoveries"; Mr. J. A. Fuller Maitland, four lectures on "Music in England during the Reign of Queen Victoria" (with musical illustrations). The Friday Evening Meetings will be resumed on April 30th, when a discourse will be given by Professor J. J. Thomson on "Cathode Rays"; succeeding discourses will probably be given by "Anthony Hope," Professor Harold Dixon, the Right Hon. Lord Kelvin, Professor H. Moissan, Mr. W. H. Preece, Mr. William Crookes, and other gentlemen.

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Chemist for Cement Works wanted about May 1st. To be capable of making full analyses, tests, and reports of different materials as required, also take complete control of washing and other tests during manufacture. To give whole time to his duties and live near works.—Apply by letter only, stating salary required, with idea of a permanency, age, and previous experience, to "Chemist," 13, Burch Road, Gravesend.

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THE CHEMICAL NEWS.

Vol. LXXV., No. 1951.

ECONOMIC PREPARATION OF HYDROXYLAMINE SULPHATE.

By Prof. EDWARD DIVERS, M.D., F.R.S., and
TAMEMASA HAGA, F.C.S., Rigakuhakushi,
Late Asst. Prof. College of Science, Imperial University.

In 1887 Raschig made known that hydroxylamine can be got from a nitrite by sulphonation followed by hydrolysis, and took out patents for its manufacture in this way. As to what extent these patents may have since been worked, and with what success, we have no information; but we cannot believe that this process has been advantageously carried out without great modification of the directions given. The one we are about to describe is very productive and economical for the preparation of hydroxylamine sulphate, a non-deliquescent salt, readily forming large crystals, and soluble in three-quarters of its weight of water at 20°.

Commercial sodium nitrite of 95 per cent purity does not contain more than 1 per cent of objectionable matters, such as chloride and nitrate, and is therefore pure enough. A concentrated solution of this salt (2 mols.) and of sodium carbonate (1 mol.), pretty closely adjusted in their proportions, is treated with sulphur dioxide till just acid, while it is kept well agitated at 2—3° below zero by immersion in ice and brine. At this temperature the conversion of the nitrite into oximidosulphonate is apparently perfect. Gently warmed with a few drops of sulphuric acid the oximidosulphonate rapidly hydrolyses, with marked rise of temperature, into oxyamidosulphonate and acid sulphate. The solution of these salts is kept at 90—95° for two days, by the end of which time all oxyamidosulphonate will have hydrolysed into hydroxylamine sulphate and sodium acid sulphate, while so small a quantity of ammonium salt is produced as can only be detected in the very last mother-liquors of crystallisation by chloroplatinic acid (potassium hydroxide being an unsuitable reagent in presence of hydroxylamine). At 80—85° five days are necessary, but then practically no ammonia is formed. At 70°, three weeks at least are necessary, while at the common temperature much oxyamidosulphonic acid remains after several months, even when much sulphuric acid has been added. On the other hand, the solution kept boiling needs seven or eight hours usually to deprive it of all sulphonate; but the boiling has disastrous effects on the hydroxlamine, destroying at least one-third of it, by converting it (through amidosulphonic acid?) into ammonia, and wasting another third as a practically inseparable mixture of its sulphate with ammonium sulphate.

To be assured of the disappearance of all sulphonate it is well to add barium chloride in excess to a little of the solution, and filter, and then boil the filtrate with potassium chlorate, which will change any sulphonate into sulphate. Sulphonation complete, the solution is neutralised with sodium carbonate, using methyl orange as indicator, and evaporated till it weighs only 10½ to 11 times as much as the sodium nitrite taken. Left to cool where its temperature will fall to 0° or lower, nearly all its sodium sulphate will crystallise out. The mother-liquor, evaporated sufficiently and cooled to the common temperature, yields much hydroxylamine sulphate, the mother-liquor from which, very slightly diluted and cooled below 0°, gives again a little sodium sulphate, and can be worked for more hydroxylamine sulphate, as before.

The crude hydroxylamine sulphate weighs about 9 parts for every 10 parts of sodium nitrite taken. It needs to be re-crystallised, but the mother-liquors can be closely worked up. On the other hand, the sodium sulphate re-crystallised, or even washed with ice-water, will give up 1 part more of hydroxylamine sulphate; so that sodium nitrite will yield, on the small scale, nearly its own weight of pure hydroxylamine sulphate. No doubt, on the large scale, the theoretical yield of 118·84 per cent could be more nearly approached.

Potassium nitrite is not well fitted for the preparation of hydroxylamine, because of the difficulty experienced in closely separating its sulphate from that of potassium. After several re-crystallisations the hydroxylamine salt contains 1·8 per cent of potassium sulphate. The addition of aluminium sulphate is not an improvement, for then the hydroxylamine sulphate, separated as far as practicable from the potassium alum, leaves behind on ignition as much as 5·7 per cent residue.—*Journal of the College of Science, Imperial University, Japan*, vol. ix., Part II., p. 291.

RESEARCHES ON MONAZITIC SANDS.

By G. URBAIN and E. BUDISCHOVSKY.

We have undertaken this enquiry to find if it is legitimate to admit the existence in the monazitic sands of a new earth; the atomic weight would be approximately = 100.

In very precise and minute researches on the fractionation earths of the yttrium series obtained from the monazitic sands, P. Schützenberger and O. Boudouard have succeeded in isolating portions which cannot be split up, presenting a character of great stability, and having an atomic weight close upon 102.

More recently Drossbach (*Berichte*, xxx., 2452), on studying a monazite, arrived at similar conclusions.

In contradiction with these results, Mr. Crookes (Chemical News, No. 1931, p. 259), having examined a specimen of the yttrium earths derived from the monazitic sands, and known as *lucium*, concludes from the spectrum analysis—notwithstanding the hesitations of Schützenberger and Boudouard—that these oxides ought to be regarded as impure yttrium.

The hypothetical element supposed to be contained in the portion of the yttrium earths precipitable by sodium hyposulphite, we shall confine ourselves in this paper to a description of the experiments which we have made on the portions of the earth precipitated by this reagent, as Mr. Crookes has demonstrated that it is a very general agent of fractionation, and that it perfectly precipitates yttrium.

The sands which we studied are the same as those which have been the subject of the beautiful researches of Schützenberger and Boudouard. We repeated the treatment of the earths with potassium sulphate until the concentrated solutions—on examination with the microscope in a concentrated solution and in a stratum of 20 to 30 c.m. in depth—no longer displayed the absorption-spectrum of didymium. The absorption-spectrum of the solution free from didymium is the following:—

	Wave-lengths.
A weakening..	656—649
A still weaker band	583—670
A narrow weak band	541 —
A broad band..	535—517
Very faint	535—526
Very strong maximum.. ..	— 522
A very faint band..	493—484

This spectrum, which is of little intensity, coincides very closely with the spectrum described for erbium.

One of us having observed that the acetylacetonates of the rare earths are soluble in most of the organic solvents and easily admit of fractionations, it seemed interesting to apply this method to those earths, to trace if we should reach results different from those of the authors cited.

We followed very closely the course of the fractionations by the determination of the atomic weights.

The method which we employed for this does not differ sensibly from that of Schützenberger and Boudouard. Thanks to the advice of Friedel we fixed upon a method of operating which seems to us out of the reach of criticism. The salts we converted into nitrates; the solution of the nitrates is mixed with sulphuric acid, and the sulphates are evaporated to dryness to expel the chief part of the free acid. The solid sulphates are introduced into small tubes, which are heated in the vapour of mercury, by means of a bottle of mercury fitted with a reflux pipe and three muffles supported vertically. We cause the sulphates to pass successively into the different muffles, weighing them from time to time until we obtain a weight constant to about $\frac{1}{5}$ m.grm. The sulphates are then transformed into oxides, by heating them in a double platinum crucible in the Fourguignon furnace until the weight is constant. The atomic weight is easily deduced from the transformation of the sulphates into oxides. We have satisfied ourselves that on heating the oxides successively in a current of oxygen, and in a current of hydrogen, they do not undergo a perceptible variation of weight.

We prepare the acetylacetates as follows:—

The nitrates in a very dilute aqueous solution (5 grms. per litre) are precipitated with ammonia. We wash by decantation, and add the quantity of acetylacetone theoretically sufficient to transform the hydrates into crystalline acetylacetonates. We filter; the crystals are fractionated at first in alcohol and then in benzene. These two reagents dissolve the acetylacetonates freely in heat, and on cooling re-deposit them in needles.

In alcohol the substances of low atomic weight are concentrated in the first crystals; after six fractionations the mother-liquors and the crystals have sensibly the same atomic weights.

Collecting the portions of adjacent atomic weights we made a series of fractionations in benzene.

These results are interesting to compare with those obtained by Schützenberger and Boudouard.—*Comptes Rendus*, cxxiv., p. 618.

THE VOLUMETRIC DETERMINATION OF ZINC BY POTASSIUM FERROCYANIDE.

By L. L. de KONINCK and EUG. PROST.

The volumetric determination of zinc, since the publication of the Schaffner process in 1856, has formed the subject of numerous researches.

Of all the methods proposed, two only seem admissible in current practice.

On the European continent the process of Schaffner seems to be almost exclusively in use. It consists in the use of sodium sulphide. In America the Galletti procedure, as modified by Fahlberg, meets with great favour. It depends on the precipitation of zinc by potassium ferrocyanide in an acid solution (Chem. News, lxvii., 5). The ferrocyanide process appears to have been less carefully studied than that of Schaffner. It is applied in three modifications:—1. In an acid solution, as originally proposed by Galletti. 2. In a simple ammoniacal solution (A. Renard). 3. In a tartaric-ammoniacal solution. The authors confine their attention to the original procedure of Galletti. They examine the influence of time, and find that an excess of ferrocyanide corresponding to 20 per cent is sufficient to produce the transformation in fifteen minutes. The order in which the solutions are mixed is without influence upon the result. Ammonium chloride promotes the precipitation. Ammonium nitrate has no action. To obtain very exact results the solutions must have a constant degree of acidity.

If the solution of zinc is treated with hydrogen sulphide, in order to throw down copper, cadmium, &c., it is necessary to re-oxidise the salts of iron by nitric acid or bromine.

The presence of bromine has no influence. The effects of nitric acid may be annulled by means of sodium sulphite. Manganese, if present, must be completely eliminated before titration.

All metals capable of reacting with ferrocyanide under the circumstances of the experiment must also be eliminated.

To the ammoniacal solution finally obtained, containing a quantity of ammoniacal compounds more or less constant, are added a few drops of sodium sulphite; the liquid is then neutralised with hydrochloric acid, and then acidulated with a constant quantity of the same acid.

To this solution is then added a measured volume of solution of ferrocyanide, constituting an excess of 20 to 25 p. c. on the quantity necessary for the exact precipitation. After digestion for at least ten to fifteen minutes, the quantity of zinc corresponding to the excess of the reagent is ascertained by titrating back by means of a neutral or very slightly acid solution of $ZnCl_2$.

Solutions to be used.

A. A zinc solution containing per litre 10 grms. of the metal, and very slightly acid. To obtain this we dissolve 10 or 20 grms. of pure zinc in a minimum of hydrochloric acid, in a flask graduated to 1 or 2 litres with the acid of moderate heat.

When the solution is complete the liquid is brought approximately to half the final volume, and the excess of acid neutralised by means of a solution of potassium carbonate until the appearance of a slight precipitate, which is made to disappear by adding hydrochloric acid drop by drop. The liquid is brought to the ordinary temperature, and the flask filled exactly up to the mark with distilled water.

B. A solution of potassium ferrocyanide. When, as is frequently the case in technical assay, the quantity of zinc present is approximately known, we take 2 c.c. of ferrocyanide per supposed centigrm. of zinc, and have thus the excess of 25 per cent which we recommend to be employed.

C. The indicator is a solution of 1 per cent uranium nitrate in an aqueous solution.

Assay of Ores.

We treat a portion of the ore of 2·5 grms., dried at 100° with aqua regia if it is a blende, or with fuming hydrochloric acid if it is a calamine. When the attack is complete we evaporate to dryness to render the silica insoluble, take up the residue from the evaporation in 5 c.c. of hydrochloric acid and a little water, and then, after heating for some time to ensure the solution of the basic salts produced by evaporation, we add 50 to 60 c.c. of water and heat to 70°. We then submit the liquid to the action of a moderate current of hydrogen sulphide; during the passage of this gas we add, in several portions, 100 c.c. of water, to facilitate the subsidence of the lead and the cadmium which would not be precipitated in a solution too strongly acid. On the other hand, we must not prolong the passage of the hydrogen sulphide beyond the necessary time, nor must we dilute too strongly for fear of precipitating zinc.

The precipitate of the sulphides is collected on a filter along with the silica, if there is no reason for collecting this separately. It is acidified with 5 per cent of hydrochloric acid charged with hydrogen sulphide.

The washing is complete when the last drops of the precipitate, rendered alkaline with ammonia, no longer give the slightest precipitate with a drop of sodium sulphide.

The filtrate is heated at ebullition until the hydrogen sulphide is expelled; it is mixed with 10 c.c. of fuming hydrochloric acid and from 10 to 25 c.c. of saturated bromine water (according to the proportion of iron), so as to re-oxidise the ferrous salts and assist the precipitation of manganese. It is then passed drop by drop, whilst constantly stirring, into a flask marked at 500 c.c., containing 100 c.c. of concentrated ammonia and 10 c.c. of solution of ammonium bicarbonate more or less saturated in the cold (about 20 to 25 per cent). It is allowed to cool, water is added up to the mark, stirring so as to render the mixture homogeneous, left for a short time to deposit the precipitate, and filtered with a dry filter.

The method described is that applicable to the preparation of the solution for the most complex ores. In the absence of metals precipitable by hydrogen sulphide the treatment with that reagent is omitted, and the re-oxidation of the iron salts is unnecessary, since they have not been reduced.

The use of bromine is needed only if the ore is manganiferous.

If the ore contains metals requiring treatment with hydrogen sulphide, but no manganese, the re-oxidation of the ferrous salts may, if preferred, be effected by boiling nitric acid.

We take 100 c.c. of the ammoniacal filtrate prepared as above directed, add a few drops of sulphite, and pour in gradually hydrochloric acid (sp. gr. 1·075) until a small morsel of litmus-paper thrown into the liquid shows, in passing to redness, that the point of neutralisation has been reached (about 30 c.c.), and we then add further 10 c.c. of the same acid.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF MAGNESIUM.*

By THEODORE WILLIAM RICHARDS
and
HARRY GEORGE PARKER.

(Concluded from p. 175).

Third Series of Determinations.

In order to remedy the most serious defect of the second series, the arrangement for drying the air and nitrogen was much enlarged and improved. By pouring sulphuric acid into the safety funnels, at the top of the many towers, from time to time, during the passage of the gas, the glass beads were kept thoroughly saturated during the whole process. The sulphuric acid having reached the bottom of the column, drained out of the tubes provided for that purpose into beakers below. It will be seen that by this means the efficiency of the apparatus was far greater than in the previous form. As a test, a very rapid stream of wet air from a water blast was passed through the apparatus and then through a weighed phosphorus pentoxide bulb for nearly two hours, without the slightest appreciable increase of weight of the pentoxide bulb. The same test was applied to the apparatus for drying the hydrochloric acid gas, with the same result.

With the help of this important addition to the apparatus, another series of determinations was now made. The somewhat lower result of this series is undoubtedly due to the more perfect desiccation of the gases; the agreement of the individual results is still not quite perfect, but the series is undoubtedly far more reliable than the second.

SERIES III.

No. of expt.	Sample of $MgCl_2$ used.	Sample of Ag used.	Weight of $MgCl_2$.	Weight of Ag.	Ratio. $MgCl_2 : 2Ag = 100 : n$.	Atomic weight of Mg.
9	1	2	1·99276	4·51554	226·597	24·349
10	1	2	1·78870	4·05256	226·565	24·363
11	1	2	2·12832	4·82174	226·551	24·369
12	2	2	2·51483	5·69714	226·542	24·373
13	2	3	2·40672	5·45294	226·571	24·360
14	2	3	1·95005	4·41747	226·531	24·377
				Average ..	.. ..	24·365

Fourth and Final Series of Determinations.

The apparatus was now put in the best possible order, and the phosphorous pentoxide tubes were re-charged, in order to make ready for a series of determinations in which the very highest exactness was to be aimed at. The purest samples of material were used, and all other precautions, learned from previous work, were taken to insure accuracy. The following determinations were consecutive, with the exception of one between Nos. 15 and 16, which was spoiled by a slight accident.

SERIES IV.

No. o exp.	Sample of $MgCl_2$ used.	Sample of Ag used.	Weight of $MgCl_2$.	Weight of Ag.	Ratio. $MgCl_2 : 2Ag = 100 : n$.	Atomic weight of Mg.
15	2	3	2·03402	4·60855	226·573	24·360
16	2	3	1·91048	4·32841	226·562	24·364
17	2	3	2·09932	4·75635	226·566	24·362
18	2	2	1·82041	4·12447	226·568	24·362
19	2	2	1·92065	4·35151	226·565	24·363
20	3	4	1·11172	2·51876	226·564	24·363
				Average ..	.. ..	24·362
				Extreme difference..		0·004

These results agree with one another as well as could possibly be expected, for the difference between the extremes in the last series corresponds to a difference of only one-tenth of a milligrm. in the weight of the magnesic chloride. Since two wholly distinct samples of this salt and three wholly distinct samples of silver were used in this series, we may conclude that all ordinary accidental errors had been eliminated; and in a critical discussion of the result we may limit ourselves to the consideration of the possible constant errors of the process.

The most serious objection to the method is, of course, the possible retention of water, of magnesic oxychloride, or of ammonic chloride by the magnesic salt.

With regard to the first two difficulties, it need only be said that the gases used for drying the magnesic chloride were as dry as present possibilities permit them to be made. The phosphorus pentoxide in the last drying tube showed no trace of liquefaction at the close of the research, but seemed to be as light and powdery as at first, in spite of the fact that several hundred litres of gas had been passed over it. Any trace of oxygen, as well as of aqueous vapour, was excluded from the hot salt; for the hydrochloric acid gas was replaced by nitrogen, and this was driven out in its turn by dry air only after the tube had cooled. A means of proving absolutely that no water remained does not exist; but it is extremely hard to see how water could have gained access to the carefully guarded magnesic chloride.

The fact that every sample of magnesic chloride used in the last series gave an absolutely clear and transparent solution in water is additional evidence of much weight; for a very small trace of oxychloride would have shown itself in opalescence. As a proof of this it may be stated that in experiment No. 12 of Series III. there was a perceptible cloudiness upon the solution of the magnesic chloride in water, owing to a known access of a trace of aqueous vapour, caused by a momentary stoppage of the

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* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxii., No. 2.

current of nitrogen. This result is, however, scarcely at all different from the others.

With regard to the possible retention of ammonic chloride by the magnesium salt, it may be said:—First, that none could be detected by means of a Nessler solution; and, secondly, that even if a small amount had been retained, it would have made but a very slight difference in the final result.

Our result is essentially the same, no matter whether the chlorine is weighed as argentic chloride (Series I.), or the amount of silver necessary to precipitate it is found (Series III. and IV.). This fact is satisfactory evidence that the silver and chlorine were both pure, as well as that no magnesic chloride was occluded by the argentic chloride. Thus:—

From the ratio $2AgCl : MgCl_2$ (Series I.), $Mg = 24·369$.
,, ,, $2Ag : MgCl_2$ (Series III.), $Mg = 24·365$.
,, ,, $2Ag : MgCl_2$ (Series IV.), $Mg = 24·362$.

Upon comparing these figures with the older ones, they are seen to agree surprisingly with Marignac's value obtained from work upon magnesic oxide and sulphate ($Mg = 24·37$). Burton and Vorce's syntheses of magnesic oxide gave a lower value for magnesium (24·28); but if these were corrected for a probable amount of gases in the magnesic oxide, the result would probably be close to the present one. The analytical chemist should not forget that the value 24·36 is 1½ per cent higher than the round number 24, which has been so commonly accepted.

For reasons which must be manifest to any careful reader of the foregoing paper, we accept the value given by the fourth and last of our series as representing the most probable atomic weight of magnesium. It remains only to state this result in terms of the usual unfortunately varying standards of reference used by the scientific world.

If $O = 16·000$, $Mg = 24·362$
If $O = 15·96$, $Mg = 24·301$
If $O = 15·88$, $Mg = 24·179$

THE ATOMIC WEIGHTS OF NITROGEN AND ARSENIC.*

By JOSEPH GILLINGHAM HIBBS.

The atomic weight of the metal molybdenum had been determined by expelling molybdic acid from sodium molybdate with hydrochloric acid gas, then weighing the residual sodium chloride.

Having found that nitric acid and arsenic acid were driven from their alkali salts with ease, leaving a chloride that was absolutely pure, and believing that the atomic masses of nitrogen and arsenic determined in this manner would afford a valuable contribution to the literature relating to these constants, a carefully conducted series of experiments was made with two nitrates and one arsenate. The results are given in detail in the following lines:—

The Atomic Weight of Nitrogen.

In the past, determinations of the atomic weight of nitrogen have been made from the density of the gas itself, from the ratio between ammonium chloride and silver, and from the decomposition of certain nitrates. The first method in particular has been frequently applied. Thomson, Dulong, Berzelius, and Lavoisier brought to light many new facts relating to the atomic weight of nitrogen; unfortunately, however, they have been affected by complications that have introduced inaccuracies.

Dumas and Boussingault (*Comptes Rendus*, 1841, xii., 1005) found the mean density of nitrogen to be 0·972; for hydrogen they found a mean density of 0·0693, which would give nitrogen an atomic weight of 14·026. Regnault obtained a more concordant series of results, the mean being 0·97137, and a density for hydrogen of 0·0692, which makes the atomic weight of nitrogen equal to 14·0244.

Clarke gives in detail his computation of the means of the results obtained by Penny, Stas, and Marignac. Their work on the determination of the atomic weight of this particular element was mainly on the ratio of ammonium chloride and silver, and the decomposition of certain nitrates. A great degree of accuracy was maintained throughout the entire investigation; but the amount of work required to obtain a single result necessarily lays the method open to a serious error of manipulation.

In this connection a paragraph from Clarke's "A Recalculation of the Atomic Weights" may be cited:—"The general method of working upon these ratios is due to Penny. Applied to the ratio between the chloride and nitrate of potassium, it is as follows:—A weighed quantity of the chloride is introduced into a flask which is placed upon its side and connected with a receiver. An excess of pure nitric acid is added, and the transformation is gradually brought about by the aid of heat, the nitrate being brought into a weighable form. The liquid in the receiver is also evaporated, and the trace of solid matter which has been mechanically carried over is recovered and also taken into account."

The method indicated in this study, and actually applied with the results appended, is decidedly less objectionable. In this method there is no distillation, no precipitate; in fact, nothing that could involve serious error.

Clarke summarises the results of Penny, Stas, and Marignac as follows:—

1.	From specific gravity of N	$N = 14·0244$
2.	,, ammonium chloride	$N = 14·0336$
3.	,, ratio number four	$N = 14·0330$
4.	,, silver nitrate	$N = 13·9840$
5.	,, potassium nitrate	$N = 13·9774$
6.	,, sodium nitrate	$N = 13·9906$
	Mean of results for N .. .,	$N = 14·0210$

If oxygen is 16, this becomes 14·0291. Stas found the atomic weight of nitrogen to be 14·044. Dumas found 14 by experiments on the combustion of ammonia and cyanogen ($O = 16$). Pelouze found 14·014 by bringing a known weight of silver nitrate in contact with a known and slightly excessive weight of ammonium chloride, which excess was titrated. Anderson found 13·95 by the decomposition of the nitrate of lead, with just enough heat for decomposition (the same method that was used by Berzelius). Marignac found 14·02 by dissolving a known weight of silver in nitric acid and then melting and weighing the nitrate found.

A.—*Atomic Weight of Nitrogen by Action of Hydrogen Chloride upon Potassium Nitrate.*

The purest salt obtainable was dissolved in water, filtered, and re-crystallised six times, a solution of which was tested for chlorides, sulphates, &c., but no impurity was found. One more crystallisation was made and the best crystals were selected. These were washed with distilled water and dried at 210° C. for three hours, powdered, and again dried, and finally placed in a weighing bottle. This compound was dried before each experiment. It was also allowed to stand in a balance case one hour before weighing. The same degree of care was exercised in the preparation of the boat for weighing.

The weighing bottle was placed on the scale pan and

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* Contribution from the John Harrison Laboratory of Chemistry. From the author's thesis presented to the faculty of the University of Pennsylvania for the degree of Doctor of Philosophy, 1896. From the *Journal of the American Chemical Society*, vol. xviii., No. 12.

TABLE A.

No.	Potassium nitrate taken.	Potassium chloride. obtained.	Correction for potassium nitrate.	Correction for potassium chloride.	Correction for weight of potassium nitrate.	Correction for weight of potassium chloride.	Molecular weight of potassium nitrate obtained.	Atomic weight of nitrogen obtained.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.		
1.	0·11084	0·08173	0·00006	0·00004	0·11090	0·08177	0·101121	14·011
2.	0·14864	0·00960	0·00007	0·00005	0·14871	0·10965	0·101120	14·010
3.	0·21056	0·15525	0·00011	0·00008	0·21067	0·15533	0·101123	14·013
4.	0·23248	0·17214	0·00012	0·00009	0·23360	0·17223	0·101121	14·011
5.	0·24271	0·17894	0·00013	0·00009	0·24284	0·17903	0·101124	14·014

Atomic weight of nitrogen = 14·0118 ± 0·000472.

TABLE B.

No.	Potassium nitrate taken.	Sodium chloride obtained.	Correction for sodium nitrate.	Correction for sodium chloride.	Correction for sodium nitrate.	Correction for sodium chloride.	Molecular weight of sodium nitrate.	Atomic weight of nitrogen.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.		
1.	0·01550	0·01064	—	—	0·01550	0·01066	85 061	14·011
2.	0·20967	0·14419	0·00009	0·00007	0·20976	0·14426	85·061	14·011
3.	0·26217	0·18029	0·00012	0·00009	0·26229	0·18038	85·064	14·014
4.	0·66610	0·46805	0·00035	0·00024	0·66645	0·45829	85·064	14·014
5.	0·93676	0·64422	0·00042	0·00034	0·93718	0·64456	85·058	14·008

Atomic weight of nitrogen = 14·0116 ± 0·000741.

TABLE C.

No.	Sodium pyroarsenate taken.	Sodium chloride obtained.	Correction for sodium pyroarsenate.	Correction for sodium chloride.	Correction for sodium pyroarsenate.	Correction for sodium chloride.	Molecular weight of sodium pyroarsenate.	Atomic weight of arsenic.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.		
1.	0·02176	0·01439	0·00001	0·00000	0·02177	0·01439	354·008	74·904
2.	0·04711	0·03114	0·00002	0·00001	0·04713	0·03115	354·042	74 921
3.	0·05792	0·03828	0·00003	0·00002	0·05795	0·03830	354·054	74·927
4.	0·40780	0·26970	0·00021	0·00011	0·40801	0·26981	354·002	74·901
5.	0·50440	0·33028	0·00026	0·00017	0·50466	0·33045	354·033	74·916
6.	0·77497	0·51222	0·00041	0·00027	0·77538	0·51249	354·034	74·917
7.	0·82853	0·54762	0·00044	0·00029	0·82897	0·54791	354·034	74·917
8.	1·19 68	0·78690	0·00056	0·00041	1·19124	0·78731	354·053	74·926
9.	1 67464	1·10681	0·00081	0·00051	1·67545	1·10732	354·057	74·928
10.	3·22485	2·13168	0·00152	0·00099	3·22637	2·13267	354·002	74·901

Atomic weight of arsenic = 74·9158 ± 0·00222.

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allowed to stand several minutes in order to regain its normal temperature. After weighing it was quickly opened and a portion of the salt removed to the boat, and again closed and allowed to stand in the balance case for several hours before re-weighing. The boat was then introduced into the combustion tube and the gas passed over it. The characteristic action took place, The only difference in the method of procedure adopted here and that described in the first section of this paper, was a longer time being given to complete the action, using a lower temperature, in order to do away with all possibility of fusion of the salt. It was then carefully removed to a vacuum desiccator and allowed to stand over night before weighing. It may be said also that experiments were only conducted on clear days to insure the non-entrance of moisture.

With potassium nitrate, no great variation of amount was taken.

Five determinations were made in this case (Table A). The atomic values used in these calculations were taken from "Table of Atomic Masses," revised by F. W. Clarke, in October, 1891.

The figures deduced from these values are, of course, subject to any change made by later revision of atomic weights. It is not so much the exact figure to which attention is called, as to the constancy of result brought forward by this method. The values used were:—

Oxygen	16·00
Potassium	39·11
Chlorine	35·45
Specific gravity potassium nitrate	2·1
Specific gravity potassium chloride	1·99

B.—*Atomic Weight of Nitrogen by Action of Hydrogen Chloride upon Sodium Nitrate.*

The same degree of care and method of procedure were here observed as in Division A. The results are given in Table B.

Atomic values used were:—

Oxygen	16·00
Sodium	23·05
Chlorine	35·45
Specific gravity sodium chloride	2·16
Specific gravity sodium nitrate	2·26

When these results are compared with those obtained by Penny and Stas by treatment of potassium chloride with nitric acid, and the treatment of potassium nitrate with hydrochloric acid (likewise for sodium), a close comparison can be made.

	Penny.	Hydrogen chloride method.
For potassium nitrate	13·9774	14·0118
For sodium nitrate ..	13·9906	14·0116

Showing a difference of—

0·0344 for potassium salt,
0·0210 for sodium salt.

When a mean of the above results is taken, the atomic weight of nitrogen equals—

13·9996 for potassium salt,
14·0011 for sodium salt.

Taking now a mean of these values, the atomic weight of nitrogen would be 14·0003.

C.—*The Atomic Weight of Arsenic.*

The atomic weight of arsenic has been obtained from the chloride ($AsCl_3$), the bromide ($AsBr_3$), and the trioxide (As_2O_3).

Pelouze, in 1845 (*Comptes Rendus*, x., 1047), and Dumas, in 1859, determined it by the titration with known quantities of pure silver in the analysis of arsenic trichloride. The mean of their results, as computed by Clarke, gives the atomic weight of arsenic 74·829. Wallace (*Phil. Mag.*, (4), xviii., 279) makes the same titration with silver in the analysis of arsenic tribromide. His value is 74·046. Kessler made a set of determinations by estimating the amount of potassium bichromate required to oxidise 100 parts of arsenic trioxide to arsenic pentoxide. He obtained a mean value of 75·002.

A mean of these results gives the following:—

From $AsCl_3$	74·829
,, $AsBr_3$	74·046
,, As_2O_3	75·002
General mean	74·918

If oxygen = 16 then the atomic weight of arsenic will equal 75·090.

Berzelius, in 1826, heated sulphur and arsenic trioxide together in such a way that sulphur dioxide alone escaped; this method gave 74·840 as the atomic weight of arsenic. But one experiment was made, so that it does not possess much value. In the above method there seems to be a wide variation in the results obtained, the difference between the extreme values is but little less than one unit.

By the hydrogen chloride method, we have but the weighing of the material used in the determination—which must necessarily enter every estimation or analysis —and a single weighing after the action of the acid gas. As in the case of nitrogen, the method seems to be as short and concise as possible.

The methods and *modus operandi* were exactly the same as those used in the determination of the atomic weight of nitrogen.

The sodium chloride obtained was perfectly white in colour. In no instance was it fused. After weighing the salt residue it showed no traces of arsenic, and was readily soluble in cold water without residue. The same conditions of atmosphere were observed.

As the specific gravity of sodium pyroarsenate could not be obtained, it was determined by means of the specific gravity bottle, against chloroform, and was found to be 2·205, while the specific gravity of sodium chloride was taken as 2·16. The atomic values used were:—

Oxygen	16·00
Sodium	23·05
Chlorine	35·45

The results here obtained, besides being to a great degree constant, compare favourably with those obtained by Pelouze (74·829) and Kessler (75·002).

A coincidence may here be shown by the fact that the mean of these values gives 74·9155, while the hydrogen chloride method gives 74·9158.

In order to give the method a thorough trial, the amounts taken cover a wide range. The smallest amount used was 0·02176 grm. of sodium pyroarsenate, and the largest 3·22485 grms. It will also be noticed that the variation in result is but 0·027 for ten determinations (Table C).

NOTES ON THE
FERROCYANIDES OF ZINC AND MANGANESE.

By EDMUND H. MILLER.

THE composition of the ferrocyanides of zinc and manganese, formed when salts of these metals are precipitated by potassium ferrocyanide, is given by Prescott and Johnson ("Qualitative Analysis," pp. 67 and 57) as $Zn_2Fe(CN)_6$ and $Mn_2Fe(CN)_6$, while the books on volumetric analysis, such as Sutton's and Beringer's, ignore the composition of this precipitate.

The prevailing idea is that in the titration of zinc by potassium ferrocyanide, a normal zinc ferrocyanide is formed. This I believe to be incorrect, for if the reaction is—

$$K_4Fe(CN)_6 + 2ZnCl_2 = Zn_2Fe(CN)_6 + 4KCl,$$

a solution of potassium ferrocyanide, 1 c.c. of which is equivalent to 10 m.grms. of zinc, would contain 32·32 grms. of $K_4Fe(CN)_6 \cdot 3H_2O$ to the litre, not 43·2 (Sutton, "Volumetric Analysis," p. 329; Beringer, "Assaying," p. 219) to 45 grms. (Furman, "Assaying," p. 205), as has been found by experiment. Using 44 grms. per litre as a basis for calculation, the reaction becomes—

$$2K_4Fe(CN)_6 + 3ZnCl_2 = Zn_3K_2(Fe(CN)_6)_2 + 6KCl.$$

This reaction is not merely one that may possibly be true, but according to Wyrouboff (*Ann. Chim. Phys.*, [5], viii., 485), the precipitate formed by the action of potassium ferrocyanide on a zinc salt, whichever is in excess, is $3Zn_2Fe(CN)_6 . K_4F_3(CN)_6 . 12H_2O$, white, while the normal salt, $Zn_2Fe(CN)_6 . 4H_2O$, is formed only by the action of hydroferrocyanic acid on a zinc salt.

This statement agrees both with the preceding reaction and with the results obtained in standardising potassium ferrocyanide solution.

The manganese precipitate with potassium ferrocyanide, as obtained in titration, is given by Stone (*Journ. Amer. Chem. Soc.*, xvii., 473) as $Mn_3Fe_2(CN)_{12}$. This is a ferri-, not a ferrocyanide, thus making necessary a change of quantivalence. Mr. Stone also states that an amount of potassium ferrocyanide which will precipitate 4 atoms of zinc will only precipitate 3 of manganese, thus basing his calculation on the formation of normal zinc ferrocyanide.

Wyrouboff (*Ann. Chim. Phys.*, [5], viii., 474) gives the precipitate obtained from potassium ferrocyanide and manganese salt, whichever is in excess, as—

$$5Mn_2Fe(CN)_6 . 4K_4Fe(CN)_6 . 4H_2O, \text{ rose white;}$$

while the normal salt $Mn_2Fe(CN)_6 . 7H_2O$, cream, is formed as in the case of zinc by hydroferrocyanic acid.

The solution used by Mr. Stone had the following strength:—

1 c.c. = 0·00606 grm. zinc.
1 c.c. = 0·00384 grm. manganese.

If the ratio were exactly four zinc to three manganese, using the most recent atomic weights, the strength of this solution against manganese would be 1 c.c. = 0·00382 grm.; while, according to Wyrouboff, $10Mn = 9K_4Fe(CN)_6$ and $6Zn = 4K_4Fe(CN)_6$, or $10Mn = 13·5\ Zn$, or $1Mn = 1·35\ Zn$, and the strength against manganese would be 1 c.c. = 0·003774 grm.

These figures show but little difference between the two ratios, and, while Mr. Stone's experimental results are undoubtedly accurate, his theory based on the formation of $Zn_2Fe(CN)_6$ and $Mn_3Fe_2(CN)_{12}$ is not satisfactorily proved.

This article is only a preliminary note regarding the composition of the ferrocyanides as they are being investigated in this laboratory.

In connection with the ferrocyanide of zinc I have found a very strong solution of hydrochloroplatinic acid, H_2PtCl_6, acidified with hydrochloric acid, a most satisfactory indicator for the titration of zinc by potassium ferrocyanide, when performed in a hot solution. This indicator is used in the same way as uranium acetate, and is less affected by a varying amount of hydrochloric acid. The end reaction is a bright emerald-green, which takes a few seconds to develop. It will not work with a cold solution.—*Journal of the American Chemical Society*, xviii., No. 12.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, April 9th, 1897.

Mr. Shelford Bidwell, President, in the Chair.

Mr. T. A. Garrett read a Paper on "*A Nickel Stress Telephone.*"

In conjunction with Mr. W. Lucas, the author has experimented upon telephones with nickel magnets. A magnetised nickel rod is wound with insulated wire, and is then fixed vertically by a clamp at its lower end. A wooden diaphragm is rigidly attached to the top of the rod, in a horizontal plane. The rod just passes through the middle of the diaphragm, where it is fixed with sealing-wax. The diaphragm is entirely supported by the nickel rod. On speaking against the top of the diaphragm, variations of longitudinal pressure, and consequently of magnetisation, are produced in the nickel; and corresponding undulatory currents are induced in the surrounding coil. The nickel wire is sometimes magnetised by stroking it with a magnet, and sometimes by passing a current through the coil. A diaphragm of pine wood gives better results than a metallic plate. The instrument does not work well as a "receiver"; an ordinary telephone is used for this latter purpose. The results obtained with a weakly magnetised nickel rod are much better than those with a strongly magnetised steel rod, indicating that the undulatory currents are due rather to magnetic variations arising from changes of stress than to the relative motions of the magnet and coil.

Dr. S. P. Thompson said that some years ago he had worked with a somewhat similar apparatus, using it as a "receiver," with wires of nickel, cobalt, and iron. Cobalt gave the best results; the metallic strips in his experiments dipped into the solenoids without contact with them. This arrangement did not work well as a "transmitter," even when a battery was included in the circuit. In some cases the rods were cut into short lengths separated by brass.

Mr. Boys asked how the nickel "stress" instrument compared in clearness and loudness with an ordinary telephone.

Mr. Shelford Bidwell had tried a nickel telephone with a mica diaphragm; depending not upon mechanical stress, but magnetic strain. It did not work well.

Dr. Chree thought the "stress" telephone might possibly be improved by choosing the right strength of magnetic field.

Mr. Appleyard said the arrangement was interesting historically, because it was, mechanically, almost identical with the original instrument used by Philip Reis as a "receiver." The authors had succeeded in getting it to work as a "transmitter." Their success was probably due to the rapidity with which the magnetisation of nickel responded to very small changes of stress or current. The Post-Office electricians had tried to introduce nickel cores into relays, on account of its magnetic sensitiveness; the results, he believed, had not been very satisfactory.

Mr. T. A. Garrett, in replying, said the "stress" telephone gave better articulation than an ordinary "watch" telephone, but the sounds were feebler. There seemed to be a field-strength proper to the instrument; he had noticed that the articulation was clearer with three cells than with six.

Mr. W. A. Price then read a Paper on "*Alternating Currents in Concentric Conductors.*"

This is a mathematical investigation of a proposed new form of submarine cable. The case is considered of two concentric conductors, interrupted alternately at different points throughout the whole length. In the mathematical treatment the cable is supposed to be laid in a circular path, and successive charges of electricity are supposed to be applied at some point at the extremity of a diameter of the circle. Expressions are given for the amplitude of the periodic charges arriving at a point diametrically opposite to the first; and for the reduction in amplitude, throughout the whole length of the cable, of an applied E.M.F. The theory indicates that under no circumstances can the "speed" of a cable of the proposed form be greater than the "speed" of a cable of ordinary type. The author has experimented upon an artificial cable connected up to represent the proposed form. The "definition" of signals is considerably better than that obtained through an artificial cable of analogous "weight" and "length" connected up in the ordinary way. Within certain limits the "definition" continues to improve as the number of sections, or subdivisions, of the cable is increased.

Mr. Blakesley said he was sorry the result did not indicate a successful type of cable. He would have been inclined to predict that the amplitude would have decreased with the number of sections. If a number of condensers were joined in series, and one end was subjected to a periodic E.M.F., the amplitude would fall off inversely as the square of the distance.

Mr. Price then exhibited a galvanometer support. The instrument is suspended from two indiarubber cords attached at the top and bottom to cross-bars of metal, thus forming a rectangle. The cross-bars are provided with knife-edges in such a way as to compensate for unequal stretching of the indiarubber. Weights can be added, if necessary, to the support, so as to increase its inertia.

Mr. H. Garrett read a Paper, communicated by Prof. W. B. Morton, on "*The Effect of Capacity on Stationary Electrical Waves in Wires.*"

The author investigates the effect produced when a condenser is inserted at a point in the secondary circuit of the apparatus used by Blondlot for obtaining stationary electrical waves in wires. The positions of successive nodes are determined in the usual way, by a bridge, with a vacuum-tube indicator. When two opposite points of the parallel secondary wires are joined to the plates of a small air-condenser, the nodes approach the condenser on either side. The amount of the displacement of the nodes—that is to say, the extent of the shortening of the apparent half wave-length—depends upon the position of the capacity along the wires. The effect is *nil* when the condenser is at a node, and a maximum when it is midway between two nodes. The state of affairs at a point of the circuit is obtained by summation of a series of separate disturbances due to the different direct and reflected trains. In obtaining a formula for the conditions of resonance, with which to compare the observations, the author adopts a method from Heaviside. It connects the frequency of oscillation with the position and capacity of the condenser.

Mr. Shelford Bidwell proposed a vote of thanks to all the authors, and the meeting was adjourned until May 14th.

Action of Nickel upon Ethylene.—Paul Sabatier and J. B. Senderens.—The authors have caused ethylene to act upon nickel obtained by reducing the oxide with hydrogen. After cooling in a current of hydrogen the metal is exposed to ethylene which has been carefully dried and purified. There is no effect in the cold, but about 300° and more readily at a higher temperature the nickel gradually sprouts, yielding a very voluminous black matter. This matter is carbon in which nickel is distributed.—*Comptes Rendus*, cxxiv., No. 12.

NOTICES OF BOOKS.

A Detailed Course of Qualitative Chemical Analysis of Inorganic Substances. With Explanatory Notes. By Arthur A. Noyes, Ph.D., Assistant Professor of Chemistry in the Massachusetts Institute of Technology (Boston). Third Revised and Enlarged Edition. New York: The Macmillan Company. 1897. 89 pp., 8vo.

An Introductory Course of Quantitative Analysis. With Explanatory Notes and Stoichiometrical Problems. By Henry P. Talbot, Ph.D, Associate Professor of Analytical Chemistry in the Massachusetts Institute of Technology (Boston). New York: The Macmillan Company. 1897. 125 pp., 8vo.

Those who follow the fashion of deprecating the rapid multiplication of chemical text-books do not fully comprehend the conditions which impel the authors to issue them.

Teachers finding themselves expected to give instruction in elementary chemistry to large classes of young men having no previous experience in manipulation, and finding it impossible to give to each member of the class that personal assistance and supervision which is well nigh indispensable to success, are compelled to plan courses of laboratory work adapted to the circumstances, and to prepare, in manuscript, directions embracing such minute details that the students cannot possibly go astray. These manuscript notes grow from year to year with the needs of successive classes, and gain in value by the experience of the teacher, until after a few years the instructor finds it more economical of the time of the student to print these notes than to communicate the statements orally. Moreover, each Institution establishes courses having different ultimate aims, one being intended to qualify the students for the pursuit of mining, another for engineering, a third for the vocation of geologist or of naturalist, and, in consequence, the character of the chemical work required is modified to suit each case. This does not imply that the fundamental facts of chemistry differ in the several courses of instruction, but that the topics treated are selected to lead the students in the direction of the goals.

Again, the amount of time that can be devoted to chemical instruction is sometimes greatly abbreviated, so that the instructor finds indispensable the utmost condensation, consistent with perspicuity. Hence standard treatises on analytical chemistry, such as those of Fresenius, are relegated to the position of books of reference, and the students are supplied with specially adapted guides.

We do not claim, but we surmise, that the books under review have arisen in some such way, and this, instead of being a disadvantage, is one of the causes of their excellence.

Professor Noyes's little work has evidently found a larger circle of friends than the few students in his own classes, for it has reached a third edition. A characteristic feature of the book is the separation of the methods of procedure from the notes upon them, the former consisting of very detailed directions for carrying out the processes, and the notes serving to explain the philosophy of the same. The section on the detection of metals is followed by one on the detection of acids, and a third on analysis by the dry method. These are succeeded by instructions for the preparation of the solutions, and an appendix on the preparation of reagents.

Professor Talbot's treatise is intended for beginners who have completed a course in qualitative analysis, and follows the same method as that of Professor Noyes. The author remarks that his book should be supplemented by reference to the works of Fresenius, Mohr, and Sutton. Instead of selecting simple salts for analysis as preliminary practice, Dr. Talbot uses approximately pure samples of appropriate minerals or industrial products: this advances the student more rapidly without greatly increasing the difficulties. Part IV., Stoichiometry, is a valuable feature.

Both Prof. Noyes and Prof. Talbot are to be congratulated on the handsome paper and typography which is furnished by Macmillan and Co., the publishers.—H. C.B.

Laboratory Manual. A Short Course of Practical Chemistry. By Alfred C. Beebe. Chicago: A. Flanagan.

The work before us is a favourable specimen of those elementary treatises on chemistry in which the English press has been so prolific, and which are now also appearing in America. The author lays some emphasis upon a reaction for the recognition of potassium, which has been proposed by Koninck and approved of by W. Crookes. It has the advantages of being cheaper than platinum chloride, and more manageable than tartaric acid. Otherwise, whilst considering the instructions conveyed in this book sound and purposive, we fail to find them superior to those met with in similar manuals.

Les Nouveautés Chimiques par 1897. Nouveaux Appareils de Laboratoires, Methodes Nouvelles de Researches apliqués a la Science et a l'Industrie. Camille Poulenc, Sc.D. Paris: J. B. Baillière et Fils. 1897.

This work has been compiled in order to give chemists and physicists an account of recent discoveries fuller and more accurate than the notices which we encounter in the literary and the political press. The first chapter is taken up with general applications of chemistry and physics, such as Dr. Joly's meldometer for the rapid and accurate determination of the fusion-points of bodies which melt at high temperatures; the pyrometric telescope of Mesuré and Nouel; the new self-correcting air-thermometer of F. G. Müller; the short thermometers of Dr. Raikow; McTree's thermo-element for determining high temperatues; the Wiborgh thermophore, for determination of elevated temperatures; the double differential thermoscope of Loesen; Dunnington's new gas-regulator; various apparatus for the production of acetylene; M. Grünberg's proposed appliance for the rapid determination of the specific gravity of ores; the universal densimeter of Courtonne; the densimeter of Pieri; the compensating densimeter of Galaine; Vandevyn's new areometer.

An important section of the book is devoted to bacteriology. The description of the novelties here are well and abundantly illustrated. Many—we might say most—of the paragraphs here inserted seem to have been gleaned from the *Chemiker Zeitung* and its Supplement the *Chemisches Repertorium.*

We hope that the "Nouveautés Chimiques" will be continued yearly, as it is calculated to prove highly serviceable to men of Science.

A Manual of Chemistry, Theoretical and Practical. Based on Watts's Edition of "Fownes's Manual." By W. A. Tilden, D.Sc., F.R.S., Professor of Chemistry in the Royal College of Science. London: J. and A. Churchill. 1897. Crown 8vo., pp. 599.

This work is somewhat complicated in its origin. The last traces of the work of Fownes, we are told, have disappeared under the hands of the successive editors in accordance with the development of chemical science, and the final result is a most satisfactory specimen of the intermediate type of chemical handbook.

A preliminary chapter has been added, giving in broad outline the leading points in the history of chemistry from the time of Boyle downwards. The author expresses the very correct opinion that such historical survey will prove useful to the student.

Dr. Tilden, whilst accepting the periodic system, does not regard it as the be-all and end-all of classification, It is pointed out as a singular fact that the discoverers of oxygen, Scheele and Priestley, remained phlogistians to the end of their lives.

After the list of the elements we find the term "metalloids" used, not as it is done in France, for the non-metals, but as a sub-class of the latter.

In speaking of the composition of the atmosphere, we find an expression which may be misunderstood. The writer means, of course, that ozone and hydrogen peroxide may replace each other, but a junior reader might carry away the impression that ozone is a synonym for hydrogen peroxide.

Dr. Tilden greatly underrates the confusion arising from the different hydrometer scales, which are far more than two or three.

The periodic law is here ascribed to Newlands, Lothar Meyer and Mendeleeff receiving the credit of having elaborated the original idea. The relations among the atomic weights of the elements, as connected with their attributes, are explained by the diagram devised by Dr. Emerson Reynolds, and subsequently modified by Mr. Crookes. Dr. Tilden does not enter upon a variety of other schemes for the classification of the metals, such as those of Chancourtois.

The section on the glass manufacture gives the composition of Bohemian plate-glass and English flint-glass, but overlooks the Jena glass, which is now rapidly and deservedly rising in favour.

According to the recent researches of Prof. Berthelot, pure copper (commercially so called) was used for tools and weapons before the introduction of bronze.

In speaking of the Bessemer process, it might have been added that the slag from the basic process (Thomas slag) is an excellent phosphatic manure, equal—and in some cases even preferable—to superphosphate.

Tin has occasioned some trouble in chemical classification. In common life it ranks as a metal, and is, indeed, one of the bodies upon which the concept of a "metal" was primarily founded. We sometimes, however, find it placed as a non-metal or a semi-metal. Dr. Tilden associates it with thorium, zirconium, and cerium.

It is impossible for us to notice all the numerous passages in this work which justify, and indeed call for, favourable comment. The index is excellent.

The Organised Science Series. First Stage.—Inorganic Chemistry. By G. H. Baily, D.Sc. (Lond.), Ph.D. (Heidelberg), Lecturer in the Victoria University, and also Assistant Examiner in the Science and Art Department. Edited by William Briggs, M.A., F.C.S., F.R.A.S., Principal of University Correspondence College. London: W. B. Clive, University Correspondence College Press. Warehouse, 13, Booksellers' Row, Strand, W.C. 8vo., pp. 210.

The title-page of this little book might justify a few questions. What, for instance, is "Organised Science"? The definition of Science is "organised knowledge"; what, then, is "organised science"? Or is it the series only which is organised, rather than any other series? Again, it may be asked, what are the characteristic features of University Correspondence College, an organisation which seems to do its own printing and publishing? Again, we find mention of a "University College Tutorial Series," which has the same general editor. How are two series connected together, if at all? There is further a weekly journal, the *University Correspondent* and *University Correspondence College Magazine.* There is, if it has not experienced the "happy despatch," a journal bearing the ominous name, the *Competition*, but issued, as far as we are aware, under different auspices. Have we not here the old unhappy game of too many cooks spoiling the broth?

It will be perceived that the "University Correspondence College" prepares students for examinations at the London University. The various chapters are fitted with sets of questions, and, in addition, there are answers to the questions and to the "chemical calculations."

The instructions given are satisfactory, but the question still arises *Cui bono?*

Abstract of Chemical Analysis. Second Part.—Quantitative Analysis. By E. Fink, Head of Practical Operations in Analysis at the Municipal School of Industrial Physics and Chemistry of the City of Paris. ("Precis d'Analyse Chimique." Deuxième Partie. — Analyse Quantitative. Par E. Fink, Chef des Travaux Pratiques d'Analyse à l'Ecole Municipale de Physique et de Chimie Industrielles à la Ville de Paris). Paris: Georges Carré and C. Naud. 1896.

This book differs little from the generality of works on the same subject and of the same extent. The balance proposed by Dr. Curie is described and figured. The weights are of course arranged on the ultra-decimal principle, with the exclusion of all pieces which are not submultiples of the preceding weight. The bases are classified as belonging to the group of arsenic, copper, iron, barium, and potassium.

The analytical methods are divided into the gravimetric, electrolytic, volumetric, and colorimetric. The instruments employed in the last method are those of Duboscq and Salleron. The tintometer is not mentioned. Quantitative spectroscopic analysis also is overlooked.

Practical Work in Physics. For Use in Schools and Colleges. By W. G. Woolcombe, M.A. (Oxon), B.Sc. (London), Senior Science Master in King Edward's High School, Birmingham. Part III. — *Light and Sound.* Oxford: Clarendon Press. London: Frowde (Oxford University Press Warehouse), Amen Corner, E.C. Crown 8vo., pp. 95.

The Preface informs us that an essential feature of the work before us is to furnish, at a trifling cost, a fairly complete experimental course in the subjects covered. As regards the trifling cost we have to consider, in the first place, the book itself; and in the second, the inexpensive character of the apparatus required. The subjects here considered "do not appeal so much to the student's power of observation as to that of his judgment." Here therefore the author, in his estimate of the educational value of physics, differs from those authorities who consider that its value consists mainly in its training and stimulating the student's faculties of observation. Who is in the right we do not undertake to decide. It will be perceived that sound is not on all fours with light, heat, and electricity. These agencies are all *molecular*, whilst sound is plainly *molar*. So that, in spite of the fact that the study of sound first made us familiar with vibratory motions, we are at a loss as to whether acoustics ought to rank with optics.

Quantitative Estimation of Urine; New System of Rapid Analysis, for Medical Men and Pharmacists. By J. Barker Smith, L.R.C.P. (Lond.). London: Baillière, Tindall, and Cox. 1897. Pp. 37.

The author of this pamphlet has had a long experience in the analysis of urine, and has naturally evolved, so to say, several new and rapid methods. Time is, of course, a great factor in carrying on work of this character, and the general practitioner will doubtless appreciate the improvements and modifications herein described.

The tests applied to urine may be arranged in two main divisions:—

I. Tests of a sample of urine rendered *alkaline*, these being used for the estimation of *acidity*, *urea*, *sugar*, *total urates*, *phosphates*, *ammonia*, *&c.*

II. Tests associated with the estimation of normal or acid urine:—*albumen*, *biliary salts*, *peptone*, *&c.*

The general procedure (*a*) is fully set forth and explained; this is followed by two sections (*b* and *c*), fully describing the special methods used, all the details being minutely gone into; possible errors and misinterpretations of results are pointed out, and many examples of actual periodic examinations are given.

Accompanying this pamphlet is a small, conveniently arranged pocket set of tables, and general instructions for the rapid thermometric method of the quantitative analysis of urine; the complete apparatus required (besides these tables) comprises only a measure, phial, and thermometer, so that with the few reagents required only a small box is needed.

CORRESPONDENCE.

THE NEW SCIENTIFIC CLUB.

To the Editor of the Chemical News.

Sir,—My attention has been drawn to the fact that my name appears on a circular signed by Mr. Robert Ingram proposing to found a Club for scientific men. I write to ask you to give publicity to the fact that I know nothing of the proposed Club, and have not sanctioned the use of my name in any way.—I am, &c.,

W. Ramsay.

12, Arundel Gardens, W.,
April 9, 1897.

CHEMICAL SOCIETY ELECTION.

To the Editor of the Chemical News.

Sir,—Your readers might be led to infer from Professor Ramsay's letter of April 3rd that I had not replied to the communication he addressed to me: this would be a mistake.

Professor Ramsay well knows that I made a full reply, in which I challenged him to put aside all verbal quibbles; and that it is I who am without an answer. He has but to say that he wishes that the letter he wrote to me, dated 27th March, and my answer to it, dated 30th March, shall be published,—I will then forthwith place both in your hands for communication to your readers.—I am, &c.,

Henry E. Armstrong.

TEACHING OF CHEMISTRY.

To the Editor of the Chemical News.

Sir,—I have read the letters of Mr. Woodward and Mr. Wigley with great interest, but cannot see in either sufficient reason to change my original position. Both the above-named gentlemen think I over-estimate the danger beginners incur when handling the simple gases. I can only say that I know of a number of serious explosions of these gases that I believe would have been avoided had their preparation been deferred till later in the course. Of course I cannot speak of English schools, but in the American schools with which I am familiar this danger is greatly increased by giving too many pupils to one teacher. In my opinion this overcrowding of classes is the most serious shortcoming in our American schools to-day, but it only aggravates the danger which is already present. In regard to the danger of explosions from careless handling of acids that is present in either qualitative analysis or the preparation of the non-metallic elements, and so cannot count against either subject, Mr. Wigley thinks qualitative analysis would not prepare the student to work with gases. I think work with chemicals and apparatus in any branch of the subject will materially aid work in other lines.

Both Mr. Woodward and Mr. Wigley seem to place small value on the educational effect of qualitative analysis. To my mind one of the most important objects of laboratory work is to teach the student to think logically and to observe accurately. Both of these objects are as well accomplished by qualitative analysis as by the preparation of the simple gases. Whether qualitative analysis becomes routine or not depends entirely upon the ability of the teacher. Surely a subject that has claimed the attention of some of the ablest chemists who have ever lived ought to contain enough intellectual matter to prevent the subject from becoming stale and profitless to the beginner. With the rare elements to study—which I should not advise at this stage of the work—I think there is no need for purely mechanical work.

To Mr. Woodward's criticism that the students *won't* reason, I may say I think we are all more or less lazy in that respect. The remedy I suggest is the one Nature uses for more advanced scholars, namely, to stimulate interest by withholding results from the experimenter. I strongly approve of text-books in which the students are never given a result when it can reasonably be withheld.

I may state my position by saying that I do not advise the abandonment of work with the simple gases and the other non-metallic elements, but I suggest that it is not suitable for the first work in the chemical laboratory. I should recommend some such chemical course as the following:—Recitations, with strict and searching questioning daily, upon the non-metallic elements and such work as is usually included in that branch of the subject in a short text-book. These recitations should be thoroughly illustrated by experiments performed by the teacher, which are recorded by the pupils. Then the essential principles of qualitative analysis should be taught by laboratory work. Finally, a review of the non-metallic elements, in which the student does the actual work himself. Here quantitative analysis could be brought in to great advantage, I think. I am not prepared to say that it ought not to be brought in sooner, for I think it is too little used; but I *think* some knowledge of chemical manipulation had best precede it. Qualitative analysis can be made quantitative also with great ease. After this review of the non-metallic elements, the subject is ready to be expanded along any line the teacher may see fit to follow.

The delay in answering the letters of Mr. Woodward and of Mr. Wigley, and the fact that I answer both gentlemen in one and the same letter, I hope will be pardoned on account of my distance from London.—I am, &c.,

Alfred C. Beebe.

Savanna, Ills., U.S.A.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 13, March 29, 1897.

The President announced the presence of Dr. Nansen at the session, whom he cordially welcomed on behalf of the Academy.

Transformations of the Sugars, and on Levulic Acid.—MM. Berthelot and André.—In virtue of its generation by means of aldehydic groups, the molecule of glucose behaves as being eminently moveable, capable of being split up at the ordinary temperature in various different directions: its constituent atoms of hydrogen and oxygen oscillate among numerous centres of carbon. In all cases it is a question of purely chemical agents. We have never ceased to think that it must be the same in the production of alcohol; the living cell which there intervenes not being the true specific agent of the reaction, but having the function of secreting such a specific agent. To this opinion adhere the majority of the physiologists who occupy themselves with the study of infectious maladies.

On the Fatty Matters Found in the Egyptian Tombs of Abydos.—C. Friedel.—The author has examined certain antique objects found at Abydos by M. Amélineau and considered to be anterior to the first dynasty. The fatty matter consisted chiefly of palmitic and stearic acids, and was doubtless the tallow of beef or of mutton. It is interesting to find that the fatty acids, such as the stearic and palmitic acid, and even the glycerides of these acids, have been capable of preservation for thousands of years. Among the substances found in small vases was pulverised lead sulphide mixed with a quantity of fatter matter; evidently a cosmetic used as antimony sulphide is still employed in the East.

Transformation of the Diamond into Graphite in the Crookes Tube.—H. Moissan.—Mr. Crookes has demonstrated in his fine researches on the phenomenon which he has named molecular bombardment that on placing diamonds in one of his tubes they quickly lose their lustre and are coated with a black layer. Having been present in his laboratory at this curious experiment I asked him for some of the diamonds which had been thus bombarded that I might study the variety of carbon produced under these conditions. Mr. Crookes having kindly sent me a diamond the surface of which had been completely blackened by this bombardment, I heated it to 60° in an oxidising mixture of potassium chlorate and fuming nitric acid prepared from sulphuric acid exactly monohydrated and potassium nitrate fused and quite free from moisture. The action on the black layer is very slow. There is produced graphitic oxide, which at an increased temperature yields pyrographitic acid which is easily destroyed by nitric acid. Hence the variety of carbon which coated the diamond was graphite. This transformation of the diamond into graphite must be very high. Mr. Crookes had already proved the platinum-iridium can be fused in his tubes, but the temperature obtained in the bombardment is much higher, since the transformation of diamond into graphite requires the high temperature of the electric arc. The higher the temperature to which graphite is raised the greater is its resistance to oxidation. The temperature reached is probably about 3600°.

Mutual Actions of Electrodes and of Cathodic Rays in Rarefied Gases.—H. Deslandres.—The author concludes that when we have in the vicinity of a cathode a conductive or insulated body which is taken as an anode or is insulated, everything ensues as if the cathodic rays were attracted. The mutual action of the rays and the cathodes takes place only when the rays interpenetrate each other.

Stannic Chlorobromides.—A. Besson.—Theory leads us to foresee the existence of the chlorobromides of the type SnX_4, $SnCl_3Br$, $SnCl_2Br_2$, $SnClBr_3$. The compound $SnCl_3Br$ forms the main part of the fraction which distils at 50—55° under the pressure of 3 c.m. The chlorobromide, $SnCl_2Br_2$, is separated from the fraction passing over between 60° and 70°. The compound $SnClBr_3$ distils over the same pressure at about 73°.

Conditions of the Direct Combination of Sulphur and Hydrogen.—H. Pélabon.—Hydrogen may still combine with sulphur as long as the temperature is not below 215°. Between 215° and 350° the combination is still limited. The direct combination of the two substances is effected the more rapidly the higher is the temperature. The maximum quantity of hydrogen sulphide formed at a given temperature increases regularly with temperature. Above 440° we reach the same limit, whether we set out from sulphur and hydrogen or from pure hydrogen sulphides. If we substitute for pure hydrogen a mixture of hydrogen and nitrogen, the maximum quantity of hydrogen sulphide formed after heating for a given time is less than with pure hydrogen; all circumstances being equal the difference is less the higher the temperature.

Action of Bromine and Hydrobromic Acid upon Ethyl Acetate.—Boleslas Epstein.—A critique of the results of M. Crafts published in the *Comptes Rendus*, vol. lvi., p. 707, 1863.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on April 5th, Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—Mr. J. H. Colls, Mr. H. E. Diamond, Mrs. J. Dundas Grant, Mr. Douglas Hall, Mr. W. Hunter, and Mr. F. M. Mackenzie, M.R.C.S. The special thanks of the Members were returned to Sir William J. Farrer for a donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures.

Gravimetric Estimation of Sugar.—G. Ambuhl (*Chem. Zeit.*, 1897, xxi., 137).—The author recommends that the cuprous oxide produced in the Fehling-Allihn process should be dried for one hour at 98·5° C., and weighed as such, instead of being reduced to the metallic state. He presents an elaborate table, showing the results of the method when applied to forty-six samples of wine, honey, and diabetic urine. In the case of wines, the figures are practically identical with those obtained by weighing the metal, being usually a trifle higher (maximum +0·09; average +0·034 per cent). With honey, the excess averages 0·23 per cent on amounts of sugar varying from 57 to 69 per cent; and with urine containing 4·25 to 6·16 per cent of sugar, the mean difference between the two processes is 0·10 per cent, but in this instance the suboxide was manifestly contaminated with organic substances, which suffer decomposition on ignition.—*The Analyst.*

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.

Gun Paper.—Will some correspondent inform me the way to make gun paper, by the quire at a time. I find when trying to make more than a single sheet the whole quire adheres and becomes one solid cake or block.—F. F.

Pemberton's Molybdate Method for Phosphoric Acid.—Will some correspondent kindly inform me where I can find any description of a modification of Pemberton's molybdate method for phosphoric acid, being the use of glue to make the yellow precipitate sink so as to enable one to better see the end reaction. The method is used, I believe, in the State Agricultural Laboratories in Switzerland.—R. C. W.

Errata.—No. 1910, p. 11, col. 1, line 19 from bottom, *for* "90°" *read* "0°." No. 1950, p. 179, col. 2, line 5 from bottom, *for* "Staining" *read* "Storing."

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THE CHEMICAL NEWS.

Vol. LXXV., No. 1952.

METHOD OF SEPARATION OF NICKEL FROM COBALT, NICKEL FROM IRON, AND COBALT FROM ALUMINIUM.

By E. PINERUA,
Laboratory of the University of Valladolid, Spain.

On account of the very close resemblance between nickel and cobalt their separation offers many difficulties, and calls for special methods. The process generally employed, viz., the potassic nitrite method, is very tedious, and above all requires certain conditions as to the proportion of cobalt present (Fleitmann, *Z. fur. Anal. Chem.*, xiv., 76, 1875).

Liebig's method, by means of cyanide of potassium, bromine, and an alkali, is very delicate.

That of Langier, which consists in precipitating the nickel and cobalt as oxalates, and dissolving these in ammonia, and exposing this solution to the action of the air, has been abandoned.

Gautre's modification (*Z. fur Anal. Chem.*, v., 75, 1866) of the cyanide of potassium and mercuric oxide process, is again not very exact.

The latest method, that of Knorre and Ilinski (*Z. fur. Ange. Chem.*, vi., 264, 1893), based on the precipitation of cobalt by nitroso-β-naphthol, which does not precipitate the nickel, is good; but we think the simplest and most rapid is that which we have recently employed at this laboratory, founded on the insolubility of chloride of nickel in a solution of ordinary ether saturated with hydrochloric acid gas at a low temperature.

The action of hydrochloric acid gas on the metallic oxides and their salts has been studied by Debray, E. Pechard, Ditté, Engel, Hanriot, Rothe, Smith and Oberholtzer, Smith and Hibbs, Smith and Meyer, Jannasch and Schmith, Bird Moyer, F. A. Gooch, F. S. Havens, and many other chemists; but we believe that, up to the present, no method of separation of the above-named metals has been published, based, as ours is, on the insolubility of the chlorides of nickel and aluminium, and the great solubility of cobalt and iron, in the solution previously mentioned.

The hydrated chlorides (0·3 grm. to 0·4 grm.) of the metals, nickel and cobalt, nickel and iron, cobalt and aluminium, are dissolved in *the smallest possible quantity of water*, and to the solution is added 10 or 12 c.m. of fuming hydrochloric acid and 10 c.m. of ordinary ether (D 15 c. = 0·725), or, better still, anhydrous ether. This must be well shaken, and through the resulting homogeneous liquid a current of hydrochloric acid gas is passed continuously until complete saturation, at the temperature of melting ice, with which the beaker or test-tube should be surrounded.* During this operation the nickel is precipitated in the state of heavy, crystalline, *yellow chloride*, and the cobalt remains in solution with an intense blue colour (Engel's acid chloride). In the presence of iron, which under these conditions would give a bright yellow solution, the colour becomes green.

Most of the commercial chlorides of nickel and cobalt, *soi-disant* pure, are really very impure. By using our process for precipitating the nickel, on the commercial chlorides of cobalt, the resultant liquid is of a bluish green instead of a pure blue colour, indicating the presence of iron.

The precipitated chloride of nickel is yellow, but sometimes the remaining liquid is of a light yellowish green colour, indicating the presence of iron and cobalt.

We have noticed, by using different solvents, phenomena which by their importance demand studying with very great attention. We are led to believe, as are the chemists Krüss and Schmidt, Remler, Winckler, de Koninck, and others, that nickel and cobalt are not actually known in a state of purity, and that they probably contain other elements still unknown.

The precipitate of chloride of nickel is washed by decantation, with ether saturated with hydrochloric acid gas, at a low temperature, collected on a filter, and thoroughly washed again on the filter; it can then be weighed and the nickel estimated in the ordinary manner (such as sulphate, for example) with very accurate results.

The same method of procedure can be utilised for the separation of aluminium and cobalt; the former metal is completely precipitated in the state of insoluble chloride, as it is when in the presence of iron, using the analogous method of Hanriot and Rothe, as modified by F. A. Gooch and F. S. Havens.*

The cobalt remains like the iron in solution; and the insoluble chloride of aluminium, washed with ether saturated with hydrochloric acid gas, can be estimated with great accuracy.

To effect the separation of nickel from iron, it is necessary to wash the chloride of nickel many times with ether to eliminate the chloride of iron which is re-dissolved, and the operation must be repeated several times.

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* Our hydrochloric acid gas was obtained by the reaction in the cold of concentrated sulphuric acid and chloride of ammonium. The apparatus employed consists of a litre flask, with three large openings at the top, and one draw-off tube at the side near the bottom. One of the three necks allows the gas to pass by means of stoppered tube; another serves for the introduction of small lumps of the ammoniacal salt; and in the third is inserted a *Welter* safety tube, by which means small quantities of sulphuric acid are added. The lower side tube is used for emptying the apparatus when necessary.

* "Method for the Separation of Aluminium from Iron," by F. A. Gooch and F. S. Havens. Contributions from the Kent Chemical Laboratory of Yale University. *American Journal of Science*, vol. ii., Fourth Series, December, 1896; Chemical News, vol. lxxiv., p. 296.

THE OCCURRENCE OF RAFFINOSE IN AMERICAN SUGAR BEETS.

By W. E. STONE and W. H. BAIRD.

Raffinose, as a distinct kind of sugar, belongs to the comparatively little met with class of tri-saccharides with the formula $C_{18}H_{32}O_{16}$. It has been shown that the sugars found in different plants, such as Eucalyptus, cotton-seed, barley, wheat, and finally in molasses and refinery products of the sugar beet, and called variously melitose, gossypose, and raffinose, are all identical with each other.

In the residual and secondary products resulting in the manufacture of beet sugar, raffinose has long caused serious and unexplainable errors, inasmuch as it crystallises with cane sugar, modifying its form and increasing the specific rotation. It was at first thought that raffinose was not originally present in the beet juices, but it has been since shown that such is not the case.

The special processes of making beet sugar from beet juices, as carried on at the Norfolk (U.S.A.) Works, are fully described; an important point to note is that, owing to the behaviour of raffinose during the process of manufacture of beet sugar, it gradually becomes more and more concentrated in the molasses and secondary products of the factory, and it has been noted that if the amount of raffinose present reaches 8 to 12 per cent, or even less, it not only destroys the accuracy of all polarimetric determinations, but seriously retards the crystallisation of the sucrose itself.

Repeated attempts, during 1895 and 1896, were made to detect raffinose by Tollens's method of producing mucic acid, but were met with failure, and the results herein given well illustrate the untrustworthiness of the mucic acid test when applied to complex mixtures of salts and organic matters, such as molasses. Numerous methods have been proposed for the isolation of raffinose, and the authors proceed to describe several of them, such as those used and described by Kodyl and Scheibler, and they finally found a combination of several of these which proved successful. This method is described at length, and from the results obtained the authors feel justified in concluding that raffinose occurs in the juices of the American sugar beet in appreciable quantities. Certain peculiarities of crystallisation of mixtures of sucrose and raffinose are pointed out, the authors finding, when examining the crystals under the microscope, that frequently solutions containing apparently but a very small amount of raffinose would completely crystallise into forms which could scarcely be distinguished from pure raffinose. This modification of the crystalline form of sucrose would seem to afford a ready means of detecting the presence of small amounts of raffinose when mixed with sucrose.—Abridged from the *Journal of the American Chemical Society*, xix., No. 2.

THE DETERMINATION OF SULPHUR IN CAST-IRON.

By FRANCIS C. PHILLIPS.

In a Paper read before the American Chemical Society in August, 1895 (*Journ. Amer. Chem. Soc.*, xvii., 891), I have detailed some experiments made in the determination of sulphur in white cast-iron by the evolution method, and have attempted to show that the loss of sulphur in its determination in such iron may be due to the formation of organic sulphur compounds not oxidisable to sulphuric acid by the usual means.

By passing the gases evolved during the solution of the iron in hydrochloric acid through a heated porcelain tube, it was found that the volatile organic sulphur compounds may be decomposed and nearly all the sulphur recovered by conversion into hydrogen sulphide, oxidation and precipitation as barium sulphate.

In judging of the correctness of an analytical method it has been necessary, in the case of the majority of the constituents of iron, to depend upon a single criterion; that method is regarded as most accurate which, being correct in its details, yields the highest percentage of the constituent sought to be determined. For it is hardly possible to add to pure iron a known percentage of sulphur, phosphorus, or carbon, and test the method by a determination of the added constituent. For the determination of sulphur in iron it has been common to regard the method of oxidation and solution of the iron by nitric acid, followed by precipitation of the sulphur in form of barium sulphate, as the most accurate, inasmuch that it yields results somewhat higher than those obtained by other modes of procedure.

It does not seem probable that an appreciable error could occur in the use of this method, unless, in the simultaneous oxidation of the carbon and sulphur of the iron, an organic sulphur compound should be formed.

It has seemed to be of interest, however, to apply a method for the determination of sulphur by which all the constituents of the metal could be completely oxidised in a dry state and at a high temperature, in order to avoid as effectually as possible the chances of loss due to the conversion of sulphur into a volatile compound not oxidisable by ordinary means to sulphuric acid.

In searching for a method which should answer these requirements, it seemed possible that by heating the iron in the form of fine powder, in presence of a mixture of alkaline carbonate and nitrate, the sulphur might be oxidised directly and completely to the condition of a sulphate without affording an opportunity for the escape of a trace of sulphur in some intermediate volatile or soluble compound. Accordingly an experiment was tried in the following way:—

An iron containing its carbon in the combined form was melted in a crucible, and poured while fused into water. The granulated metal was crushed in a steel mortar to an extremely fine powder. The powder so obtained was sifted through bolting sheeting.

Two and one-half grms. of the sifted iron were mixed with 10 grms. of a mixture of equal parts of sodium nitrate and carbonate in a platinum crucible. The crucible was covered and heated over a Bunsen burner. At a red heat a sudden and rather violent reaction occurred, and, having been begun, was easily maintained with very little aid from the burner flame. The reaction appeared to be complete in a few minutes. After heating for a half hour the crucible was cooled, and its contents softened in water. A residue of a reddish brown powder, consisting of ferric oxide with a little ferrous oxide, was obtained. This residue was found to contain no sulphuric acid, and, on digesting with hydrochloric acid, dissolved without effervescence, showing that none of the particles of the original iron had remained unoxidised. From the results of this experiment, and others which need not be detailed here, it seemed to be possible to oxidise finely divided iron so completely by heating with sodium carbonate and nitrate, that its sulphur might be converted quantitatively into sulphuric acid.

The mixture of sodium carbonate and nitrate, although tending to oxidise finely divided iron, seems to exert a less powerful action upon the carbon contained in the iron, and this carbon may appear as a black residue after the fused mass has been softened and extracted by water and the ferric oxide dissolved in hydrochloric acid.

It seems to be important for the success of the method that in the oxidation of the iron the carbon should also be nearly or completely oxidised, for if the carbon remained unburned a portion of the sulphur might escape oxidation. In general it may be said that the order of oxidation of these three elements by the method used is as follows:—1, iron; 2, carbon; 3, sulphur; the iron being the most easily oxidised, and the sulphur the most difficult to oxidise. This order is not exactly what we should anticipate; but it is to be remembered that unless the iron grains are fine enough to be penetrated by oxygen, and changed completely into a soft powder of ferric oxide, the sulphur and carbon have no opportunity to oxidise at all. If the iron could be used as an impalpable powder the order of oxidation would probably be different. The marked resistance of the carbon to oxidation has been frequently observed, even when using more sodium nitrate in the fusion than is theoretically enough to completely oxidise both iron and carbon, supposing that the sodium nitrate is reduced only to nitrite in the process.

Experiments of a similar kind were tried with ferromanganese. A metal containing about 80 per cent of manganese was used. By crushing in a steel mortar this iron was very easily reduced to a powder fine enough to pass through bolting sheeting. On heating the powder with the mixture of sodium nitrate and carbonate a most violent reaction occurred, the metal burning with a long flame, extending several inches above the crucible. In order to control the reaction it was found necessary to melt one-half of the fusion mixture to be used in the crucible, and then add slowly the other half, previously mixed with the powdered metal, while stirring constantly. In this way the reaction could be easily controlled. On sofening the fused mass in water it was found that the iron had been peroxidised and the manganese changed to binoxide. No trace of sodium manganate was ever formed, the solution in water being after filtration invariably colourless. No carbon was found in the residue. The oxidation of the carbon is much more easily effected in the case of iron containing a high percentage of manganese. In all the trials made the silicon of the iron was oxidised, but it was found that when the fused mass is softened in water very little silica enters into solution as an alkaline silicate, the greater portion remaining insoluble and in a flocculent form.

Experiments were then tried with a grey iron. This form of iron could not be crushed to a fine powder, and an experiment was made in reducing it from small drillings by means of a chilled iron rubber and plate, such as is ordinarily used for grinding ores. Several grey irons were tried in this way. Some could not be powdered by the method just mentioned, the grains tending to flatten instead of being crushed. Others were readily reduced, but the powder was not in any case fine enough for sifting through bolting sheeting. It was found, in the case of a grey iron reduced to powder by the method of grinding, that on fusion with the mixture of sodium nitrate and carbonate, used in the preceding experiments, the graphitic carbon of this iron was more readily burnt than the combined carbon of white iron.

As it had proved to be a somewhat difficult matter to oxidise completely the carbon of the iron in the various experiments made with the fusion method, notably in the case of white iron, some trials were made in the use of sodium peroxide. This proved to be a more efficient oxidising agent for iron and its contained carbon than sodium nitrate. For these trials a mixture was used consisting of forty-five parts each of sodium peroxide and sodium nitrate, together with ten parts of sodium carbonate.

White iron was oxidised and its carbon burnt during a fusion lasting less than ten minutes.

On heating ferromanganese with this mixture the iron was found to be completely oxidised. The carbon was burnt, and the manganese was oxidised and converted into sodium manganate, yielding a deep green solution when the fused mass was digested in water.

An admixture of sodium carbonate to sodium peroxide tends in all cases to diminish its action upon finely-divided iron at a high temperature, and renders the process more easily controlled. It seemed to be possible to base a method for the quantitative determination of sulphur in certain kinds of cast iron upon the reactions described above.

An indispensable condition of success in the use of the method is found in the extreme fineness of the iron. In the case of white irons the fineness of the powder has been secured by crushing in a steel mortar until the powder passed through a sieve of bolting sheeting or bolting cloth.*

Some grey irons cannot be crushed or ground. To these the method is not applicable. For grey irons, however, the evolution method answers all requirements.

The following details are given of the method finally employed:—

1. *White Iron.*—About 1½ grms. of the finely-powdered and sifted metal was intimately mixed with 8 grms. of the sodium peroxide mixture above mentioned, or with 4 grms. each of sodium carbonate and nitrate. The somewhat violent reaction set up on the application of strong heat to the platinum crucible was completed in a few minutes. The crucible was heated for about twenty minutes in all. After cooling, the contents were softened in water, the solution decanted, and the residue ground, while wet, in a mortar. The solution and residue were then digested in a beaker on the water-bath for one hour after addition of 2 c.c. of strong bromine water. The liquid was then filtered, acidulated with hydrochloric acid, evaporated to dryness to separate the small portion of silica which had entered in solution, and filtered. The sulphuric acid was determined in the filtrate in the usual manner. The barium sulphate obtained was always white. If the fusion mixture contains sodium carbonate and nitrate, but no sodium peroxide, the crucible must be heated for a longer time, but a portion of the carbon of the iron may still remain unoxidised.

Character of iron used.	Fusion mixture employed.	P.c. of sulphur found by fusion.	P.c. of sulphur found by the method of oxidation by nitric acid.
White iron A crushed in mortar and sifted through bolting sheeting.	Contained equal parts of sodium carbonate and nitrate.	0·112	0·101
		0·112	0·098
		0·111	0·096
		0·107	0·099
		0·114	0·100
		0·114	0·102
		0·106	0·102
		0·108	0·104
		0·107	
		0·103	
	Means	0·109	0·100
White iron B crushed and sifted.	Contained— 45 parts $NaNO_3$ 45 parts Na_2O_3 10 parts Na_2CO_3.	0·155	0·143
		0·150	0·149
		0·130	0·143
		0·139	0·147
		0·166	
		0·156	
		0·156	
		0·161	
		0·151	
	Means	0·151	0·145
Ferromanganese crushed and sifted.	Contained equal parts of sodium nitrate and carbonate.	0·022	0·012
		0·027	0·013
		0·018	0·012
		0·018	0·010
		0·018	
		0·019	
		0·016	
	Means	0·020	0·012
Grey iron drillings powdered by rubber and plate. Not sifted.	Contained equal parts of sodium nitrate and carbonate.	0·034	0·027
		0·030	0·030
		0·036	0·026
		0·034	0·028
		0·033	0·028
		0·034	0·022
	Means	0·033	0·027

2. *Ferromanganese.*—In this case it is better to use a mixture of equal parts of sodium nitrate and carbonate, omitting the sodium peroxide.

Ten grms. of the mixture were divided into two portions, one of which was fused in a crucible. The other portion, mixed with 2 or 2½ grms. of the finely-powdered iron, was then slowly added. Although too violent combustion of the iron is to be avoided, it seems to be important, for the success of the method, that a reaction of decided intensity should occur during the fusion.

Sodium nitrate possesses an advantage over sodium peroxide in its greater purity, the former compound being readily obtainable with practically insignificant traces of sulphur.

Natural gas was the fuel used for the Bunsen burner in heating the charges. This gas was found, by repeated experiments, not to contain a sufficient quantity of sulphur

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* Two different materials are sold which are suitable for the sifting. One is called bolting cloth, the other bolting sheeting. The bolting cloth used in these experiments contained about eighty-five meshes to the linear inch, while in the bolting sheeting about one hundred and thirty-five were counted. The material having the smaller number of meshes is made of coarser threads, however, and yields, on account of the smaller openings, a finer powder. Bolting cloth is, on this account, better suited to the preparation of a sample of white iron for a determination of sulphur by the method described.

to affect the purity of the sodium carbonate when heated in a platinum crucible in the same manner as in the case of the determinations described.

The usual occurrence of sulphur compounds in coal-gas would preclude its use in the application of the method.

From the experiments, the results of which are stated in the accompanying table, there seems to be some reason to suppose that not quite all the sulphur of the iron is converted into barium sulphate when the metal is oxidised and dissolved by nitric acid. That it has been completely recovered by the process of fusion cannot be positively asserted.*

The method I have described is not proposed as a substitute for any existing method. The purpose of the present work was merely to ascertain as far as possible whether, by a process of direct oxidation of the iron in a dry state, a larger proportion of the sulphur could be recovered in weighable form than by the usual method of oxidation and solution in nitric acid.

My thanks are especially due to Mr. F. B. Smith for great care and attention to detail in conducting the experiments I have detailed.—*Journal of the American Chemical Society*, xviii., 1079.

THE APPLICATION OF IODIC ACID TO THE ANALYSIS OF IODIDES.†

By F. A. GOOCH and C. F. WALKER.

It has long been understood that iodic acid is easily and completely reduced by an excess of hydriodic acid with the liberation of iodine according to the equation—

$$HIO_3+5HI=6I+3H_2O.$$

To apply this reaction to the quantitative estimation of iodic acid, it is only necessary to add to the free iodic acid or soluble iodate an excess of a soluble iodide, to acidify—best with dilute sulphuric acid,—and to titrate the iodine thus set free with sodium thiosulphate, one-sixth of the iodine found being credited to the iodic acid.

It has been shown recently by Riegler (*Zeit. Anal. Chemie*, xxxv., 305) that this reaction may be also applied to the quantitative estimation of iodides, the iodine set free upon the addition of a known excess of iodic acid to the iodide solution being removed by petroleum ether, and the residual iodic acid titrated directly with sodium thiosulphate.

The present investigation was undertaken to define more particularly the limit of applicability of the reaction and to establish, if possible, a direct method for the quantitative estimation of iodides, dependent upon the action of iodic acid or an iodate in the presence of free sulphuric acid, neutralisation of the solution by means of an acid carbonate, and titration of the free iodine by arsenious acid—five-sixths of the iodine thus found being credited to the iodide to be estimated. It has been found that by fulfilling certain necessary conditions, the proposed method is entirely successful, so far as concerns the estimation of iodine in iodide solutions free from large amounts of chlorides as bromides.

In a system containing a considerable quantity of free iodine with variable amounts of the other reagents mentioned, as well as possible impurities, it is conceivable that secondary reactions may occur, depending largely on conditions of mass, time, and temperature, and of a sort likely to alter the amount of recoverable iodine, or to exert an excessive oxidising influence on the arsenious acid finally titrated. It has been established by Schönbein, Lunge and Schoch, and others, that iodine forms compounds with the alkalis of the type R—O—I, and Phelps (*Am. Journ. Sci.*, ii., 70, 1896) has recently found that the formation of some such compound, accompanying the iodate naturally expected, is distinctly recognisable when iodine and barium hydroxide interact at ordinary temperatures. It has been shown, also, in a former paper from this laboratory (Roberts, *Am. Journ. Sci.*, xlviii., 157) that free iodine or an iodide interacts very easily with iodic acid in the presence of dilute hydrochloric acid with the formation of iodine monochloride, according to the equations—

$$HIO_3+2I_2+5HCl=3H_2O+5ICl.$$

$$HIO_3+2KI+5HCl=3H_2O+2KCl+3ICl.$$

Moreover, organic compounds containing the groups $-I=O$ and $-I{=O \atop =O}$, in which iodine seems to be analogous to nitrogen, result in great variety from the oxidation of halogen substitution products. It would seem, therefore, that the formation of inorganic reduction products of iodic acid under the conditions likely to obtain in this analytical process might be by no means beyond the bounds of possibility.

A few simple qualitative tests to determine the possibility of interaction between small quantities of iodine and iodic acid alone met with negative results. Thus, a single drop of a decinormal solution of iodine, made as usual in potassium iodide, gave when added to 10 c.m.^{3} of decinormal iodic acid a distinctive colour to chloroform. Similar results were obtained when the iodine was employed in aqueous solution in which there was no alkaline iodide. A few drops of an aqueous solution of iodine treated (in either order) with 10 c.m.^{3} of a saturated solution of potassium bicarbonate and 10 c.m.^{3} of decinormal iodic acid gave the same distinctive colour to chloroform as came from the same amount of iodine in the absence of the iodic acid. So it appears that if in the system under consideration, reactions do occur between iodic acid and iodine to alter the amount of iodine recoverable, such action is not appreciable between small amounts of these materials. This, however, does not preclude the possibility of perceptible changes under the mass-action of a large amount of iodine.

The reactions of hydrochloric acid, and probably of hydrobromic acid, in the presence of varying amounts of iodic acid, iodine, and iodide, as well as the reaction of the alkaline carbonate upon such mixtures, are doubtless complex, more or less reversible, and dependent upon proportion and dilution. The tendency of the former reactions is toward the reduction of the molecule of iodic acid, and the formation of the chloride or bromide of iodine. Thus, Miss Roberts (*loc. cit.*) demonstrated that a solution of hydrochloric acid, so dilute that by itself it is without effect on iodic acid, acts upon a mixture of iodic acid with either free iodine or an iodide to form iodine monochloride. The action of the acid carbonate upon the iodine chloride or bromide may produce a salt of the oxy-acids and free iodine.

The practical effects, under the conditions of analysis, of the reaction between iodine, iodic acid, and the halogen acids in presence of sulphuric acid, and of reactions which may occur upon neutralisation by an acid carbonate, were studied in detail in a number of experiments.

The preliminary experiments of Table I. were made to bring out the effect of neutralising with the acid carbonate and subsequently titrating with an alkaline arsenite a solution containing sulphuric acid and a considerable amount of free iodine. The danger of mechanical loss of iodine during the effervescence accompanying neutralisation, as well as by spontaneous volatilisation from the surface during the process of titration, was minimised by effecting the neutralisation in the trapped Drexel washing

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* The method of preparation of a sample for analysis in the case of the more brittle forms of iron, by crushing in a steel mortar and sifting, is suggested in Regnault's "Elements of Chemistry," translated from the French by Betton, 1867, ii., 112.

† Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Fourth Series, vol. iii., No. 16.

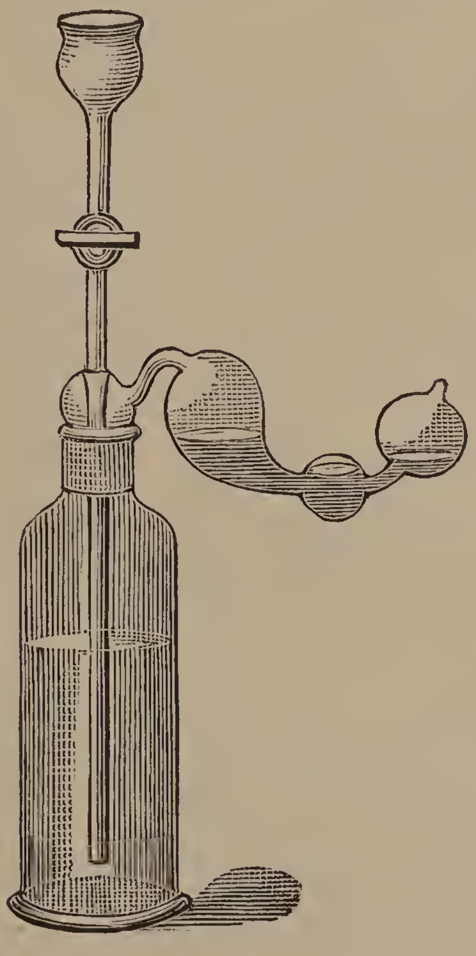
TABLE I.

Effect of the Carbonate.

[5 c.m.³ H_2SO_4 (1 : 3). Total volume of liquid, 250 c.m.³.]

	I (in KI) taken. Grm.	$KHCO_3$ in excess. C.m.³.	I found. Grm.	Error. Grm.
1.	0·0713	Very small	0·0707	0·0006 −
2.	0·0715	Very small	0·0710	0·0005 −
3.	0·0713	10	0·0710	0·0003 −
4.	0·0710	10	0·0706	0·0004 −
5.	0·0723	10	0·0717	0·0006 −
6.	0·0713	20	0·0709	0·0004 −
7.	0·0713	20	0·0709	0·0004 −
8.	0·3565	Very small	0·3560	0·0005 −
9.	0·3568	Very small	0·3561	0·0007 −
10.	0·3567	10	0·3563	0·0004 −
11.	0·3596	10	0·3588	0·0008 −
12.	0·3565	10	0·3565	0·0000
13.	0·3572	20	0·3560	0·0012 −
14.	0·3567	20	0·3569	0·0002 +

bottle, to be described later, and making the titration in the same tall washing cylinder without transfer. To varying amounts of a recently standardised decinormal solution of iodine were added successively 5 c.m.³ of dilute sulphuric acid and varying amounts of potassium bicarbonate in excess of that necessary to neutralise the free acid, decinormal arsenious acid in slight excess of the iodine, 5 c.m.³ of starch emulsion, and decinormal iodine to colouration, the total volume of the liquid being not greater than 250 c.m.³. The results show plainly that while the loss, mechanical or otherwise, in the treatment of reasonably large amounts of fairly concentrated iodine is perceptible, it is still well within permissible limits (amounting to a little less than 0·0005 grm. in the mean), and obviously independent of the excess of the carbonate in the solution, and of the amount of free iodine present.



In the experiments of Table II. the proposed process of analysis was tested upon potassium iodide taken by itself in varying amounts of a $\frac{1}{10}$ normal solution and carefully standardised by the method formerly elaborated in this laboratory (Gooch and Browning, *Am. Journ. Sci.*, xxxix., 188). The apparatus employed was a Drexel washing bottle of 500 c.m.³ or 1000 c.m.³ capacity, according to requirements, with stopcock and thistle-tube fused to the inlet-tube and a Will and Varrentrapp absorption-trap sealed to the outlet, as shown in the accompanying figure. The iodide for the test was drawn from a burette into the bottle and carefully washed down, and potassium iodate in excess of the amount theoretically necessary (namely, 5 c.m.³ of a 0·5 per cent solution for every portion of 20 c.m.³ of the iodide solution), was added, and the volume of the liquid was adjusted to the volume at which it was desired that the iodic and hydriodic acids should react. The stopper with the thistle-tube and trap was now placed on the bottle and the trap was half-filled by means of a pipette with a 5 per cent solution of potassium iodide. Five c.m. of dilute (1 : 3) sulphuric acid were added through the thistle-tube and washed down; the stopcock was closed, and the solution gently agitated, if necessary, to insure a complete separation of iodine. Potassium bicarbonate in saturated solution to an amount about 10 c.m. in excess of that required to neutralise 5 c.m.³ of dilute (1 : 3) sulphuric acid, was poured into the thistle-tube, and allowed to flow into the bottle slowly enough to avoid a too violent evolution of gas. The stopcock was closed, and the solution agitated by giving to the bottle a rotary motion, at the same time keeping the bottom pressed down upon the work table, to prevent a possible splashing of the iodide out of the trap into the yet acid solution. When the neutralisation of the solution had been completed, the bottle was shaken until the last trace of violet vapour was absorbed in the liquid. The greater part of the solution in the trap was then run back into the bottle, the stopper removed, and the tube and trap carefully washed; the washings being added to the bulk of the solution. Decinormal arsenious acid was introduced from a burette to the bleaching point, 5 c.m.³ of starch emulsion were added, and the solution was titrated back with decinormal iodine (usually only a few drops) to colouration.

TABLE II.

Effect of Dilution.

	KI taken. Grm.	KI found. Grm.	Error. Grm.	Approximate volume upon addition of H_2SO_4. C.m.³.	Volume H_2SO_4 (1:3 used. C.m.³.
1.	0·0772	0·0768	0·0004 −	150	5
2.	0·0772	0·0765	0·0007 −	150	5
3.	0·1544	0·1546	0·0002 +	150	5
4.	0·1544	0·1541	0·0003 −	150	5
5.	0·3087	0·3090	0·0003 +	150	5
6.	0·3087	0·3088	0·0001 +	150	5
7.	0·3859	0·3864	0·0005 +	150	5
8.	0·3859	0·3860	0·0001 +	150	5
9.	0·0772	0·0754	0·0018 −	300	5
10.	0·0772	0·0757	0·0015 −	300	5
11.	0·1543	0·1532	0·0011 −	300	5
12.	0·1544	0·1524	0·0020 −	300	5
13.	0·0772	0·0744	0·0028 −	500	5
14.	0·0772	0·0737	0·0035 −	500	5
15.	0·1544	0·1521	0·0023 −	500	5
16.	0·1544	0·1512	0·0032 −	500	5
17.	0·3859	0·3827	0·0032 −	500	5
18.	0·3859	0·3831	0·0028 −	500	5
19.	0·0772	0·0744	0·0028 −	500	10
20.	0·0772	0·0757	0·0015 −	500	10
21.	0·3859	0·3828	0·0031 −	500	10
22.	0·3859	0·3827	0·0032 −	500	10

Blank tests made upon a solution obtained by mixing the maximum amount of the iodate with 5 c.m.³ of dilute sulphuric acid (1 : 3), neutralising as usual with potassium bicarbonate, adding the iodide from the trap and 5 c.m.³ of starch emulsion, showed that a single drop of iodine was invariably sufficient to bring out the starch blue. Occasionally it was found that the mixture, particularly when chlorides or bromides were present, of itself developed a trace of colour, but by no means a reading tint. A correction of the one drop of iodine necessary to bring out the colour reaction in the blanks was applied uniformly in the analytical process.

The number of centimetres of decinormal arsenious acid required to bleach the free iodine, multiplied by 0·01383 (log. 2·140822) gives the number of grms. of potassium iodide taken for analysis, being equivalent to five-sixths of the iodine liberated in the solution.

From these results it appears that the degree of dilution of the solution at the time when the mixed iodide and iodate are acidified has an important influence on the completeness of the reaction. Thus, the mean error of the determinations in which the volume at the time of the reaction did not exceed 150 c.m.^{3} was practically nothing, while the errors at volumes of 300 c.m.^{3} and 500 c.m.^{3} amounted to 0·0016 grm. and 0·0028 grm. respectively. It is obvious that the doubling of the amount of sulphuric acid used in acidifying does not increase the amount of iodine liberated at the highest dilution. The plain inference is that the interaction between the iodide and iodate should be brought about in a volume of liquid not much exceeding 150 c.m.^{3}.

In the following series of experiments, recorded in Table III., the effect of the introduction of a chloride or bromide into the iodide (before the iodate is added) was studied. The volume of the liquid at the time of acidifying was fixed at 150 c.m.^{3}, approximately, and 5 c.m.^{3} of the dilute sulphuric acid (1 : 3) were used. The mode of procedure was otherwise similar to that of the foregoing series.

Table III.

Effect of Chloride and Bromide.

	KI taken. Grm.	KI found. Grm.	Error. Grm.	NaCl taken. Grm.	KBr taken. Grm.
1.	0·0772	0·0795	0.0023+	0·2	—
2.	0·0772	0·0784	0·0012+	0·2	—
3.	0·0771	0·0823	0·0052+	0·5	—
4.	0·0773	0·0819	0·0046+	0·5	—
5.	0·1544	0·1588	0·0044+	0·5	—
6.	0·1544	0·1590	0·0046+	0·5	—
7.	0·0772	0·0802	0·0030+	—	0·2
8.	0·0773	0·0853	0·0080+	—	0·2
9.	0·0772	0·0873	0·0101+	—	0·5
10.	0·0772	0·0861	0·0089+	—	0·5
11.	0·1544	0·1646	0·0102+	—	0·5
12.	0·1543	0·1626	0·0083+	—	0·5

The influence of sodium chloride and potassium bromide in increasing the amount of iodine liberated is plain. The increase comes without doubt from the iodate, and is doubtless due to the formation of iodine chloride or bromide, during the acidifying, by the interaction of the free iodine, the iodic acid, and the hydrochloric or hydrobromic acid, according to the reactions previously discussed. It is plain, therefore, that the value of the process in the determination of iodine in an iodide is restricted of necessity to those cases in which it is known that chlorides or bromides are not present to any considerable extent. For determining the standard of a solution of nearly pure potassium iodide, employed in so many laboratory processes, it should find useful application.

In Table IV. are comprised a number of experiments made exactly like those which seemed to give the best results in the series of Table II. The iodide and an excess of iodate (5 c.m.^{3} of the 0·5 per cent solution to every 20 c.m.^{3} of N/40 iodide) were made to interact in a volume of about 150 c.m.^{3}, 5 c.m.^{3} of sulphuric acid (1 : 3) were used to bring about the reaction, 10 c.m.^{3} of potassium bicarbonate were added after the neutralisation of the sulphuric acid was complete, and the free iodine was estimated by titrating decinormal arsenious acid, the manipulation being like that previously described in detail.

Table IV.

Analysis of Pure Potassium Iodide.

	KI taken. Grm.	KI found. Grm.	Error. Grm.
1.	0·0814	0·0816	0·0002+
2.	0·0814	0·0813	0·0001−
3.	0·0814	0·0805	0·0009−
4.	0·0815	0·0809	0·0006−
5.	0·0814	0·0808	0·0006−
6.	0·0814	0·0806	0·0008−
7.	0·0814	0·0812	0·0002−
8.	0·1628	0·1624	0·0004−
9.	0·1628	0·1617	0·0011−
10.	0·1628	0·1621	0·0007−
11.	0·1628	0·1619	0·0009−
12.	0·1628	0·1624	0·0004−
13.	0·1628	0·1621	0·0007−
14.	0·1628	0·1626	0·0002−
15.	0·2442	0·2451	0·0009+
16.	0·2442	0·2442	0·0000
17.	0·2442	0·2439	0·0003−
18.	0·3256	0·3258	0·0002+
19.	0·3256	0·3256	0·0000
20.	0·3256	0·3258	0·0002+
21.	0·3256	0·3272	0·0016+
22.	0·3256	0·3256	0·0000
23.	0·4071	0·4076	0·0005+
24.	0·4071	0·4080	0·0009+
25.	0·4071	0·4073	0·0002+

The average result of a series of several determinations in which a great excess (0·1 grm.) of potassium iodate was used, proved to be practically identical with that of a similar series in which only a small excess of the iodate was employed, so that it appears to be unnecessary in any practical work to restrict the amount of iodate below the amount necessary to decompose the maximum quantity of potassium iodide which we have handled, namely, 0·4 grm.

It appears that for the estimation of iodine in a soluble iodide free from notable amounts of chlorides or bromides, this method, depending as it does upon a single standard solution, is simple, fairly accurate, and rapid.

SODIUM PEROXIDE AS A THIRD GROUP REAGENT.

By S. W. PARR.

Sodium peroxide as a reagent has properties of a very unusual and striking character. These properties are no less valuable than peculiar, and indicate for this substance a prominent place in analytical work. The immediate object of this paper is to note the advantages and adaptability of sodium peroxide to qualitative analysis. By this means its numerous characteristics can be best illustrated. The specific data indicating its use in certain lines of quantitative analytical work will be given later. The methods herein set forth have been employed in this laboratory during the past year by large classes in qualitative analysis. This practical test of the processes involved has abundantly demonstrated their value.

In the ordinary procedure for the separation of the metals the greatest difficulty arises in the third or iron group. These complications may be briefly enumerated as follows:—

(*a*). The separation of zinc in the presence of chromium.

(*b*). The unsatisfactory separation of cobalt and nickel from the other members of the group by the action of dilute hydrochloric acid on their sulphides.

(*c*). The variations arising from the presence of phosphates, &c.

It is not necessary to enlarge upon these difficulties. The one most commonly ignored in methods is usually outlined, and yet a very serious obstacle is the one designated under (*a*). Zinc and chromium enter into a combination which, to a very large extent, resists the action of ammonia and ammonium salts. The use of barium carbonate to obviate this difficulty is cumbersome. By use of sodium peroxide we may oxidise the chromic compounds present to sodium chromate, and thus completely eliminate it as a factor in any precipitation likely to be employed, excepting of course such as would involve a reduction and return to the condition of a chromic salt.

The method of procedure is as follows:—The solution should be slightly acid. A small porcelain spoonful of the peroxide is slowly sifted in with constant stirring. The solution is then heated to complete the decomposition of the peroxide, and finally boiled for some minutes after the oxygen seems to be all driven off. The completeness of the oxidation may be easily tested by filtering from any insoluble constituents, acidifying, boiling, and making ammoniacal. A precipitate may be aluminum or unoxidised chromium. Filter and wash free from all sodium chromate, re-dissolve in a little nitric acid, and treat as before with a small amount of sodium peroxide. A yellow colouration is due to the chromium which escaped oxidation by the first treatment. However, if properly conducted, the first operation should be complete. Similarly, the insoluble residue on the filter, if suspected of being a zinc-chromium compound, may be washed free from chromate, dissolved in dilute nitric acid, and treated again with the peroxide. The only condition so far governing the completeness of the transformation to the chromate form is the necessity of starting the oxidation with the chromium entirely in solution. Precipitated chromium hydroxide will undergo this transformation, but less readily, and especially if the precipitate is the double one of zinc and chromium. Hence the advisability of beginning the oxidation with the solution containing some free acid, preferably nitric. The quantity of free acid is immaterial, less than 1 c.c. being sufficient. It should be noted, however, that the amount of sodium peroxide should cause the solution to pass quite beyond the neutral condition, since the oxidation is only partial while in the acid state. It might be expected that the moment the addition of sodium peroxide passed the neutral point the precipitation of chromium would commence, and the completeness of the oxidation be lessened in consequence, but I have not found this to be the case. The oxidising action of the peroxide is so pronounced that it precedes the precipitating action, hence the reason for using the dry sodium peroxide. A cold saturated solution of the peroxide will operate but incompletely. Hydrogen peroxide will also act similarly, but even less completely than the solution of sodium peroxide. For obvious reasons also the operation is performed on the solution before heating, and it is better to shake the powder in gradually than to drop the reagent in at once.

We are ready now to note the effect of such treatment as above indicated, upon the other members of this group, assuming that any or all may be present, including cobalt and nickel. The results are as follows:—

(*a*). Aluminum compounds are in solution in the form of sodium aluminate, not different from the ordinary result from using sodium hydroxide in excess. It is assumed, of course, that the sodium peroxide has exceeded the free acid in sufficient amount to provide sodium hydroxide in excess.

(*b*). Zinc is similarly in solution as zincate.

(*c*). Iron precipitates as a very dense, reddish brown precipitate, the exact composition of which is being made a matter of investigation. The precipitation is complete, no re-solution being effected upon boiling. The filtration is performed with great facility. The precipitate is almost insoluble in concentrated nitric acid; soluble in dilute acids on heating. If phosphates are present none are precipitated with the iron, but all pass through and are found in the filtrate.

(*d*). Manganese behaves exactly as iron, precipitating presumably as the hydrated dioxide, MnO_2xH_2O, having all the properties of that compound as to colour, solubilities, &c. Similarly also phosphates are not precipitated. It should also be noted that from this precipitate can most readily be obtained the delicate test for the presence of manganese by formation of permanganic acid by means of nitric acid and lead peroxide or Pb_3O_4.

(*e*). Cobalt precipitates also a black hydrated cobaltic oxide with solubilities the same as in the case of iron and manganese. No phosphate is precipitated with the cobalt. The precipitate, in conjunction with dilute acid and potassium iodide, liberates free iodine, imparting an intense blue to starch solution. This latter property, however, is common to the precipitates of iron and manganese under (*c*) and (*d*).

(*f*). Nickel precipitates, as the ordinary green nickelous hydroxide, $Ni(OH)_2$, easily soluble in acid, either concentrated or dilute. As to phosphates, in the case of nickel, if present in large amounts, small quantities are found in the precipitated nickel. A re-solution and re-precipitation with sodium peroxide, however, eliminates all the phosphate from the precipitate. The behaviour of nickel in thus precipitating as the nickelous compound indicates for its higher form of oxidation a less degree of stability than exists in the case of cobalt. This property suggests the readiest and most delicate method for the detection of nickel, even in the presence of the three precipitates enumerated above, thus:—Boiling this precipitate of nickel with bromine water converts it at once into the black nickelic hydroxide, which has the property of decomposing potassium iodide with water alone, no acid being required, as in the case of iron, manganese, and cobalt. It is necessary, of course, to boil off the free bromine, which is readily accomplished. The action upon a potassium iodide starch solution is very marked.

The above facts suggest a method for the iron group which is indicated by the accompanying table. It is given here to illustrate the adaptability of some of the well-known but more positive and satisfactory tests for the several metals.

In the presence of phosphates the method so far employed has been as follows:—Upon dissolving the precipitate from the ammonium sulphide in concentrated nitric acid, a very little of the solution is tested for phosphoric acid in the usual manner. If present, granulated tin is added and the boiling continued. Filter from the insoluble tin phosphate, make ammoniacal, re-precipitate with ammonium sulphide, and proceed as with phosphoric acid absent. Any method not involving the use of tin, and depending upon the non-formation of the phosphates of iron, manganese, and nickel, is as yet unsatisfactory. Having removed the barium and strontium with sulphuric acid before the precipitation with ammonium sulphide, the oxidation and precipitation by means of sodium peroxide may be performed as usual; but before filtering, the solution is made acid with acetic acid, and boiled a little further and filtered. The filtrate now may contain, besides the aluminum, zinc, and chromium, the nickel which is readily soluble in acetic acid, and the calcium and magnesium which has been brought along by means of the phosphoric acid. A little of the cobalt, however, dissolves with the acetic acid, and a solvent has not been found thus far for the calcium phosphate and nickel hydroxide that will not dissolve traces of the other three metals of the precipitate.

One other application to qualitative analysis may be mentioned as having proved valuable. In testing for acids a ready method for distinguishing between carbon dioxide and sulphur dioxide, when both are present, is found in the use of a solution of sodium peroxide. Conducted into this solution, the above gases form sodium carbonate and sodium sulphate respectively. With lime-water the solution will give a copious precipitate if the carbonate has been formed, and with an acidulated solution of barium chloride the sulphate test is obtained.

The precipitate obtained in the ordinary method by means of ammonium hydroxide and ammonium sulphide contains, as hydroxides and sulphides, iron, manganese, cobalt, nickel, aluminum, zinc, and chromium, and is brought into solution by means of 10 to 15 c.c. of concentrated nitric acid with heat. Nearly neutralise with sodium hydroxide, then sift in slowly with stirring sodium peroxide in excess. Boil.

Precipitate A contains iron, manganese, cobalt, and nickel.

(*a*). Test for iron by dissolving a small portion of the precipitate in dilute hydrochloric acid and adding potassium thiocyanate. The blood-red colouration is due to ferric thiocyanate.

(*b*). For manganese, to 5 c.c. of water add 5 c.c. concentrated nitric acid and 5 to 10 grms. Pb_3O_4. Stir into the warm mixture a little of the precipitate and let stand. A purple solution is permanganic acid.

(*c*). In absence of iron or manganese, stir a little of the precipitate into dilute hydrochloric acid, and add solution of potassium iodide and starch. In presence of iron and manganese use the bead test.

(*d*). Boil some of the precipitate with bromine water till all bromine is expelled, add water and solution of potassium iodide and starch, $Ni(OH)_3 + KI = Ni(OH)_2 + KOH + I$, imparting the blue to the solution.

Solution A contains all the aluminum, zinc, and chromium. The yellow colour is evidence of chromium. Acidify with hydrochloric acid, boil, and add ammonium hydroxide.

Precipitate B consists of aluminum hydroxide, and any chromium hydroxide that may have escaped oxidation. Dissolve in nitric acid, and repeat the precipitation with sodium peroxide, or apply the blowpipe and cobalt test for aluminum.

Solution B contains zinc and chromium.

(*a*). Test for zinc by adding to a portion a few drops of potassium ferrocyanide. A heavy white precipitate indicates zinc.

(*b*). If further verification of chromium is needed, make the solution acid with hydrochloric acid, and boil with a little alcohol added. The chromium reverts to the green chromic chloride.

Many other features incidental to the properties above outlined have developed, mainly of interest in quantitative methods. It is hoped that the data will be of sufficient value to warrant further notice.—*Journal of the American Chemical Society*, xix., p. 347.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending March 31st, 1897.

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

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

London, April 10th, 1897.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined one was recorded as "turbid," the remainder being clear, bright, and well filtered.

There has been a large excess of rain recorded at Oxford during the month, the actual fall being 2·61 inches; as the average fall for thirty years is only 1·50 inches, we have had an excess of 1·11 inches.

Our bacteriological examination of the London waters gives the following results:—

	Microbes per c.c.
Thames water, unfiltered (average of 27 samples)	9187
Thames water, from the clear water wells of five Thames-derived supplies (average of 159 samples)	33
Ditto ditto .. .. highest	372
Ditto ditto .. .. lowest	2
New River, unfiltered (average of 27 samples)	1160
New River, from the Company's clear water well (average of 27 samples)	30
River Lea, unfiltered (average of 27 samples)	1080
River Lea, from the East London Water Company's clear water well (average of 27 samples)	22

Last month we drew attention to the abnormal bacterial contents of some samples taken from the wells of the Grand Junction Water Works at Hampton, connected with the supply of the country district. The Engineer has now informed us that the Company in May last authorised extensive additions and alterations to their filtering plant af Hampton; these are in course of construction. The Board, however, having had our recent communications on the subject brought to their notice, have now authorised the Engineer to carry out more extensive alterations than had been previously contemplated. We have had a consultation with the Engineer, at which he submitted the general plans of the proposed new filtering plant, which in our opinion will meet the difficulty.

Since the beginning of the month the water from the Hampton Works has steadily improved, and for the last ten days it has been in a satisfactory condition.

At this season of the year there is always a considerable amount of fish spawn in the river, clogging up the filters, and rendering very frequent cleaning necessary. This, added to the recent heavy rainfall, has put a severe strain on the filtration plant of the different Companies. The results, however, show that they have been well able to cope with the difficulties.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

THE HYDROLYSIS OF ACID AMIDES.

By IRA REMSEN.

A number of years ago, with the assistance of advanced workers in this laboratory, I carried out a series of investigations on the oxidation of substitution-products of aromatic hydrocarbons, the results of which went to show that, when the oxidising agent is chromic acid, an oxidisable residue, situated in the ortho position with reference to an atom or group that is not oxidisable, is almost completely protected from oxidation, whilst similar groups in the meta or para position are easily oxidised. Later, experiments were tried on the reduction of nitro compounds of different structure, but, although results of some value were thus obtained, these have not been published, as I have hoped that the method of making the measurements might be improved. Still later, my attention was drawn to the marked difference between benzoic sulphinide (saccharin) and parasulphaminebenzoic acid (Remsen and Burton, *Am. Chem, Journ.*, xi., p. 403) towards boiling dilute acids. The former is easily converted into the corresponding acid ammonium salt, while the latter remains unchanged.

About a year ago I requested Mr. E. E. Read, of this laboratory, to make some experiments on the relative ease with which the three nitrobenzamides are converted into their ammonium salts by dilute acids. Mr. Read has since devoted himself with much skill and energy to this work, and the results reached are most interesting. A method has been devised by which it is possible to measure with a considerable degree of accuracy the rate of the hydrolysis. The experiments thus far completed have been carried out with hydrochloric acid of three concentrations and with sulphuric acid of three concentrations. The details of the experiments will be communicated later, and it will then be seen that the curves showing the rate of change are remarkably regular. A striking difference is shown in the action of the three nitrobenzamides. The following results obtained with half normal hydrochloric acid may serve as an example:—

Time in hours.	Per cent of *o*-amide changed.	Per cent of *m*-amide changed.	Per cent of *p*-amide changed.
½	—	21·1	24·4
1	—	42·8	48·2
1½	—	50·1	63·4
2	—	65·0	71·2
3	3·3	80·5	84·5
4	3·9	88·9	91·9
5	—	92·6	94·6
6	6·2	94·2	96·9
7	—	—	—
8	8·6	—	—

The orthoamide is seen to resist the action of the hydrolysing agent to a very marked degree, so that it was difficult to measure the amount of the change if the heating was not continued for at least three hours. On the other hand, the meta and para amides yield readily, the para somewhat more so than the meta.

It seems highly probable that other aromatic acid amides that contain an atom or group in the ortho position to the group $CONH_2$ will conduct themselves in a similar way. These phenomena are suggestive of those studied in this laboratory many years ago, to which reference has already been made. Apparently the single nitro group in the ortho position with reference to the carbamide group, $CONH_2$, *protects* this from the action of dilute acids, as the nitro group in the ortho position to methyl protects this from oxidation by chromic acid, as shown in my earlier experiments. There is also some analogy between these protection phenomena and those recently studied by Victor Meyer and his students—an analogy which Meyer does not appear to have recognised.

The object of this note is to inform chemists that we are in possession of a method that makes measurements of the kind given above comparatively easy, and that we propose to apply the method to the study of as large a number of cases as possible, with the object of determining—

1. Whether the influence of ortho groups upon the hydrolysis of acid amides is always the same; and
2. How various atoms and groups differ in their effect upon the rate of hydrolysis.

This work will require some time, and it seems best to postpone the publication of the results until the investigation is completed.

(The substance of this note was communicated by me to the National Academy of Sciences, at the New York meeting held November 18, 1896).—*American Chemical Journal*, April, 1897.

WHO SHALL BE HEN-WIFE.

"Na ye maun gan wi' me the noo, Wullie" (his name was Charles), said Henrietta, as she flung a brawny arm round the lad's neck; "sure my friend Jemmie's as Scotch as they make 'em."

"Na, na, lass; I maun gan wi' Wilhelmina, an' my name's no Wullie,—hang it!—and ye need na gar me a crick in my—what do you call it in this lingo?—craig. Your fren' Jemmie's a fause loon; didna she deceive the kirk and get the mickle rebuke o' the meeneester?"

"Then ye'll no mair keep company wi' me (hang this jargon!)" said Henrietta, who was English, and found Kailyardish trying.

Said Charles, "I care no for ye, an I ne'er lo'ed ye nor e'r any but the Scots lassie Wilhelmina.

"You're a rude little boy," said she.

"Stay y're havers, and no clack like siccan," said the Chem. Soc.. afflicted by the *genius temporum*, and involuntarily speaking the lingo.

"An' why shall we no have a bit clavers? Sair, I ken I'm as winsome as Jemmie," said Wilhelmina, as she tried to pull Wullie to her side.

"Bide a wee," said a voice. It was Jemmie's.

There was a confused struggle; Wullie squealed and kicked, the Chem. Soc. awoke with a start, and found Jemmie installed as hen-wife, and the kailyard resuming its normal gentlemanly demeanour.

Ian McCrockett.

EDINBURGH UNIVERSITY GRADUATION CEREMONIAL.

Professor Sir Ludovic Grant, Bart., Dean of the Faculty of Law, introduced Professor James Dewar, F.R.S., Royal Institution, London, to receive the degree of LL.D.

The University recalls with pride that the distinguished physicist and experimentalist who now stands before us received his earliest training in science and first impulse towards research within her precincts. For Professor Dewar was a pupil of Professor Tait's, and thereafter acted as assistant to Professor, now Lord, Lyon Playfair, when he held the Chair of Chemistry in Edinburgh. Since that period Professor Dewar has been called to many offices which are the prerogative of the highest scientific eminence. He was a member of the Government Committee on Explosives, and of the Royal Commission on the Metropolitan Water Supply, and is now President of the Chemical Society, Jacksonian Professor of Natural Experimental Philosophy in the University of Cambridge, and Fullerian Professor of Chemistry in the Royal Institution. But a bare recital of his appointments conveys no adequate idea of Professor Dewar's services to science. Despite the duties of official life, he has devoted himself untiringly to experimental research, and his investigations have been productive of the most remarkable results, and constitute his chief claim to academic recognition. In particular may be mentioned the discoveries he has made regarding the liquefaction of gases, and the properties of matter at a very low temperature. In many instances his experiments demanded the highest courage, no less than perseverance and skill, for they were fraught with extreme personal danger. His Alma Mater rejoices to follow the example already set by the Universities of St. Andrews and Glasgow, by conferring upon her distinguished alumnus the honorary degree of Doctor of Laws. (Applause). — *Scotsman*, April 12, 1897.

NOTICES OF BOOKS.

An Outline of the Theory of Solution and its Results. For Chemists and Electricians. By J. Livingston R. Morgan, Ph.D. (Leipzig), Instructor in Quantitative Analysis, Polytechnic Institute, Brooklyn (New York). New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1897. 63 pp., 12mo.

This little book should be in the hands of every student of chemistry who cares to make himself acquainted with recent developments in chemical philosophy, and every student who does *not* care should be required to pass an intelligent examination on its sixty-three pages.

The author has compiled a very clear, condensed, and up-to date account of the modern theory of solution and its influence on chemical philosophy; he shows its development logically and historically as based on electrolytic dissociation, from the laws governing the behaviour of gases. The results obtained by van't Hoff, Arrhenius, and Ostwald (to whom the book is dedicated) are admirably stated, and without being overloaded with mathematical expressions. Students of analytical chemistry who have not the time to digest the larger treatises of Ostwald and Le Blanc, will find this little work valuable in removing the empiric character of their studies and processes; the laboratory worker will learn *why* an excess of a precipitant is efficacious, and *why* certain salts are added to water used in making precipitates, and *why* indicators in volumetric analysis act as they do.

The theory of solution is daily becoming more and more important for theoretical and practical chemistry, as well as for electricity, and Dr. Morgan has supplied an excellent introduction to the larger treatises.

One typographical error cannot be overlooked: Helmholtz appears twice as "Helmholst," but the book is neatly printed.

H. C. B.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 14, April 5, 1897.

Preparation of Iron Carbide by the Direct Union of the Metal and of Carbon.—Henri Moissan.—If we heat pure iron and the carbon of sugar to the high temperature of the electric furnace, and then allow the regulus to cool slowly, we find in the metal merely a small trace of combined carbon. We thus obtain a grey casting which solidifies towards 1150°. If the metal is run into a mould at the temperature of 1300° to 1400° it contains on cooling graphite and a larger quantity of combined carbon; this is white cast metal. Lastly, if we cool abruptly in water iron saturated with carbon at 3000°, there is produced an abundant crystallisation in the metal, and we may separate from it a pure definite crystalline carbide, CFe_3. This carbide is identical with that of steel. All these facts are explained simply on admitting that iron carbide, like ozone and silver oxide, may be formed at a very high temperature and then be decomposed progressively on a reduction of temperature. We find a notable quantity in steel, the melting-point of which is high, rather less in white cast metal, and very little in grey castings. In all our experiments we have observed the formation of the carbide only in the liquid metal.

Nomination. — The Academy proceeded to the nomination of a member in the Section of Astronomy, *vice* M. Tisserand, deceased. M. Radau obtained the absolute majority of the votes, and was accordingly proclaimed elected.

A letter was read from H. Wilde, F.R.S., President of the Manchester Literary and Philosophical Society, addressed to M. Berthelot, criticising as improper the expression the "Periodic Law," and offering to the Academy the sum of £5500 (=137,500 frcs.) to be invested in French securities and the interest applied to the foundation of an annual prize of 4000 frcs. to be awarded to the author of any discovery or research in astronomy, physics, chemistry, mineralogy, geology, and mechanics, which in the judgment of the Academy shall be considered the most meritorious. The award of this prize will be international, and may be retrospective. (See Chemical News, vol. lxxv., p. 177).

Partial Polarisation of the Radiations emitted by some Sources of Light under the Influence of the Magnetic Field.—N. Egoroff and N. Georgiensky.—Some months ago Dr. Leeman, of the University of Leyden, made remarkable experiments on the influence of a fairly strong magnetic field on the emission of flames in a Bunsen Burner (sodium and lithium). He demonstrated that the perturbation undergone by the ions under the influence of the magnetic focus produce new periods and luminous vibrations (expansion of the spectral rays of sodium and lithium). Subsequently Dr. Leeman, led by the theoretic views of Prof. Lorentz, has demonstrated the peculiar polarisation of these new vibrations.

New Cadmium Lamp for the Production of Interference Fringes.—Maurice Hamy.—The resistance of the lamp when in action is equal to that of one-fifth m.m, of air. A decided rise of temperature above 350° increases this resistance, so that the discharge no longer takes place in the apparatus. Besides the four radiations—red, green, blue, indigo—the spectroscope has enabled me to identify all the known visible rays of cadmium in the light given out by the lamp; and besides a faint ray in the red (λ 632), the rays of sodium, a fine ray in the green (λ 515), invisible in the spectrum of the spark, striking into the air between the electrodes of cadmium.

Researches on Nickel Steels. Meteorological Properties.—Ch. E. Guillaume.—A mechanical paper.

Nature of various kinds of Radiations produced by Bodies under the Influence of Light.—G. Le Bon.—This paper will be inserted as early as possible.

New Oxide of Phosphorus.—A. Besson.—The composition of this phosphorous oxide is shown by the formula P_2O.

Metastannyl Chloride.—R. Engel.—This paper will be inserted in full.

Action of High Temperatures upon Copper, Bismuth, Silver, Tin, Nickel, and Cobalt Sulphides.—A. Mourlot.—We can completely desulphurise the bismuth and copper sulphides, but the desulphuration of bismuth is by far the more difficult. Silver sulphide on exposure to the highest temperatures yields a volatile product still retaining traces of sulphur. Cobalt and nickel yield sulphides relatively stable, CoS and Ni_2S. Tin sulphide undergoes a partial volatilisation and furnishes a crystalline regulus of protosulphide, a new example of a sulphide stable at a high temperature.

Combinations of Gaseous Ammonia and Methylamine with the Haloid Compounds of Lithium.—J. Bonnefoir.—A thermo-chemical paper.

Action of Tannin and of Gallic Acid upon certain Alkaloids.—Oeschner de Coninck.—The author examines the action of dry pulverulent tannin upon pure nicotine and nicotine in aqueous solution. The result was negative, as also in the case of alcoholic and ethereal solution.

Preparation of Sodium Carbide and Mono-sodic Ethylene.— Camille Matignon.— The author describes the *modus operandi* which he has adopted.

Observations Concerning the Freezing Temperature of Milk.—J. Winter.—A controversial paper in reply to MM. Bordas and Génin.

Non-identity of the Lipases of Different Origins.—M. Hanriot.—The blood of the eel contains the same lipase as the blood of the horse, but in a much greater quantity.

Certain Properties of the Ferment of Fracture of Wines.—P. Cazeneuve.—The author enquires into the action of sulphurous acid, which in a small proportion destroys the action of an oxidase, and thus prevents the "fracture" of wines.

Novel Method of obtaining the Perfume of Flowers.—Jacques Passy.—The author uses water in place of the fats used in the process of *enfleurage.*

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. ii., No. 2.

Economical Treatment of the By-products of Distillation of Starchy Products.—A report presented on behalf of the Committee of Chemical Arts by M. de Luynes on the procedures adopted by MM. Bonard and Boulet, who, when treating the distillery residues by the procedure described and figured in this paper, utilise them for the production of oils and matters suitable for cattle-foods.

Revue Universelle des Mines et de la Metallurgie. Series 3, Vol. xxxvii., No. 3.

This issue contains no chemical matter.

MISCELLANEOUS.

Tuberculin O and R.—Prof. Koch has succeeded in the production of two new preparations which he names as above, both of which possess an immunising action against the bacilli of tuberculosis. The preparation is injected beneath the skin at first in small quantities, and the dose is then gradually increased.

Test for Formaldehyd.—L. Kentmann (*Pharm. Gen. Anz.*, 1896, viii., 356).—If the suspected liquid is floated on an equal volume of a solution of 0·1 grm. of morphine hydrochloride in 1 c.c. of strong sulphuric acid, a red violet colour is produced within a few minutes, provided the formalin exceeds one part per 6000.—*The Analyst.*

MEETINGS FOR THE WEEK.

TUESDAY, 27th.—Royal Institution, 3. "Volcanoes," by Dr. Tempest Anderson, B.Sc.
—— Society of Arts, 8. "Delft Ware," by Dr. J. W. L. Glaisher, F.R.S.
WEDNESDAY, 28th.—Society of Arts, 8. "Asbestos and Asbestic—with some Account of the Recent Discovery of the latter at Danville, in Lower Canada," by Robert H. Jones.
THURSDAY, 29th.—Royal Institution, 3. "Liquid Air as an Agent of Research," by Prof. Dewar, F.R.S., &c. (The Rev. Canon Ainger being unable through illness to begin his lectures on this day).
—— Chemical, 8. "Monochlordiparaconic Acid and some Condensations," by H. C. Myers, Ph.D. "Decomposition of Iron Pyrites," by W. A. Caldecott, B.A.
FRIDAY, 30th.—Royal Institution, 9. "Cathode Rays," by Prof. J. J. Thomson, F.R.S., &c.
SATURDAY, May 1st.—Royal Institution, 3. "The Greek Theatre according to Recent Discoveries," by the Rev. J. P. Mahaffy, D.D. Annual Meeting, 5.

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THE CHEMICAL NEWS.

Vol. LXXV., No. 1953.

RESEARCHES ON THE EARTHS CONTAINED IN THE MONAZITE SANDS.

By MM. SCHÜTZENBERGER and BOUDOUARD.

Crystalline cerium sulphate obtained by the treatment of monazite sands has yielded us, on analysis, figures which lead for the corresponding metal to an atomic weight decidedly higher than that resulting from the analysis of the cerium sulphate obtained from cerite (140·5 to 141 in place of 139 to 139·5 for the formula Ce_2O_3). As this result shows the probable presence of a strange earth bordering on cerium, we have sought to isolate the latter, which we have effected in the following manner:—

1. The monazite sands, reduced to powder, are treated with sulphuric acid in heat. The excess of the sulphuric acid is evaporated, and the residue is treated with water.

2. The solution is saturated with potassium sulphate, which precipitates the earths of the cerium group in the state of double cerium sulphates, insoluble in water charged with potassium sulphates. The precipitate is washed with a saturated solution of potassium sulphate, then suspended in water, and decomposed in heat by an excess of caustic soda. The hydrated oxides, precipitated and washed, are dissolved in nitric acid and re-precipitated with ammonia, washed, re-dissolved in nitric acid, and finally precipitated by oxalic acid.

3. The oxalates, washed and dried, are converted into nitrates by nitric acid. The nitrates are dried and melted at 325°, with 8 parts of saltpetre (Debray's process), unto tranquil fusion. The cerium oxide (binoxide), insoluble, is separated from solution of saltpetre water and the nitrates of didymium and lanthanum. After washing, it is transformed into sulphate by the action of sulphuric acid; the dissolved sulphate is precipitated with oxalic acid; the washed oxalate is converted into nitrate, which is dried and melted a second time at 320°, with 8 parts of saltpetre. This second treatment serves to eliminate small quantities of didymium entangled in the first fusion. We thus obtain a light yellow oxide, finely divided, which is first converted by sulphuric acid into yellow cerium sulphate, and then into cerous sulphate, $(SO_4)_3Ce_2$, by a moderate ignition of cerium sulphate, $(SO_4)_2Ce$.

4. The white cerous sulphate is dissolved in water in the cold, and the solution is heated in a capsule on the water-bath. During the evaporation of the liquid, being kept between 75° and 80°, an abundant crystallisation separates out. When the deposit of crystals formed in heat ceases to appear, the mother-liquor is decanted off.

The crystals separated are dehydrated, dissolved in cold water, and the solution is again concentrated by heat, with separation of crystals and of a mother-liquor.

The same operation is repeated several times, and the mother-liquors obtained from the successive crystallisations are added to the first.

We thus obtain (1) a sulphate crystallised in brilliant colourless prisms, containing 13·5 per cent of crystalline water, entirely eliminated at about 300°, which we designate as A; (2), a mother-liquor, B.

The crystals A, dehydrated and dissolved in water, were precipitated with a large excess of a solution of neutral ammonium oxalate. The liquor heated for some hours on the water-bath is filtered when quite cold, and the cerium oxalate is washed with a solution of ammonium oxalate until the filtrate is no longer rendered turbid on the addition of nitric acid. The operation seems to eliminate the traces of thorium which may have become mixed with the cerium.

The cerium oxalate is afresh converted into sulphate. The analysis of this sulphate, after desiccation at 440°, gave—(1) for 2·7196 of sulphuric anhydride, 1·6491 of calcined rose-coloured oxide; calculating this oxide as CeO_2 we have, for the atomic weight of the metal, Ce = 140·5; (2) for 2·6017 of anhydrous sulphate we found 3·1904 barium sulphate, whence we deduce Ce = 141·05.

The determination of the sulphuric acid by barium chloride requires certain precautions, which have been indicated by one of us in a former paper on cerium.

The augmentation of the atomic weight of the cerium of monazite cannot, therefore, be due to the presence of thorium which would have been removed by the treatment with ammonium oxalate. Still, for greater security, we applied to the dilute solution of this sulphate the method indicated by Lecoq de Boisbaudran, by heating it gently for a long time with an excess of copper oxide precipitated and dehydrated at 100°. The cupric oxide precipitates the thorium, but not the cerium. Very little copper passed into solution, and the filtrate had a greenish colour. When freed from copper by hydrogen sulphide, and concentrated on the water-bath, this liquid yields crystals, like the former in appearance, but differing in composition:—

1. Hydrated sulphate, 3·9288; anhydrous sulphate obtained, 3·4012; water, per cent, 3·47.
2. Anhydrous sulphate employed, 2·3075; oxide (white) obtained by calcination, 3·928, whence Ce = 138·6, considering the oxide as dioxide.
3. Anhydrous sulphate employed, 2·3667; barium sulphate obtained, 2·9320, whence Ce = 138·1.
4. Anhydrous sulphate employed, 2.7475; barium sulphate obtained, 3·4045, whence Ce = 138·1.
5. Anhydrous sulphate employed, 2·4176; barium sulphate obtained, 2·2940, whence Ce = 137·7.

In all the analyses effected with similar products, purified with copper oxide, the determination by calcination of the sulphate gives for the atomic weight of the cerium a value a little higher than that resulting from a determination of the sulphuric acid.

This is the inverse of that always observed on analysing cerium sulphates which have not undergone the purification with copper oxide. The atomic weight deduced from the calcination of the sulphate, and calculating the residual oxide as dioxide, is sensibly below that deduced from the contamination of the sulphuric acid.

Examination of the Mother-liquors, B.—These mother-liquors, diluted with water, are directly treated with an excess of copper oxide precipitated and dehydrated at 100° whilst in the water.

A notable quantity of copper is dissolved, and the excess of this oxide is found mixed with a large proportion of a precipitated white hydrate. The deposit is washed, and added to the precipitate formed by the A crystals under the influence of cupric oxide.

The filtrate, freed from copper by means of hydrogen sulphide, yielded crystals of cerous sulphate similar to the foregoing, that is to say to about Ce = 138·0.

Examination of the Precipitate yielded by Copper Oxide.—This is stirred up in water and dissolved in a *slight* excess of sulphuric acid. The lukewarm solution is freed from copper by means of hydrogen sulphide. It still presents very distinctly the characters of the cerium salts. On treatment with soda it gives, after the addition of an oxygenated water, an orange-yellow precipitate. On the other hand, it reveals the presence of large proportions of thorium or of analogous bodies; it is thus that, when concentrated on the water-bath, it yields an abundant white flocculent deposit formed of felted needles, which, on analysis, lead to atomic weights bordering on that of thorium.

In order to separate the cerium from the thorium, we saturated the liquid with sodium sulphate. After some time there is formed a scanty precipitate of double sulphate, which was separated after twelve hours, and washed with a solution of sodium sulphate saturated in the cold.

This double sulphate, decomposed in heat with caustic soda, gave an oxide which when converted into sulphate offers the characters of cerium sulphate. Its analysis gave :—

1. Anhydrous sulphate employed, 2·3014; barium sulphate obtained, 2·7570, whence Ce=147·8.

2. Anhydrous sulphate employed, 3·3074; calcined oxide obtained, 2·0074, whence Ce=141·6.

3. Hydrated sulphate, 3·6582; anhydrous sulphate obtained, 3·1611; water per cent, 13·5.

4. Anhydrous sulphate employed, 1·7673; calcined oxide obtained, 1·0730, whence Ce=141·1.

The solution of this sulphate crystallises during the evaporation in crystalline crusts, adhering to the bottom of the capsule, and which appear homogeneous to the desiccation of the last drop of the liquid. From these results we may calculate that the oxide obtained by the calcination of the sulphate has a composition close upon $2Ce_2O_3 \cdot Ce_2O_4$.

Examination of the Saturated Solution of Sodium Sulphate separated from the foregoing Precipitate. — The earth withdrawn from this liquid by means of caustic soda, washed, dissolved in nitric acid, precipitated anew with ammonia, and washed, still shows the presence of cerium compounds. Its solutions give with soda a white precipitate, which becomes reddish yellow on the addition of oxygenated water.

We succeed in separating the ceric part which occasions these coloured reactions, by treating the neutral solution of the sulphate in the cold with an excess of neutral ammonium sulphate. The greater part of the precipitate dissolves; the insoluble portion, when filtered and washed, calcined, and again transformed into sulphate, gives a salt very soluble in water and does not deposit crystals during evaporation. The liquid thickens on concentration, forming on the surface films like those of a solution of gum. On evaporation we obtain a colourless mass, amorphous and transparent, which if kept for some time in a stove at 100° becomes opaque and crystalline.

The analysis of the crystals which give the coloured reactions of cerium furnished the following numbers :—

1. Anhydrous sulphate employed, 2·566; barium sulphate obtained, 2·975, whence Ce=157·45.

2. Anhydrous sulphate employed, 2·6684; calcined oxide obtained, 1·6320, whence Ce = 144·3, calculating the calcined oxide as bioxide. From these results we may attribute to this oxide the formula already found, that of an intermediate oxide.

The earths bordering on cerium oxide, with a nigh molecular weight, give, on the calcination of their sulphate, not a bioxide, but an intermediate oxide.

This explains the disagreement constantly observed between the results of the determination of the sulphuric acid, and on the calcination of the sulphate whenever it has not been purified with copper oxide.

In fine, we have separated :—

1. A cerium with an atomic weight near 138, and rather lower, the solution of which does not precipitate copper oxide.

2. A cerium of an atomic weight near 148, the sulphate of which is precipitable by copper oxide, and also by sodium sulphate.

3. A cerium of an atomic weight near 157, the sulphate of which is precipitable by copper oxide, but not by sodium sulphate. The solutions are characterised by taking a gummy aspect during concentration.

These three earths give yellow ceric salts, decomposable by heat into white cerium salts. Oxygenated water with soda precipitates them of an orange-red. Ammonium oxalate precipitates them, all three, and the precipitates are not soluble in excess. Spectroscopic examination (sparks with chloride) does not show any difference between the three salts.

The part soluble in neutral ammonium oxalate, and not precipitated by sodium sulphate, does not present the coloured reactions of cerium, but belongs to the thorium group. The experiments hitherto effected have led us to a homogeneous product.—*Comptes Rendus*, cxxiv., p. 481.

THE BEHAVIOUR OF BACTERIA WITH CHEMICAL REAGENTS.

By TH. PAUL and B. KRÖNIG.

From the authors' experiments with the spores of splenic fever and those of *Staphylococcus pyogenes* it results that—

1. With the exception of platinum, the salts of gold, silver, and mercury have a specific toxic action.

2. The disinfective action of the metallic salts depends not alone on the concentration of the metal in solution, but also on the specific properties of the salts and the solvent. Behring's view that the disinfective value of the mercury solutions depends alone on the percentage of soluble mercury cannot be rightly admitted.

3. Solutions of metallic salts in which the metal is an ingredient of a complex ion, and the concentration of its ion is hence very trifling, exert merely a very slight antiseptic action.

4. The effect of a metallic salt depends not merely on the specific action of the metallic ion, but also on that of the anion.

5. The haloid compounds of Hg (including the cyanides and sulphocyanides) disinfect according to their degree of dissociation.

6. The disinfective action of aqueous mercuric chloride is lowered by the addition of metallic chlorides.

7. The strong acids act at concentrations of 1 litre and upwards, not only corresponding to the concentration of their hydrogen ions, but also by means of the specific properties of the anion. The strong acids, even if more dilute, and the weak organic acids seem to act in the proportion of their degree of dissociation.

8. The bases KOH, NaOH, and LiOH, when dissociated, disinfect almost equally; $NH_4(OH)$, when much less dissociated, disinfects very little.

9. The oxidising agents, NHO_3, $H_2Cr_2O_7$, $HClO_3$, $HMnO_4$, act according to their position in the series laid down according to their electric behaviour. Chlorine does not rank in this series, but has a very powerful specific action.

10. The disinfective action of the halogens, Cl, Br, I, decreases, like their general chemical behaviour, with the increase of atomic weight.

11. The statements Scheurlein that solutions of phenol disinfect better on the addition of salts was verified.

12. The known fact that substances dissolved in alcohol and ether are almost without action on the spores of splenic fever was confirmed by the author's observations.

13. Aqueous alcohol of known percentage heightens the disinfective action of $HgCl_2$ and $AgNO_3$. — *Chemiker Zeitung*.

Determination of Organic Matter in Potable Water. —Dr. E. Fricke.—It is an unpleasant property of centinormal oxalic acid that it gradually loses its efficiency. A recent solution of oxalic acid of which 10 c.c. are just faintly reddened by an equal volume of permanganate, after being kept for eight days required only 9·5 c.c. for adjustment, and after four weeks its value had fallen to 8 c.c. permanganate. The appearance of flocculent matter showed that the oxalic acid is decomposed by fungi. As it is very inconvenient to prepare a new standard solution every day or two I tried adding to the oxalic solution 1 grm. boric acid per litre, and I find that after ten weeks it has remained unchanged. The boric acid has no action upon the permanganate.—*Chem. Zeitung*, No. 26, 1897.

THE IRONSTONE OF THE WEALD.

By Dr. T. L. PHIPSON.

Of the various ironstones examined of late years in this laboratory, none are more interesting than that of the Weald. This particular portion of the Earth's crust, which lies just below the green sand of the chalk formations, is rarely met with on the surface of the globe. It presents the characters of a fresh-water formation, and has been found to contain the remains of some gigantic reptiles. There exist a few small patches of it in the South of England. The fresh-water *Paludina* shells are one of its characteristics.

I have made a careful examination of the ironstone of this formation, and have found that it consists of a yellowish white or grey *carbonate of iron*, generally coated with hydrated peroxide in the form of brown hæmatite, which in its turn passes into reddish orange or yellow ochraceous stones containing much silica.

The carbonate of iron of the coal measures is also, evidently, of fresh-water origin; for, among the ores of this kind forwarded to me from South Staffordshire, I have met with a beautiful little specimen of a fresh-water mollusc (*Unio*) presenting exactly the composition of these spathic ironstones.

But whilst the carbonate of iron of the coal strata contains a notable amount of phosphates and sulphates, that of the Weald is remarkably pure in this respect.

The Weald ironstone has given me from 34 to 42 per cent of metallic iron; 14 to 46 per cent of silica (which is the chief impurity), and about 2 to 3 per cent of oxide of manganese, with similar quantities of magnesia and alumina, and a little lime, but only faint traces of sulphates and phosphates.

These spathic ironstones seem to have been formed from ancient chalybeate springs, such as are rather frequent at the present day, especially in Germany, where the process is still in action, the iron being dissolved from the rocks through which issue constantly vast streams of carbonic acid. Near Neubau, in Waldeck, for instance, I have seen bubbles of carbonic acid varying in size from that of a walnut to that of a man's head, bursting on the surface of springs, incessantly, day and night; and this volcanic action has been continuous there as long as man can remember.

The almost complete absence of phosphorus and sulphur in the ironstone of the Weald is rather remarkable, since spathic ironstone is generally different in this respect. In olden times, when forests abounded in the South of England, this ore was smelted and made good iron. I have heard it stated that the old iron-railings of St. Paul's Cathedral were obtained from this source; and among the samples forwarded to me for analysis, and picked up on the surface of the ground, I have met with pieces of slag that appear to be Catalan slag.

Casa Mia Laboratory, Putney, S.W,
April 27, 1897.

MODIFICATION OF THE THALLEOQUIN TEST FOR QUININE.

By F. S. HYDE.

It is extremely important for the success of this test that the reagents employed should be dilute. Some authorities give the quantity of each reagent necessary, without stating the proper dilution, thereby causing much inconvenience.

The light green colouration produced on porcelain by contact of the quinine salt with weak bromine or chlorine water and ammonia, is not nearly so striking as the brilliant emerald-green colour obtained by using dilute solutions in a test-tube.

Usually the analyst deals with unknown quantities, or mere traces, but for experiment it will be found convenient to use from 3 to 5 m.grms. of the quinine salt for each test. (With larger amounts there is a tendency to form bulky precipitates).

For example, place 3 to 5 m.grms. (0·003 to 0·005 grm.) quinine sulphate in a test-tube, and add about 5 c.c. distilled water. Acidulate with *one* drop (not more) of dilute sulphuric acid (1 : 4), which immediately dissolves the quinine sulphate with a blue fluorescence. An excess of the acid should be avoided.

At this point various authorities recommend the addition of weak bromine or chlorine water; but the writer has found that if a clear, filtered solution of calcium hypochlorite (bleaching powder) be substituted for the bromine or chlorine water, the results will be more satisfactory so far as certainty and brilliancy of the test are concerned.

The points to be observed are as follows:—After acidulation with one drop of sulphuric acid (1 : 4) the hypochlorite solution is added through a small filter to the quinine solution in the test-tube, until the blue fluorescence just disappears, and the solution acquires a faint golden tint; then add a few drops of dilute ammonia (1 : 3), when a clear emerald-green colour should appear. (Thalleoquin test).

The tint thus produced seems to be more brilliant than that obtained through the agency of bromine water.

On the addition of a slight excess of dilute sulphuric acid to this green solution, a blood-red tint will be produced, which may be considered confirmatory. This is not always the case, however, when bromine water has been used in the preliminary operation.

Potassium or sodium hypobromite is not applicable, on account of the strong alkali, which tends to precipitate the white quinine base, and thus interfere with the brilliancy of the test. Chlorinated soda (Labarraque's solution) likewise gives uncertain results, the tints varying from yellowish green to violet.—*Journal of the American Chemical Society*, xix., p. 331.

THE ACTION OF ACID VAPOURS ON METALLIC SULPHIDES.[*]

By JEROME KELLEY, Jun., and EDGAR F. SMITH.

Experiments made in this laboratory on the action of the vapours of hydrochloric acid upon the sulphide of arsenic proved that the latter is wholly volatilised. The purpose of the present communication is to record further observations along analogous lines. Thus, when washed and dried arsenic trisulphide is exposed to the action of hydrobromic acid gas, it volatilises completely. Indeed, the action commences in the cold with the formation of a liquid that passes out of the containing vessel upon the application of a very gentle heat. In evidence of this, two quantitative experiments may be given:—

Arsenic sulphide taken. Grm.	Arsenic sulphide expelled. Grm.
0·2945	0·2941
0·4632	0·4628

Antimony trisulphide, like that of arsenic, is volatilised by hydrochloric acid gas. It was quite probable that a like deportment would be observed if hydrobromic acid gas should be substituted. This was found to be the case. When the gas came in contact with the sulphide it became liquid and volatilised as soon as a gentle heat was played upon the boat in which the sulphide was contained.

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[*] Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xviii., No. 12.

Antimony sulphide taken. Grm.	Antimony sulphide expelled. Grm.
0·1473	0·1469
0·0938	0·0935

Upon substituting stannic sulphide for antimony sulphide, an experience similar to that observed with antimony and arsenic sulphides followed. There was a complete volatilisation with but a trifling residue, which proved to be carbon from filter-paper that had adhered to the metallic sulphide.

Stannic sulphide taken. Grm.	Stannic sulphide expelled. Grm.
0·1880	0·1880
0·5527	0·5521
0·4174	0·4169

The oxides of arsenic, antimony, and tin (at least in the stannic form) can be volatilised in a current of hydrochloric acid gas. This is also true of the sulphides of arsenic and antimony, but how the two sulphides of tin would act under like conditions was not known.

Experiments recently made demonstrate the perfect volatility of stannic sulphide in this way. With stannous sulphide it was found that by the continued action of the gas in the cold there followed a complete conversion into chloride without any volatilisation. That the residue was the chloride was evident from its action upon a mercuric salt solution. The figures obtained in the several trials were:—

Stannous chloride found. Grm.	Stannous chloride theory. Grm.
0·3544	0·3523
0·4893	0·4903

Several attempts were made to separate stannous and stannic sulphides by this procedure. The results were unsatisfactory. In order to drive out the stannic salt completely it is necessary to heat the mixture, and this caused a partial volatilisation of the stannous chloride, so that quantitative results could not be obtained.

Comparatively few metallic sulphides have been studied in the direction indicated in the preceding lines, so that it is probable that a wider application of the method will disclose interesting behaviours, and that probably new separations can be brought about in this way. The action of the vapours of haloid acids has also been tried on natural sulphides with a fair degree of success.

THE ESTIMATION OF MOLYBDENUM IODOMETRICALLY.*

By F. A. GOOCH.

In a former paper from this laboratory (Gooch and Fairbanks, *Am. Journ. Sci.*, IV., ii., 157, 1896) several modes of applying hydriodic acid to the reduction of molybdic acid were studied. It was found, first, that the digestion process of Mauro and Danesi (*Zeit. Anal. Chemie*, xx., 507) is of very limited applicability, owing to the fact that the reaction of reduction is reversible. Secondly, it appeared that the use of the same reaction by Friedheim and Euler (*Ber. d. D. Chem. Gesell.*, xxviii., 2066) in a distillation process, so arranged that the iodine set free in the reduction might be caught in the distillate and titrated to serve as the measure of the reducing action, was not sufficiently regular because of inattention to minor details. It was shown that by taking care to adjust the conditions constant results might be obtained. Thirdly, the fact was developed that by simply boiling the solution under well-defined conditions in an ordinary Erlenmeyer flask, partly closed by a simple trap, the reduction of the molybdic acid proceeded regularly, and that the addition of standard iodine to the solution made alkaline with sodium bicarbonate served to restore the original condition of oxidation of the molybdic acid. The results of this treatment were shown to be accurate.

In a recent paper (*Ber. d. D. Chem. Gesell.*, xxix., 2981) Friedheim has seen fit to make our modifications of the distillation process the subject of attack. Friedheim's comments upon the third method discussed—as well as upon a subsequent application of the process ("An Iodometric Method for the Determination of Phosphorus in Iron," by Charlotte Fairbanks)—are evidently prompted wholly by personal opinion and demand no further attention. With reference to Friedheim's denial of the necessity of modification in the Friedheim and Euler treatment the case is different.

The process of Friedheim and Euler consists, it will be remembered, in treating the soluble molybdate, or the solution of molybdic acid in sodium hydroxide, with potassium iodide and hydrochloric acid in a Bunsen apparatus, boiling until the solution is of a clear green colour, collecting the iodine distilled in potassium iodide, and titrating it with sodium thiosulphate. We found that the development of the green colour was not a sufficient criterion of the exact reduction of the molybdic acid to the condition of the pentoxide and of the removal of the iodine which should be theoretically set free. To accomplish that end we found it safer and more convenient to start the distillation with a definite volume (40 c.m.^{3}) of liquid and boil until a definite volume (25 c.m.^{3}) was reached, care being taken with regard to the strength of acid and the excess of potassium iodide employed. Experience showed unmistakably that in order to avoid the decomposing action of the air upon the hot vaporous hydriodic acid in the retort, it was necessary to go beyond the measures advised by Friedheim and Euler (namely, to warm the retort and its contents slowly, heating to boiling only when the connecting tube was well filled with iodine vapour, and the tendency toward back-suction of the liquid in the receiver began to appear), and to conduct the operation in a simple little apparatus (the retort holding about 100 c.m.^{3}) put together entirely with sealed and ground joints, as shown in the figure of the former paper, so arranged that a current of purified carbon dioxide could be passed through retort and receiver during the distillation. With this apparatus we were able to determine with accuracy the point of concentration at which the free iodine left the liquid, the molybdic acid having been converted to the condition of the pentoxide. It was found that if dependence is placed upon the occurrence of the so-called clear green colour of the liquid to determine the end of the distillation, it may frequently happen that free iodine remains in the residue. This takes place, it will be observed, in the atmosphere of carbon dioxide, so that the presence of the free iodine can by no possibility be attributed to the action of atmospheric air upon the hydriodic acid remaining after the distillation is complete. On the other hand, it appeared that, if the distillation is pushed too far, the molybdenum pentoxide may be still further reduced, with consequent evolution of more than the expected amount of iodine. The attainment of an exact degree of reduction with the expulsion of the corresponding amount of iodine becomes, therefore, a matter of chance unless further precautions are taken. We found in our experiments that if amounts less than 0·3 grm. of the molybdic acid are introduced in soluble form into the 100 c.m.^{3} retort with a not too great excess of potassium iodide, and the 40 c.m.^{3} of liquid so constituted that 20 c.m.^{3} of it shall be water and 20 c.m.^{3} the strongest hydrochloric acid, the reduction proceeds with a fair degree of regularity in the manner expected. We found it important to restrict the excess of potassium

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* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Fourth Series, vol. iii., March, 1897.

iodide so that it shall never exceed the theoretical requirement by more than 0·5 grm.

Our determinations with the pure molybdenum trioxide showed errors varying from 0·0010 grm. + to 0·0007 grm. − ; the variations from theory in the experiments with ammonium molybdate ranged from 0·0011 grm. + to 0·0011 grm. −. If these results are compared with those given by Friedheim and Euler, the advantage is a little in favour of the latter ; but a scrutiny of the figures given by Friedheim and Euler developes the fact that the apparent accuracy of their work is founded upon miscalculations. This fact was known to us at the time of our former writing, but we did not consider it essential then to make the matter public. The recent attack of Friedheim makes that course now necessary.

Herewith is reproduced a table of results obtained by Friedheim and Euler in the test of their method upon ammonium molybdate, shown by analysis to contain 81·49 per cent of molybdenum trioxide. The figures which are incorrect are enclosed in brackets :—

Original Figures of Friedheim and Euler.

Molybdate taken. Grm.	$Na_2S_2O_3$ used. C.m.^{3}.		MoO_3 found. Grm.	Per cent of MoO_3 referred to molybdate taken.
0·2674	30·8	1 c.m.^{2} = 0·00709 MoO_3.	0·2184	[81·71]
0·4418	50·8		0·3601	81·51
0·4075	[40·7]*		0·3317	81·40
0·3281	37·33	1 c.m.^{3} = 0·007086 MoO_3.	0·2644	[81·85
0·4340	49·43		0·3502	81·69
0·4098	46·63		0·3304	81·67
0·4305	49·08		0·3478	81·78]

* Probably 46·7.

Appended is a re-calculation of the percentage of the trioxide found, with columns showing the percentage error and the error stated in fractions of a grm. Changes from the figures of Friedheim and Euler are in modern-faced type.

Re-calculation of the Results of Friedheim and Euler.

Corrected per cent of MoO_3 found, referred to the molybdate.	Error in per cent of MoO_3 found compared with MoO_3 taken.	Error of MoO_3. Grm.
81·68	0·23 +	0·0005 +
81·51	0·03 +	0·0001 +
81·40	0·12 −	0·0004 −
80·58	1·12 −	0·0030 −
80·69	0·99 −	0·0035 −
80·62	1·05 −	0·0035 −
80·79	0·86 −	0·0030 −

These figures of their own (properly calculated) are sufficient to show the inadequacy of the method of Friedheim and Euler. We ourselves were occasionally able to get results from the method of Friedheim and Euler quite as good as these ; it must be said, however, that most of our results obtained by their unmodified method have been even worse than their own.

In another series of six determinations, in which molybdenum trioxide was the starting point, Friedheim and Euler were more successful, the errors varying from 0·0006 grm. + to 0·0006 grm. −. Thus, Friedheim and Euler establish by their own results the fact that the hitting of the right point at which to stop their process of boiling is a matter of chance. In spite of the probability that some of the iodine which they found in the receiver was liberated by atmospheric action, the fact remains that their results are in many cases very low. That is, they did not boil long enough.

The difficulty appears again in the modification of their method which Friedheim and Euler apply to the determination of molybdenum trioxide associated with vanadium pentoxide (*Ber. d. D. Chem. Gesell.*, xxviii., 2072), namely, the distillation with phosphoric acid and potassium iodide of the residue left after reducing the vanadium pentoxide by hydrochloric acid and potassium bromide, according to the method of Holverscheit. We reproduce the part of their table which refers to the determination of the molybdenum, adding, however, columns containing the errors and corrected percentages.

MoO_3 taken.	MoO_3 found.	Per cent MoO_3 F. and E.	Error. Grm.	Per cent MoO_3. Re-calculated.
0·15037	0·15005	99·79	0·00032 −	99·79
0·16895	0·16879	99·90	0·00016 −	99·90
0·17758	0·17729	99·84	0·00029 −	99·84
0·24975	0·24962	99·95	0·00013 −	99·95
0·33151	0·33607	[99·87]	0·00456 +	101·38

Four of the five determinations are accurate, but the fact that all figures are carried out to the fifth decimal place does not keep three good sized figures out of the error column for the fifth determination.

It is hardly necessary, in the light of a comparison of the results of Friedheim and Euler with ours, to discuss further the unreliability of the unmodified process. The necessity of a proper control of the volume, strength of acid and excess of potassium iodide, as well as proper protection from atmospheric oxidation, is real.

On a former occasion the unpleasant necessity presented itself (Gooch and Browning, *Am. Journ. Sci.*, xlv., 334) of pointing out the fact that certain unfounded criticisms on the part of Friedheim and Meyer were based upon an unfortunate use by them of impure reagents; the difficulty in the present case, for Friedheim and Euler, seems to reside in the arithmetical process.

DETERMINATION OF POTASH AND PHOSPHORIC ACID IN FODDERS.

By H. W. WILEY.

In the comparative analyses of soils during the past three years we have grown a great number of pot cultures and determined the mineral plant-foods in the resulting crops. The following modified potash method, devised by Mr. K. P. McElroy, while not sacrificing accuracy, has made it possible for one analyst to determine the potash, often in duplicate, in more than ten samples a day. Since the quantity of the crop harvested from a poor soil is often small, it is desirable that the phosphoric acid and potash be determined in the same sample.

The method in use for the determination of potash in feeding stuffs, in the laboratory of the United States Department of Agriculture is a simple modification of the ordinary Lindo-Gladding method, as prescribed by the Association of Official Agricultural Chemists. It is as follows :—

Burn 8 grms. of the substance over a low flame to a proximate whiteness. Burning after addition of sulphuric acid does not give more potash than burning alone, and it is more troublesome. Transfer the ash to a 200 c.c. flask, using about 50 c.c. of water ; add 5 c.c. of strong hydrochloric acid, and place on the steam-bath for an hour, or boil from five to ten minutes. Add a little iron chloride to precipitate all phosphoric acid as ferric phosphate, then 10 c.c. of strong ammonia, and then from 5 to 10 c.c. of ammonium carbonate solution (200 grms. per litre of the commercial salt). Replace on the steam-bath and heat for an hour, and allow to stand over night. Complete the volume to the 200 c.c. mark with water, and shake three times at intervals of five or ten minutes. Grease the inside of the neck of the flask, and pour its contents on a dry folded filter. When all is transferred to the filter and run through, wash down the neck of the flask with a little water, put the funnel into the flask, and stand aside till the filter dries. The roll up the filter, and push down nto the flask. Add dilute nitric acid, digest, make volume up to the mark, and use an aliquot part for the determination of phosphoric acid.

Transfer 50 c.c. of the filtrate containing the potash, equivalent to 2 grms. of material, to a platinum dish, cover, and heat on the steam-bath till evolution of gas ceases. Remove the cover, and rinse it and the sides of the dish with a stream from the wash-bottle. Evaporate to dryness, and heat in an air-bath till all water is removed in order to avoid loss by decrepitation in the subsequent ignition. Heat over a low gas flame till the bulk of the ammonium chloride is removed, cool, and add 1 c.c. of sulphuric acid (1 : 1); then heat on a hot plate till fuming begins, then over a flame till all the sulphuric acid is driven off and the residue in the dish is white. Every portion of the dish should reach a low but distinct red heat, the bottom first and then the sides. The reason for the preliminary driving off of the bulk of the ammonia as sal-ammoniac is that ammonium sulphate melts and sputters, involving danger of loss. Cool the dish, and add one or two drops of strong hydrochloric acid, then from 50 to 75 c.c. of water, washing down the sides of the dish with a jet from the wash-bottle. Add platinum chloride solution in amount equivalent to 150 m.m. of metallic platinum for materials not containing over 4 per cent of potash. Very few reach this limit. Evaporate on the water-bath as usual, and take up with alcohol of 80 (volume) per cent. Filter through a Gooch crucible, keeping the insoluble material in the dish as far as possible. Wash with four more portions of alcohol, decanting through the crucible each time. Finally rinse down the sides of the crucible with a stream of alcohol from a wash-bottle. Cover the residue in the dish with the half-saturated solution of ammonium chloride prescribed in the official method for the determination of potash, and stir thoroughly. Decant through the Gooch crucible, and treat with five or more portions of sal-ammoniac solution, decanting through the crucible each time. Finally wash into the crucible with 80 per cent alcohol. When the transfer is complete, rinse the sides of the crucible thoroughly, and finally fill it twice with alcohol, of course constantly filtering with a vacuum. Dry for an hour at 100° and weigh.

Pour about 150 c.c. of boiling water through the weighed Gooch crucible. If the platinum potassium chloride is not wholly dissolved, again bring the filtrate to a boil and pour through once more. Store this filtrate finally in a large flask, containing aluminium clippings, to reduce the platinum. Bring a fresh portion of water (150 c.c.) to a boil, and pour through the Gooch crucible. Remove the crucible from the vacuum apparatus, wipe, and dry in an air-bath, with good ventilation, for two hours, at 110°. Weigh once more. The loss in weight is the double chloride. The second portion of hot water is used to dissolve the double salt in the next crucible operated upon, after being once more brought to a boil. —*Journal of the American Chemical Society*, xix., p. 320.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting, March 25th, 1897.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Professor P. Frankland, Ph.D., B.Sc., F.R.S., delivered the Pasteur Memorial Lecture.

It was pointed out that, although the name of Pasteur was associated with the progress of so many branches of science, it appeared that his remarkable success in such varied fields of investigation was in large measure due to the chemical discipline under which he had grown up, and in his having almost for the first time extended the experimental methods and close reasoning of the chemist to other sciences, in which previous investigators had been mostly occupied with matters of a superficial character. Reference was then made to Pasteur's birth, on December 27, , 1822, his early life and entrance as a student into the Ecole Normale, to his being retained as an assistant there by Balard, and to his interest being awakened in the study of crystallography by Delafosse. His classical researches on the tartrates and malates were then described, and the principal results discussed from a practical and theoretical point of view. It was shown of what enormous importance for the development of chemical theory had been the introduction by Pasteur of the conception of molecular symmetry and dissymmetry, whilst the wide applicability of his methods of investigating stereoisomeric compounds was indicated in outline. The manner in which he was next led to investigate fermentation phenomena was then described, his conflict with Liebig was touched upon, and his overthrow of the so-called "chemical fermentation theory" detailed. Reference was then made to his participation in the spontaneous generation controversy, and to his victories over Pouchet, Joly, Musset, and Bastian, the last champions of the doctrine of abiogenesis. The practical aspects of Pasteur's, fermentation studies were briefly considered, the famous "Etudes sur la bière"; "sur le vin," and "sur la vinaigre," as well as process known as *pasteurisation*. The direct influence of these fermentation studies on medicine, surgery, and public health was pointed out, and the manner in which they had led to the magnificent work of Lister on the antiseptic treatment of wounds was indicated. Pasteur's investigation of the destructive silkworm diseases, *pébrine* and *flacherie*, was then dealt with, and his gradual attraction into the field of pathological research traced. His studies on anthrax, his recognition of the bacillus of malignant œdema, and his discovery of the *Staphylococcus pyogenes* and of the *Streptococcus pyogenes* were referred to. Then the manner in which he came upon the possibility of attenuating viruses and preparing vaccines were described; the lecture concluded with an account of the methods of protective inoculation devised by Pasteur, first for fowl-cholera, then for anthrax, for swine-measles, and his final triumph in successfully elaborating a curative treatment for rabies.

Lord Lister, P.R.S., proposed, and Sir Henry Roscoe seconded, a vote of thanks to Professor Percy Frankland, which was carried unanimously.

Anniversary Meeting, March 31st, 1897.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Professor Collie, F.R.S., and Dr. Wynne, F.R.S., were appointed scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year, the ballot being closed at the conclusion of the President's Address.

The Longstaff Medal was then presented to Professor Ramsay for the discovery of helium, and for his share in the investigation of argon. The President referred to the circumstances under which the first announcement of the discovery was made, and expressed the pleasure he felt in presenting him with the Medal.

The President began his Address by thanking the Fellows, and more especially the Officers and Council, for the kindness with which they had aided him during his year of office, and expressed his pleasure at the progress of the Society during the past year. He referred to the arrangements made for the reading of papers, and suggested means by which the discussions might be made more useful.

The publication of the Jubilee volume, largely drawn up by Dr. Armstrong, was mentioned, and the services rendered by Mr. Warington in its preparation were acknowledged. The Hofmann Memorial Lectures had also been issued. Lothar Meyer and Pasteur Memorial Lectures had been delivered in the year, and arrangements had been made for the Kekulé Lecture. Reference was also made to the work of the Council through the year, to the death of Sir William Grove, an original member of the Society, and to the munificent donation of one thousand guineas by Mr. J. J. Tustin.

The remainder of the Address was devoted to the consideration of the question whether the changes which matter undergoes are different in their nature.

The numerical strength of the Society was as follows:—

Number of Fellows, March 31st, 1896		2019
since elected		130
reinstated by Council		7
		2156
Removed on account of non-payment of two annual subscriptions	25	
Withdrawn	29	
Deaths	23	
		77
Number of Fellows, March 31st, 1897		2079
Foreign Members		27

The following have died:—I. M. T. Anderson; John Curragh; Captain Marshall Hall; G. Harley, F.R.S.; James Hart; John Hughes; W. Lapraik, Ph.D.; J. B. L. Mackay; A. H. Mason; H. A. Nott; Baron F. von Mueller, F.R.S.; W. J. Palmer; Sir J. Prestwich, F.R.S.; Edward Rawlins; G. F. Schacht; James Scorgie; T. Shimidzu; T. J. Smith; Charles Tomlinson, F.R.S.; W. H. Walenn; Richard Weaver; W. H. Wood; T. G. Wormley, M.D.

The number of communications made to the Society during the year was 173.

One hundred and seventeen papers and three Memorial Lectures were published in the *Transactions* for 1896, occupying 1702 pages, whereas in the preceding year 116 papers were published, occupying 1172 pages.

The following were the statistics relating to the Abstracts:—

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	716	1201
PART II.		
General and Physical Chemistry		319
Inorganic Chemistry		287
Mineralogical Chemistry		267
Physiological Chemistry		182
Chemistry of Vegetable Physiology and Agriculture		153
Analytical Chemistry		430
Total in Part II.	684	1638
Total in Parts I. and II. ..	1400	2839

Eight hundred and fifteen volumes had been borrowed from, and 163 books, 310 volumes of periodicals, and 24 pamphlets added to the Library.

Professor **Odling**, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the *Transactions*.

Dr. **Frankland**, F.R.S., seconded the motion, which was carried by acclamation.

The **President** having returned thanks,

Dr. **Thorpe**, F.R.S., the treasurer, gave an account of the balance sheet, which he laid before the Society, duly audited.

The receipts had been:—By admission fees and subscriptions, £4134; by sale of Journal and advertisements, £702 14s. 9d.; and by dividends on invested capital, £415 10s. 6d. The expenses had been:—On account of the Journal, £3089 8s. 1d.; on account of the Proceedings, £237 18s. 1d.; on account of the General Index, £464 3s. 9d.; on account of the Library, £355 2s. 0d.; on account of the Jubilee, £336 12s. 1d.; House expenses, £199 17s. 4d.; the total expenditure being £5385 4s. 7d. Grants amounting to £308 had been made to the Fellows from the Research Fund during the year.

Sir F. **Abel**, F.R.S., proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Mr. **Phipson Beale**, Q.C., and carried.

The **Treasurer**, in responding, proposed a vote of thanks to the auditors.

Mr. J. H. M. **Page** seconded the motion, which was unanimously adopted, and acknowledged by Mr. H. B. **Baker**.

Dr. W. J. **Russell**, F.R.S., proposed a vote of thanks to the Officers and Council.

Professor **Tilden**, F.R.S., seconded the motion, which was unanimously adopted.

Dr. **Dyer** responded on behalf of the Council.

Professor H. B. **Dixon**, F.R.S., proposed a vote of thanks to the Editor, Sub-Editor, Abstractors, and Indexers, which was seconded by Mr. **Friswell**, and carried.

Mr. **Groves**, F.R.S., responded.

The scrutators having presented their report to the President, he declared that the following had been duly elected:—

President—James Dewar, M.A., LL.D., F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., M.D., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. Vernon Harcourt, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Lord Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—Francis Robert Japp, M.A., Ph.D., LL.D., F.R.S.; Ludwig Mond, F.R.S.; William Ramsay, Ph.D., F.R.S.; J. Emerson Reynolds, D.Sc., F.R.S.; W. Chandler Roberts-Austen, C.B., F.R.S.; William A. Tilden, F.R.S.

Secretaries—J. Millar Thomson; Wyndham R. Dunstan, M.A., F.R.S.

Foreign Secretary—Raphael Meldola, F.R.S.

Treasurer—T. E. Thorpe, LL.D., F.R.S.

Other Members of Council—P. Phillips Bedson, D.Sc.; Bennet Hooper Brough; Otto Hehner; C. T. Heycock, M.A., F.R.S.; Herbert McLeod, F.R.S.; Rudolph Messel, Ph.D; H. Forster Morley, M.A.; James Wyllie Rodger; T. Kirke Rose, D Sc.; Alexander Scott, M.A., D.Sc.; Arthur Smithells, B.Sc.; Sydney Young, D.Sc., F.R.S.

The question having been raised as to whether the number of votes cast for each candidate for the Presidency should be declared, the **President** stated that this had not been the custom, but he would take the sense of the meeting on the point. A majority being in favour of a declaration of the numbers, the President conferred with the scrutators and then stated that there was a difficulty in announcing the numbers, owing to a question having arisen in reference to the validity of certain voting papers, in which the instruction to erase the printed name had not been complied with.

Inasmuch as the rejection of these irregular papers would only increase the majority and not affect the result of the election, and as it now appeared that the announcement of the numbers would involve re-counting the votes, the President suggested that the Fellows should be content with the scrutators' report. The ruling of the President as to the validity of the irregular papers having been requested, he stated that, in his opinion, they were invalid.

Questions having been asked as to the by-laws governing the election, the **President** stated that the election had been conducted in strict accordance with the by-laws, and he therefore declared the election valid.

In the evening, at 7 p.m., the Fellows and their friends dined together at the Criterion Restaurant, Mr. A. G. Vernon Harcourt, the retiring President, in the Chair.

The following toasts were proposed:—

By the **Chairman**: 1. Her Most Gracious Majesty the Queen. 2. Their Royal Highnesses the Prince and Princess of Wales and the others members of the Royal Family.

By the Right Hon. Lord **Lister**, *President of the Royal Society*: 3. Prosperity to the Chemical Society.

By **William Crookes**, *Esq.*, *F.R.S.*: 4. The Learned and Scientific Societies, coupled with the name of Sir John Evans, K.C.B., Treasurer of the Royal Society.

By Dr. J. H. **Gladstone**, *F.R.S.*: 5. The Guests, coupled with the name of Professor Michael Foster, Secretary of the Royal Society.

By Dr. W. J. **Russell**, *F.R.S.*: 6. The retiring President.

By Dr. **Armstrong**, *F.R.S.*: 7. The Secretaries, coupled with the name of Professor J. M. Thomson.

Ordinary Meeting, April 1st, 1897.

Prof. **Dewar**, F.R.S., President, in the Chair.

Messrs. William Douglas, Ernest Goulding, T. H. Lee, and W. A. Davis were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Barlow, Hillfield, Muswell Hill, N.; James Brierley, 12, Brunswick Square, Southampton; Alexander Duckham, Crooms Hill, Greenwich Park, S.E.; Harold William Harrie, 298, Amhurst Road, Stoke Newington, N.; Sydney Hill, 11, Salisbury Street, Hull; Willie Lee Mallinson, Gawthorp Green, Kirkheaton; Edmund Howd Miller, M.A., Ph.D., Columbia University, U.S.A.; Joseph Previte Kennedy Orton, B.A., Ph.D., 20, Loughborough Road, Brixton, S.W.; Charles Alfred West, 105, Sydney Street, Chelsea, S.W.; Paul Thomas White, Horton Field, West Drayton.

Mr. **Cassal** asked whether the President would take steps to carry into effect the wishes of a majority at the Anniversary Meeting, that a recount of the ballot papers should be made, and the votes recorded for the two nominees for the Presidency announced to the Fellows.

Mr. **Vernon Harcourt** said that, although a majority at the Anniversary Meeting had declared themselves in favour of the announcement of the numbers, it had not been found possible to make any exact announcement without going through the voting papers again, and he had hoped that, having regard to all the circumstances, it would be generally felt best to accept the result of the election as it had been recorded by the Scrutators, especially as a succinct and accurate account of what had happened at the Anniversary Meeting had been included in the minutes.

The **President** said he considered the subject closed, but promised to bring the question before the Council. He could not see that any good would result from a recount of the voting papers for the mere purpose of delaring the exact numerical majority by which the President had been elected. He hoped that long before the Council met the matter would be forgotten.

Of the following papers those marked * were read:—

*50. "*The Hydrolysis of Perthiocyanic Acid.*" By F. D. **Chattaway**, M.A., and H. P. **Stevens**, B.A.

When potassium thiocyanate is treated with sulphuric acid, many different substances are produced; thiocyanic acid, however, is always first liberated, and then reacts in various ways determined by the conditions of the experiment.

The best known reaction, usually represented as a simple hydrolysis of thiocyanic acid, is that by which carbon oxysulphide is commonly prepared. Other actions, however, go on, and the carbon oxysulphide is invariably mixed with carbon dioxide, sulphur dioxide, hydrocyanic acid, and carbon bisulphide.

The authors have observed that, in addition to these, a considerable amount of thiourea is produced. This thiourea has been found to be a decomposition product of perthiocyanic acid, which is always formed in considerable quantity when acids act upon thiocyanates, and the paper deals mainly with the hydrolysis of this acid.

Perthiocyanic acid is easily hydrolysed, either by heating with water under pressure, or by heating with strong sulphuric acid, thiourea, carbon oxysulphide, and sulphur being formed.—

$$H_2N_2C_2S_3 + H_2O = CS(NH_2)_2 + COS + S.$$

As the action only takes place at a comparatively high temperature, one or other of these products is invariably decomposed. When perthiocyanic acid is heated with water to about 200° in closed tubes, this action may be considered to take place first; but at the high temperature the thiourea is transformed completely into ammonium thiocyanate, while the carbon oxysulphide reacts with water, giving carbon dioxide and hydrogen sulphide, so that the final action is—

$$H_2N_2C_2S_3 + 2H_2O = NH_4NCS + CO_2 + H_2S + S.$$

When perthiocyanic acid is heated with 60 per cent sulphuric acid, a similar hydrolysis must also take place; a certain amount of the thiourea, however, escapes transformation, but the sulphur and carbon oxysulphide are oxidised by the sulphuric acid, sulphur dioxide and carbon dioxide being produced.

The thiourea found among the products of the action of strong sulphuric acid on potassium thiocyanate, is, without doubt, formed in this way by the action of the strong acid on the perthiocyanic acid first produced.

Discussion.

In reply to questions from Mr. Groves and the President, Mr. **Stevens** stated that they had not been able to analyse the liquid supposed to be hydrogen disulphide, but they were satisfied as to its identity from a comparison of its properties with those of hydrogen disulphide specially prepared for the purpose.

*51. "*The Composition of Cooked Fish.*" By **Katharine** I. **Williams**.

Twenty-two species of fresh fish and five species of preserved fish and oysters were examined after cooking.

Determinations were made of the following constituents:—Water; carbon and hydrogen; nitrogen (total) by Ruffle's method; nitrogen by soda-lime combustion; ash; sulphur; phosphorus; fat; proteids; carbohydrates convertible into glucose; nitrates extracted by dilute alcohol; heats of combustion. The results are recorded in a series of tables.

Discussion.

In reply to questions from Mr. Groves, Mr. Hehner, Mr. Sutherland, Mr. Cassal, and Prof. Dunstan, Miss **Williams** stated that the fish, in each case, had been analysed in the condition in which it would be eaten. Details of the mode in which the fish had been prepared were given in the paper. The common opinion that fish contained much phosphorus seemed to be erroneous. Little or none of the phosphorus would be removed in cooking.

*52. "*On the Oxidation Products of αγ-Dimethyl-α′-Chloropyridine.*" By Emily Aston, B.Sc., and J. Norman Collie, Ph.D., F.R.S.

The present communication is an account of the continuation of some work of one of the authors with A. P. Sedgwick (*Trans.*, 1895, lxvii., 399). The substance αγ-dimethyl-α′-chloropyridine was obtained by the action of phosphorus pentachloride on pseudolutidostyril. When oxidised with potassium permanganate, two isomeric acids are obtained, each having the formula—

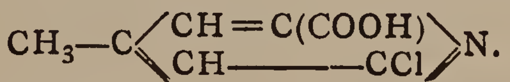
$$C_5H_2(CH_3)(COOH)NCl.$$

One (m. p. 98°) is much more soluble in water than the other and crystallises with 1 mol. of water; it produces with ferrous sulphate an orange-brown colouration. When strongly heated, it decomposes with much charring and evolution of carbon dioxide and some hydrogen chloride; the residue furnished α-chloro-γ-methylpyridine,—

$$C_5H_3(CH_3)NCl, \text{ b. p. } 194°.$$

Prolonged treatment with tin and hydrochloric acid gave γ-methylpicolinic acid, and this substance when distilled yielded picoline or γ-methylpyridine.

This acid (m. p. 98°) is, therefore, α-chloro-γ-methyl-α′-pyridine carboxylic acid.



$$\mathrm{CH_3{-}C}\left\langle\begin{matrix}\mathrm{CH{=}C(COOH)}\\ \mathrm{CH{-\!-\!-\!-}CCl}\end{matrix}\right\rangle\mathrm{N.}$$

The second acid obtained by the action of potassium permanganate on αγ-dimethyl-α′-chloropyridine is much less soluble in water. It melts at 214°, and on heating completely decomposes without forming chloropicoline. With ferrous sulphate it furnished a precipitate instead of a colouration. Tin and hydrochloric acid only reduced it very slowly, and it was found to be impossible to separate the chlorine free acid from the unchanged compound. A small quantity of free α-picoline was, however, obtained by distilling the impure reduced acid, thus proving that this acid (m. p. 214°) was the α-chloro-α-methyl-α′-pyridine carboxylic acid.

$$\mathrm{COOH{-}C}\left\langle\begin{matrix}\mathrm{CH{=}C(CH_3)}\\ \mathrm{CH{-\!-\!-\!-}CCl}\end{matrix}\right\rangle\mathrm{N.}$$

Attempts were made to obtain the dicarboxylic acid from both the acids by oxidising with potassium permanganate, but without success.

NOTICES OF BOOKS.

The Carbohydrates of Wheat, Maize, Flour, and Bread; and the Action of Enzymic Ferments upon Starches of Different Origin. By W. E. Stone, Ph.D., Professor of Chemistry, Purdue University. Washington: Government Printing Office. 1896.

The investigations described in this report constitute part of the enquiries being carried on to enable the Secretary of Agriculture to investigate and report on the nutritive value of various articles of food.

It has long been customary to estimate the quantity of carbohydrates in grains and flours by difference, that portion of the material not found to be of the nature of fat, ash, moisture, fibre, or of nitrogenous character, being regarded as of carbohydrate nature. The investigations here recorded have been made with the object of discriminating between the various carbohydrates known to be present in cereals, and to trace the effect of the separation of the grain into its parts, as occurs in milling. The different kinds and qualities of wheat, maize, and flour examined, as well as the methods employed, are then fully gone into, and it is important to note that each constituent has been actually determined, and that no result has been obtained by "difference," each carbohydrate, with the exception of cellulose, having been brought to the form of reducing sugar, in which state it was titrated with Fehling's solution.

Both classes of wheat examined were found to contain small amounts of sucrose, ranging from 0·5 per cent upwards; the principal carbohydrate present is starch, which reached 30 per cent. This proportion was considerably increased by milling, which, by eliminating a good deal of the fibre, brought the amount of starch up to 35, and even 45 per cent.

Breads made from these flours were then examined, and, contrary to expectation, it was found that the action of bread-making and baking does not change the nature or condition of the carbohydrates of wheat and maize to any great extent; in the case of wheat flour with one apparently abnormal exception, not more than 10 per cent of the total starch originally present was changed in any way.

The attention of investigators has of late been directed to the action of enzyms on carbohydrates. Recent researches show that different yeasts produce certain specific enzyms, each with an ability to convert some particular class of carbohydrate, such as lactose, maltose, or sucrose; for instance, ordinary yeast inverts the two latter, but not the former, while others will produce enzyms converting either sucrose or lactose, but not maltose. The susceptibility of starches to the more important enzyms, viz., those occurring in grains, or more especially *diastase*, those occurring in saliva, partilarly ptyalin, and those occurring in the pancreatic secretion, were the subject of the next studies. In addition, a few experiments were made with a new diastatic enzym developed by the fungus *Eurotium oryzæ*, discovered by Mr. Jokichi Takamine, and known commercially as "Taka-koji" or "Taka-diastase." The results have a practical bearing on the comparative digestibility of different starches. The action of diastase on starch is increased by minimal amounts of acids, and, on the other hand, it is checked or altogether stopped by greater amounts of acids, and the smallest amounts of alkalis, or alkaline salts.

The ability of diastase to convert large amounts of starch into soluble compounds is remarkable; some authors estimate it at as much as 200,000 times its own weight. There has been much discussion as to the nature and number of the intermediate products of the decomposition of starch; but it is now considered probable that they consist of the various forms of dextrin, which gradually become changed to maltose and isomaltose. Under precisely similar conditions the action of different enzyms on different starches varies considerably, some starches requiring eighty times as long as others for complete saccharification, but they all preserve the same relative order with regard to the commoner enzymic ferments; with taka-diastase, potato-starch was completely converted in seven minutes, this being much quicker than with any of the others; and it is reasonable to assume that the relative degree of susceptibility exhibited by starches in the experiments described would still hold good when subjected to the same enzyms in the process of digestion; in fact, we understand that "taka-diastase" is being largely and increasingly used in cases of dyspepsia with excellent results.

Commercial Fertilisers and Chemicals, Inspected, Analysed, and Admitted for Sale, in the State of Georgia, up to September 1st, 1896. By Dr. George F. Payne, State Chemist. Atlanta, Georgia: G. W. Harrison, State Printer.

This book is chiefly devoted to a recital and exposition of the State laws of Georgia regulating the sale of manures. These laws certainly do not err on the side of undue lenity. All manures have to be sold under an analysis, setting forth the moisture at 212° F., the insoluble phosphoric acid, the available phosphoric acid, the ammonia actual and potential, and, lastly, the potash.

The fact that the purchaser waives the inspection and official analysis "shall be no protection to any person selling or offering fertilisers for sale." In addition to the labels attached to the packages, there are to be fixed on each box, barrel, &c., leaden tags numbered progressively. Any tags left in possession of the manufacturer or merchant at the close of the season shall not be used for another season, nor shall they be redeemable by the Department of Agriculture. The analysis of the State chemist is to be held by an official known as the "ordinary."

The analysis given by the State chemist or his substitute is held to be conclusive evidence against a charge of "*partial* or *total* failure of consideration." Hence it seems that if the dealer's analysis is fully confirmed by the State chemist, the dealer is not, as a matter of course, entitled to his money. This, however, is still more equitable than our English practice. With us a purchaser of manures may ignore for a year or more all applications for payment, and at last, when he finds that his creditor is in earnest, may still be allowed to plead defective quality—a plea which, if well founded, should have been urged in answer to the first application for payment.

Agricultural Journal, published by the Department of Agriculture, Cape of Good Hope. January 14, 1897. Cape Town: Townhend, Taylor, and Snashall.

This issue is very rich in useful observations. Across the Free State border there are several farms being visited by rinderpest, whilst the colonial area is still entirely free. Inoculation with garlic in the dewlap has proved useless, as has also drenching with petroleum and carbolic acid.

In the Richmond district droves of wild ostriches have made their appearance, and are doing damage.

The vapour of carbon bisulphide is strongly recommended for dealing with destructive insects, care being of course taken to keep lighted candles and matches at a distance.

In South Africa, as far as it is known, there are no soils rich in potash.

Dr. R. Morloth strongly recommends basic slags for suppying the needful phosphate on the Cape Flats and the whole of the Western province.

The Law and Practice of Letters Patent for Inventions. By Lewis Edmunds, D.Sc., Q.C., of the Inner Temple and of the Oxford Circuit. Second Edition, by T. M. Stevens, D.C.L., of Gray's Inn and of the South-Eastern Circuit, Barrister-at-Law. London: Stevens and Sons, Limited. 1897. 8vo., pp. 943.

A work of this kind presents to the authors unusual difficulties, on account of the complicated nature of the subject matter which lies on the border land between law and technology, whether the invention relates to physics, chemistry, or mechanics.

A further complication is that such works are rightly expected to deal with Patent Law and Practice as at present existing, whilst the inventor not improbably and not unreasonably demands to see where such law and practice might be improved to the encouragement of our national industries. The Patent Law Amendment Acts of 1852 and 1883 have involved important alterations, both in law and practice, which the authors have set forth fully and clearly.

One of the great defects of our patent system is that it is not imperial. To obtain the protection of an invention for the whole of Her Majesty's dominions costs, if we remember rightly, about £1100. Now, what we want is a system of imperial patents, obtainable on equal terms, and with equal advantages, in London, Calcutta, Cape Town, Sydney, or other suitable central cities.

Another defect in our patent arrangements is the very "one-sided reciprocity" with alien countries which we have agreed to. Thus a German or a French subject can obtain and uphold a British patent just as easily as a British subject. But if the latter applies in Berlin for the protection of an invention, his application, after prolonged correspondence, may be refused.

In most countries a patent is granted to any applicant *inter alia* on the condition that it is actually and continuously worked on a commercial scale in the country or countries in which it is patented. In Britain no such stipulation prevails, and an article made under any existing and unexpired British patent may be imported from abroad.

A deficiency in the British patent system is that it protects the so-called invention and sale of quack medicines, foods, cosmetics, &c., in which the inventor claims to have some exclusive right or secret. Here we might advantageously copy the German patent law, which refuses patents for medicines, &c. But we might justly and wisely go a step further, and cut off the stratagem by which a German quack evades the law, *i.e.*, by refusing protection to methods for manufacturing "nostrums" or secret and "proprietary" articles whatever.

The work before us will be found invaluable to patentees, counsel, solicitors, patent agents, and all persons who have to take into consideration the value of an invention. We do not hope that it may be of service to the pseudo-inventors—"sifters" as they are called in the manufacturing districts—who are always trying how near they can sail to some valuable novelty.

CORRESPONDENCE.

A RECLAMATION.

To the Editor of the Chemical News.

Sir,—My attention has been called to "A Reclamation" in the Chemical News of March 19th (vol. lxxv., p. 134). This note conveys an erroneous impression. The author of it, who is apparently Kippenberger (not Riffenbach) is made to say that "he published this research by Gomberg in the *Zeitschrift für Analytische Chemie*, 1896, p. 466, as a supplement."

On reference to this article I find that Kippenberger, in a "Nachtrag" to the article cited refers to the article of Gomberg and comments on it at some length, but nowhere charges that Gomberg did anything improper. Anyone reading the note in the Chemical News would, I think, conclude that Gomberg stole the article, and that the *Journal of the American Chemical Society* had no right to publish it. This, I think, does injustice both to Gomberg and to the Society, and I wish to correct this false impression.—I am, &c.,

Edward Hart,
Editor of the *Journal of the American Chemical Society.*

Easton, Pa., April 6, 1897.

Physiological and Pathological Action of the X Rays.—M. Sorel.—The X ray exerts a powerful action upon the cell and its contents, and its prolonged application would be imprudent, at least in certain subjects, near the important organs such as the stomach, the heart, the lungs, and the eyes. In a great number of cases the body of a dead animal is always much more opaque to the X rays than the body of a similar animal immediately after death and still warm.—*Compt. Rend.*, cxxiv., No. 15.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 15, April 12, 1897.

Law of the Discharge of Electrised Uranium into the Air.—Henri Becquerel.—The author gives in this paper the law of the loss of electricity by uranium as a function of time and of the potential of the electrised bodies. Salts of uranium which he has preserved for more than a year protected from any known radiation continue to emit, with an intensity scarcely decreased, radiations which produce photographic impressions through opaque bodies.

Photography of König's Flames.—M. Maraze.—This paper requires, or rather consists of, eight photographic proofs.

Experiments made with a New Kathodic Apparatus generating X Rays, and with several Vessels sealed on the same Gaseous Circuit.—Foveau de Courmelles and G. Segny.—On observing the luminous, fluorescent, and kathodic effects produced we find that the internal pressure in an exhausted tube is not equal at all points; that towards the extremity the vacuum is much more complete than at the other extremity of the same gaseous circuit, and that the molecules which are able to remain in such highly rarefied media are driven with extreme violence towards the most extreme point of the circuit of the apparatus. The authors signalise the rapidity and definiteness of the results obtained with the vacuum tube.

Formation Heats of Formic Aldehyd.—Marcel Delépine.—A thermochemical memoir. The formation heat of gaseous formic aldehyd from its elements is +25·4 cals., and of dissolved aldehyd is +40·4 cals.

Formation of Ammonium Cyanide and its Manufacture.—Denis Lance.—Ammonia gas passing over carbon at a temperature between 1000° and 1100° C. always yields ammonium cyanide. The yield of cyanogen is more considerable if we use a mixture of ammoniacal gas, nitrogen, and hydrogen. The yield reaches its maximum at 1100° C., and when the gases are in the following proportions:—NH_3 = 1·26th of the mixture formed by N and 10H. In these conditions at least 70 per cent of the nitrogen of the ammonium cyanide is derived from the free nitrogen of the mixture, *i.e.*, from the nitrogen of the air.

MISCELLANEOUS.

The Stas Memorial.—Invitations have been sent by the Organising Committee to all subscribers to attend the Inauguration of the Monument erected to Stas. The ceremony will take place on May 11th, at 4 p.m., in the garden of the Palace of the Academies, Brussels.

Iron and Steel Institute.—The Annual Meeting of the Institute will be held at the Institution of Civil Engineers, Great George Street, Westminster, on Tuesday and Wednesday, the 11th and 12th days of May, 1897, commencing each day at 10.30 o'clock a.m. The following is a list of Papers that are expected to be read and discussed:—

"On the Permeability of Steel-making Crucibles," by Professor J. O. Arnold and F. K. Knowles.

"On the Practice of the Combined Open-hearth Process of Bertrand and Thiel," by E. Bertrand.

"On the Agricultural Value of Sulphate of Ammonia from Blast-furnaces," by F. J. R. Carulla.

"On the Specific Heat of Iron," by Professor W. N. Hartley, F.R.S.

"On Charging Open-hearth Furnaces by Machinery," by Jeremiah Head.

"On the 'Weardale' Re-heating Furnace," by H. W. Hollis.

"On the Effect of Phosphorus on Cold Shortness," by Baron Hanns Juptner von Jonstorff.

"On the Determination of Hardening and Carbide Carbon," by Baron Hanns Juptner von Jonstorff.

"On Malleable Cast Iron," by G. P. Royston.

"On Carbon Changes connected with Malleable Cast Iron," by G. P. Royston.

"On Microscope Accessories for Metallographers," by J. E. Stead, Member of Council.

"On Central Blast Cupolas," by T. D. West.

Silver Hydride. — Edwin J. Bartlett and W. F. Rice (*Am .Chem. J.*, xix., 49-52).—Silver hydride, AgH, was prepared by precipitating a dilute solution of silver nitrate with dilute hypophosphorous acid in excess. The solution becomes wine-coloured at first, changing to black, and after a few minutes black spongy flakes are precipitated, which are filtered at once. The filtrate, on long standing or boiling, deposits metallic silver. Silver hydride is not decomposed by water.—*Journ. American Chemical Society.*

Paraisobutylphenoxyacetic Acid. — W. P. Bradley and F. Kniffen (*Am. Chem. Journ.*, xix., 70—76).—Paraisobutylphenoxyacetic acid was prepared by heating paraisobutylphenol and chloracetic acid dissolved in sodium hydroxide. The mixture was neutralised with sulphuric acid, treated with an excess of sodium carbonate, and extracted with ether to remove any excess of phenol. The resulting liquid was then evaporated to a small bulk, acidified, and the acid extracted with ether. The compound is a cream-white solid, melts at 86·5°, and crystallises from ligroin in radial crystals. The barium and magnesium salts crystallise well. The amide, prepared from the methyl ester, crystallises from ligroin in white plates, which melt at 134°. The anilide, metanitranilide, ortho- and paratoluides, and hydrazide are described. A tetranitro derivative of the anilide was formed by the action of fuming nitric acid. The fact that the four nitro-groups are divided equally between the two benzene rings was proved by the action of potassium hydroxide, which decomposed the compound into the ortho- and paradinitraniline.—*Journ. Amer. Chem. Soc.*

MEETINGS FOR THE WEEK.

Monday, 3rd.—Society of Arts, 4.30. (Cantor Lectures). "Design in Lettering," by Lewis Foreman Day.
—— Royal Institution, 5. General Monthly Meeting.
Tuesday, 4th.—Royal Institution, 3. "Volcanoes," by Dr. Tempest Anderson, B.Sc.
—— Society of Arts, 4.30. "The Arctic and Antarctic," by Aubyn Trevor-Battye.
Wednesday, 5th.—Society of Arts, 8. "The Railway to India," by C. E. D. Black.
Thursday. 6th.—Royal Institution, 3. "Liquid Air as an Agent of Research," by Prof. Dewar, F.R.S., &c.
—— Chemical, 8. Ballot for the Election of Fellows. "A Bunsen Burner for Acetylene," by A. E. Munby, M.A. "Reactions between Lead and the Oxides of Sulphur," by H. C. Jenkins and E. A. Smith.
—— Society of Arts, 4.30. "Kafiristan—its Manners and Customs," by Sir George Scott Robertson, K.C.S.I.
Friday, 7th.—Royal Institution, 9. "Romance," by "Anthony Hope."
Saturday, 8th.—Royal Institution, 3. "The Greek Theatre according to Recent Discoveries," by the Rev. J. P. Mahaffy, D.D.

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THE CHEMICAL NEWS.

Vol. LXXV., No. 1954.

RECENT DETERMINATIONS OF THE ELECTRICAL CONDUCTIVITY OF ALUMINIUM.

By JOSEPH W. RICHARDS and JOHN A. THOMSON.

Many and various values have been determined for the electrical conductivity of this metal. The causes have been as follows:—

(1). The impurity of the metal used. Until 1886, the best commercial aluminium rarely surpassed 98 per cent in purity, and it was not until 1889 that commercial metal of 99 per cent was put on the market. As will be shown later, the effect, even within these narrow limits, is to change the conductivity nearly 10 per cent.

(2). The reference of the conductivity to copper or silver as standards. In such cases, the exact purity of the copper or silver and the physical condition of these metals, whether hard or soft, must be known in order to give the comparison its proper value; but these were in most cases either unknown or neglected. Even at the present time, the absolute conductivity of pure soft copper or silver cannot be said to be fixed closer than within 1 per cent, so that figures for conductivity of aluminium, given only with reference to copper or silver, cannot, at best, have an accurate significance.

(3). Lack of an accurate standard of absolute resistance. The adoption of standard units of resistance, by international concert, and the consequent multiplication of registered copies, has made it an easy matter to use in experiments certified instruments of accurately known resistance, and thus to dispense with self-constructed units of comparison in favour of more accurate standards.

(4). Imperfect methods of measurement. Of late years, several ingenious arrangements have been devised for eliminating from the calculations of experiments the resistance of connections, always an uncertain quantity, and more refined instruments for measuring and balancing electric currents have been constructed, thus permitting of increased accuracy in results.

In the following experiments the specimens tested were kindly furnished by the Pittsburgh Reduction Company, and were all analysed by Mr. Handy, of the Pittsburgh Testing Laboratory, so that their composition was accurately known. The conductivity is given in absolute measurement, so that no reference to any other metal as a standard can affect the results. This was rendered possible by the use of a certified standard resistance coil of 1 "International" ohm, whose possible error is not over 0·02 per cent, and by the use of the *Carey Foster* method of comparison. The metal was in wire, of 50-foot lengths, the diameter of which was measured by a micrometer and checked by weighing and determining the specific gravity. The wires were wound on wooden bobbins and immersed in oil, the temperature of which was given by a thermometer. The galvanometer used was a reflecting instrument, sufficiently delicate for all purposes. The standard coil was immersed in water, and the room was kept at a constant temperature. The bridge wire used was carefully calibrated, and all readings were taken several times. Two separate wires were tested in case of Experiment 1, the result given being the mean of two results, which differed only one-hundredth of 1 per cent from each other.

For the reduction from the working temperature to 0° C. an experiment was made with wire No. 1, which showed that between 27° C. and 0° C. its temperature coefficient was 0·00392 per degree. This coefficient was used for the nearly pure wires, while for 4 and 5 a slightly lower coefficient, determined by Mr. Scott, was used. It appears that the purer the metal the greater its temperature coefficient.

Conductivity tests of a similar set of wires were made by Mr. C. F. Scott, electrician of the Westinghouse Electric Company, Pittsburgh. They were made by comparison with pure copper, with a Wheatstone bridge. These results can only be compared with ours by assuming a certain value for the conductivity of copper, and even then we cannot say how nearly the copper used by Mr. Scott would approach that standard. Sir W. Thompson's value for the specific resistance of copper is 1580, Dewar's 1562. In the following table we reduce our results to each of these standards, and add Scott's results for comparison:—

Relative Conductivity (Copper = 100).

	Richards and Thomson. Using for copper the resistances (1580)	(1562).	C. F. Scott. Actual resistance of copper employed not known.
1. Soft	65·0	64·2	—
1. Hard . ..	64·4	63·7	63·1
2. Soft	62·3	61·6	—
2. Hard . ..	61·1	60·5	62·2
3. Hard . ..	55·5	54·9	56·2
4. Hard . ..	56·0	55·4	58·5
5. Soft	52·9	52·3	—
5. Hard . ..	52·5	51·9	55·0

Temperature Coefficient for 1° C.

	C. F. Scott. (Between 15° and 80° C.).	Richards and Thomson. (Between 0° and 27° C.).
1.	0·00385	0·00392
2.	0·00385	—
3.	0·00360	—
4.	0·00361	—
5.	0·00359	—

In connection with the results of Mr. Scott and ourselves, we may mention for comparison those of Charpentier-Page, who used what he calls *pure* aluminium, which may safely be assumed to be the No. 1 grade of European aluminium, averaging 99 per cent pure. He finds as follows:—

	Analysis.						Resistance at 0° C. of a wire 1 metre long by 1 m.m. diameter, in ohms.	Specific resistance at 0° C., *i.e.*, resistance of 1 c c. in absolute (C.G.S.) units of resistance.	
	Aluminium.	Iron.	Copper.	Silicon.	Sodium.		Hard.	Hard.	Annealed.
1.	99·66	0·10	0·00	0·16	0·008	—	0·031245	2453·7	2432·2
2.	99·58	0·25	0·00	0·16	0·052	—	0·03290	2584·0	2535·0
3.	98·77	0·20	0·57	0·45	0·012	—	0·03627	2848·0	—
4.	97·16	0·25	2·26	0·30	0·032	—	0·03590	2819·6	—
5.	94·39	0·25	3·07	0·24	0·052	1·50	0·03583	3011·4	2984·7

	Specific resistance (Calculated to 0° C.).	Compared with copper. (1580). Per cent.	(1562). Per cent.
Soft	2659	59·4	58·8
Hard.. ..	2684	58·9	58·2

It should be noticed that these results fall exactly between our Nos. 2 and 3, also just where its composition would most probably lie. The results also agree closely with ours in showing almost exactly 1 per cent greater conductivity for the annealed than for the hard-drawn wire.

Dewar and Fleming have also recently found as the specific resistance of "Swiss aluminium about 99 per cent pure" the value 2563 at 0° C., which is 60·9 per cent of that of copper, according to their own measurements. This also fits in well with our determinations, but the comparison would have been much more satisfactory if the exact composition of their metal had been determined.

C. K. McGee determined, in 1890, the conductivity of aluminium analysing 98·52 per cent pure to be 54·8 per cent that of copper when unannealed. This metal was nearly identical with our No. 3 in composition, and the results are the same within 1 per cent.

The conclusions we would draw from these experiments and comparisons are that—

The conductivity of hard drawn commercial aluminium is strongly affected by impurities, being, approximately,—

		(Copper=100).
98·5 per cent pure aluminium	.. .. ..	55·0
99·0 ,, ,,	.. .. ..	59·0
99·5 ,, ,,	.. .. ..	61·0
99·75 ,, ,,	.. .. ..	63·0—64·0
100·0 ,, ,,	probably ..	66·0—67·0

Annealed wire has a conductivity very nearly 1 per cent greater than the unannealed.—*Journal of the Franklin Institute*, March, 1897.

STANDARD IODINE SOLUTION FOR SULPHUR DETERMINATIONS.

By EDWARD K. LANDIS.

THE following calculation shows an easy method of preparing Payne's iodine solution, with the least amount of calculation.

Reactions.

$K_2Mn_2O_8+10FeSO_4+8H_2SO_4=5Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O$.

$K_2Mn_2O_8+10KI=10I+6K_2O+2MnO$.

$H_2S+2I=2HI+S$.

2 atoms I = 2 atoms Fe = 1 atom S.

32 grms. S = 112 grms. Fe.

1 grm. S = 3·5 grms. Fe.

When 5 grms. are taken for analysis, 0·01 per cent = 0·0005 grm., and this multiplied by 1000 = 0·5 grm. in a litre.

Let x = value of 1 c.c. $K_2Mn_2O_8$ in Fe in grms.

$$\text{Then } \cfrac{0{\cdot}5}{\cfrac{x}{3{\cdot}5}} = 0{\cdot}5 \times \frac{3{\cdot}5}{x} = \frac{1{\cdot}75}{x}.$$

Therefore 1·75 divided by the value of one c.c. potassium permanganate in iron in grms. gives the number of c.c. of potassium permanganate to be added to the potassium iodide and sulphuric acid and diluted to one litre, to form iodine solution of such strength that one c.c. will be equal to 0·01 per cent sulphur when using five grms. of sample.—*Journ. American Chem. Soc.*, xix., No. 3.

SOME EXPERIMENTS WITH CATHODE RAYS.*

By A. C. C. SWINTON.

THE extensive employment of the focus form of Crookes tubes as the most efficient known means of generating X-rays, has rendered advisable the more complete investigation of the cathode ray discharge in tubes of this description.

Hitherto, the usual method of investigating the characteristics of a cathode ray discharge apart from its mechanical properties, and beyond what is visible to the unassisted eye, has been by allowing the rays to fall upon a screen of some brightly fluorescent material, such as glasses of various descriptions, or screens covered with fluorescent salts. With all of these the maximum amount of fluorescence appears to be produced by such comparatively weak cathode rays, that in some cases the special effects produced by the more powerful rays seem to be more or less entirely masked, while the well-known phenomenon of the fatigue of fluorescent substances, when exposed to the more active rays, conduces to the same result.

Surface Luminescence of Carbon when exposed to Cathode Rays.

I have found in some cases that by replacing the usual screen, made of or covered with fluorescent material, by one of ordinary electric light carbon, much appears which was previously invisible. When a concentrated stream of powerful cathode rays are focussed upon a surface of carbon in this manner, a very brilliant and distinctly defined luminescent spot appears on the surface of the carbon at the point of impact of the rays, the remainder of the carbon remaining black. This luminescent spot seems to have a very close relation to the fluorescent spots on glass and on other fluorescent materials under similar influence. The effect is evidently a purely surface effect, as when the cathode stream is rapidly deflected by means of a magnet the luminescent spot on the carbon moves with no perceptible lag. Further, though, as is also the case with glass, the whole of the carbon becomes gradually heated to a considerable extent if much power be employed for a long period of time, these luminescent spots are instantaneously produced on carbon of very considerable brilliancy with but a comparatively low power. Again, just as glass is known to become fatigued under the influence of cathode rays, so that after a time it refuses to fluoresce so brightly as before, so carbon is similarly fatigued, though only after having been very strongly acted upon. Carbon, like glass, also recovers its property of giving a surface luminescence to some extent, though it does not seem to entirely recover, at any rate, at all rapidly.

That the rays which produce the luminescence of the carbon are the same rays that cause fluorescence of the glass can be proved by deflecting the rays from the carbon on to the glass by means of a magnet.

As it is exceedingly difficult, if not impossible, to obtain carbon plates which do not contain hydrocarbons and other volatile matter which are rapidly given off and reduce the vacuum very quickly when the carbon becomes at all heated, it is necessary to keep the tube connected to the mercury pump, so that the vacuum can be restored after each experiment. This arrangement was followed in all the experiments described below, except where specific mention is made to the contrary.

Apparent Form of the Cathode Ray Discharge in a Focus Tube.

As is well known, in tubes of the ordinary focus type with a single spherical concave cathode, the rays coming

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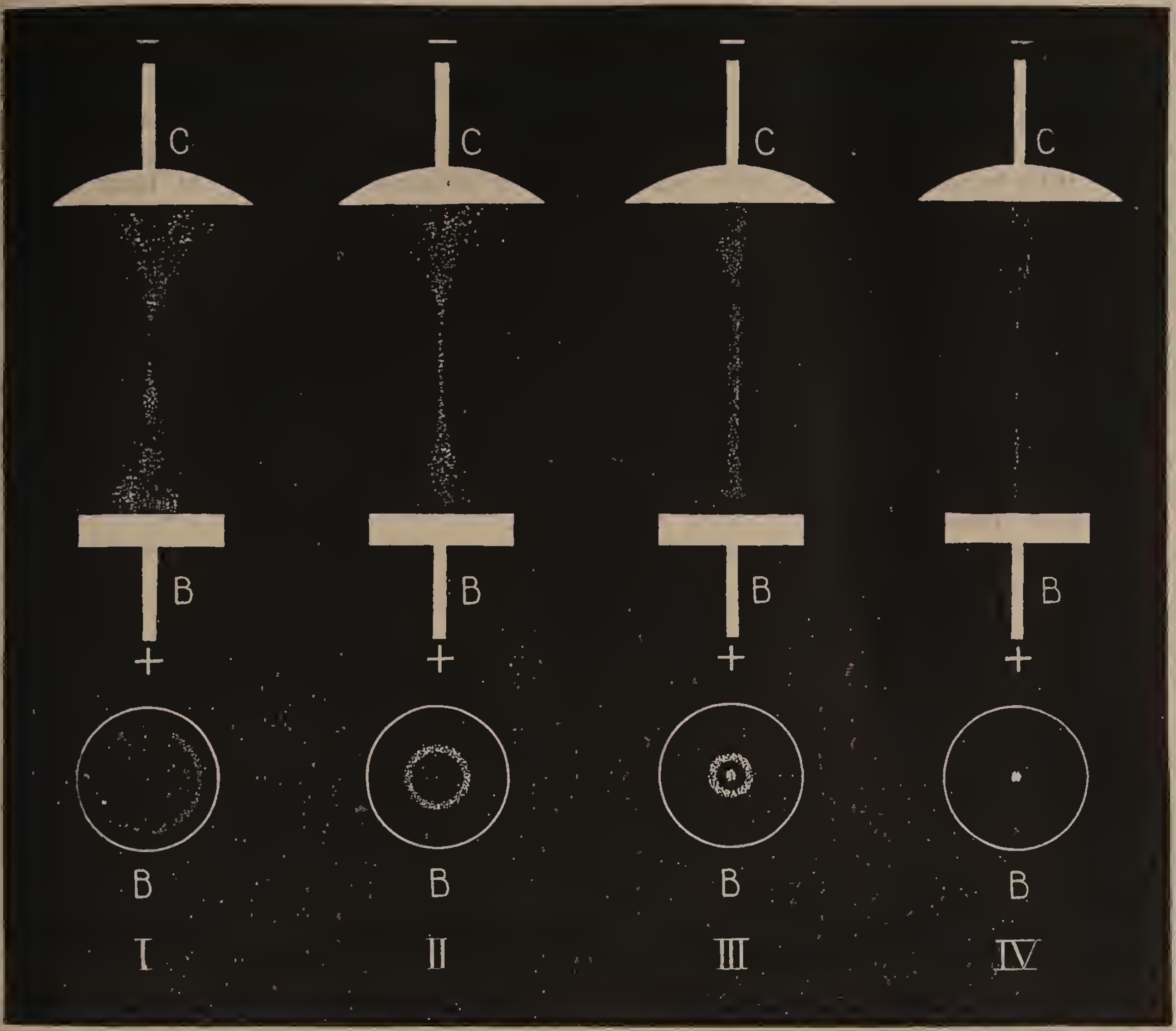
* A Paper read before the Royal Society, March 11, 1897.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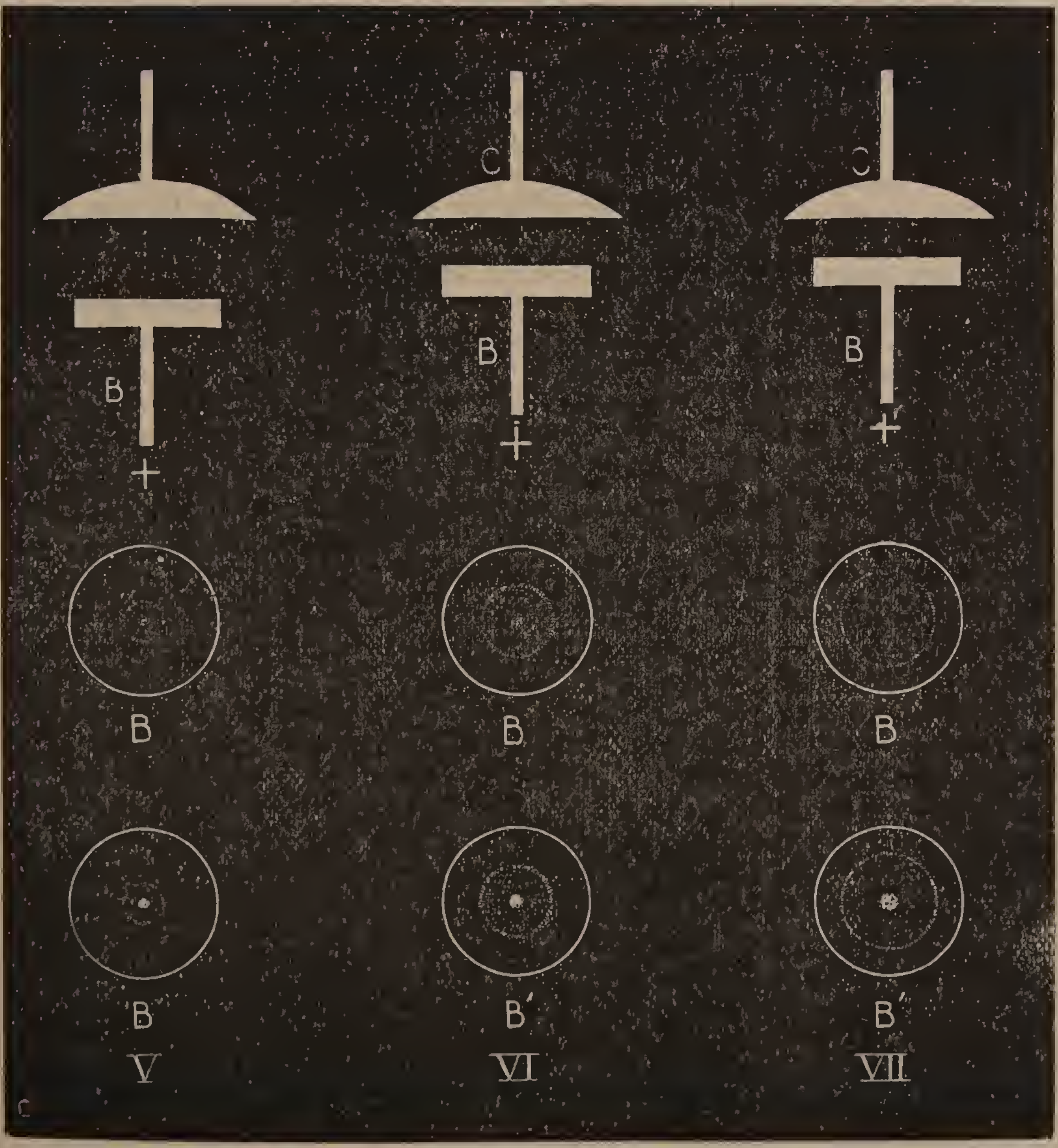
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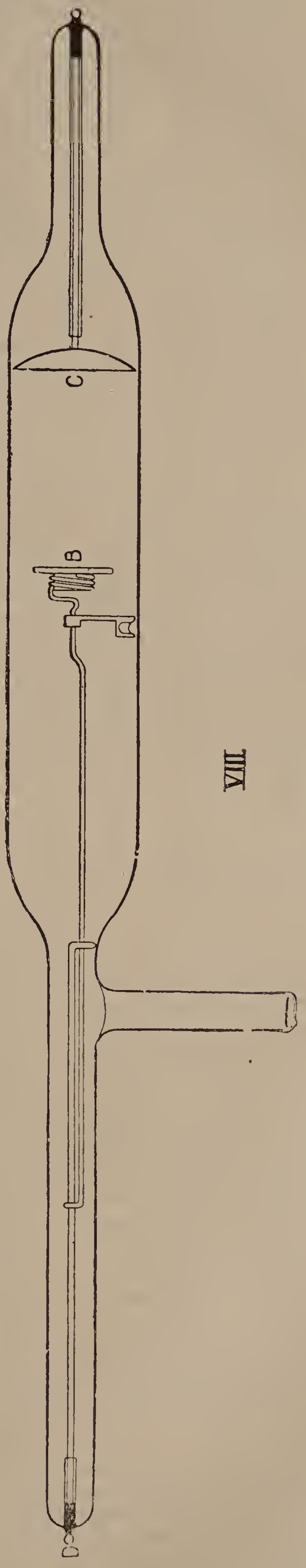
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off normally to the cathode surface appear to converge in more or less of a cone to a focus, and, if the vacuum be not too high, to diverge again immediately in another cone upon the other side of the focus. At higher vacua the rays, after passing the focus, do not appear to diverge again at once, but seem to form themselves into a description of thread which connects the convergent and divergent cones, and is longer or shorter according as the vacuum is higher or lower. The angle of the divergent cone appears, however, to be always proportional to that of the convergent cone. The focus, or perhaps more correctly the point at which this thread commences, seems always to be more distant from the cathode than the centre of curvature of the latter, but the variation in this respect seems to be less and less the higher the exhaustion. This is no doubt due to the mutual repulsion of the rays, and accords with the assumption that the rays consist of charged particles, which travel more and more rapidly the higher the exhaustion. Probably for the same reason cathodes that are only slightly concave focus further in proportion beyond their centres of curvature than do deeply concave cathodes for the same vacuum.

Apparent Hollowness of the Divergent Cone of Rays.

When the divergent cone is thrown upon a thin platinum disc, as in the ordinary focus tube, and sufficient electric power—say, from a 10-inch Rumhkorff coil—is employed, the platinum quickly attains to a red heat. With platinum, either the whole disc becomes uniformly heated, or in the event of the diameter of the cone of rays where it strikes the platinum being small, compared with the area of the platinum, that portion of the platinum covered by the base of the cone becomes uniformly heated to a higher temperature than the remainder. This is as much as can usually be seen with platinum, though rather more is sometimes visible with aluminium; but if, instead of either metal, the disc is made of ordinary electric light carbon, I have found that the luminescent portion of the carbon, instead of comprising the whole disc, or consisting of a uniformly heated circle, will in some cases take the shape of a brilliantly luminescent and apparently white hot ring, with a well-defined dark, and seemingly quite cold, interior. As the dimensions of the cone of rays are increased or decreased by decreasing or increasing the vacuum, the luminescent ring will be found to increase or decrease correspondingly in diameter, at the same time being brighter when small than when large. Further, when the ring is very small it will usually have a very brightly luminescent central spot, with a dark intervening portion between this spot and the ring, and when the vacuum is further increased the ring will gradually close in upon the spot until only the latter remains.

Figs. 1, 2, 3, and 4 show diagrammatically these hollow effects, as produced by spherical aluminium cathodes, 1·125 in. diameter and 0·708 in. radius of curvature, for four degrees of vacuum, 1 being the lowest and 4 the highest exhaustion. The upper portion of each of these figures represents the general appearance of the cathode discharge between the spherical concave aluminium cathode C at the top, and the carbon anti-cathode B at the bottom, as accurately as it is possible to represent evanescent coloured appearances in monochrome. The other appearances, due to the dark space and fluorescence of the glass, are omitted for the sake of simplicity. Beneath each of the elevational views of the cathode discharge will be found a plan view of the carbon anti-cathode, showing for each condition of vacuum the effect of the cathode discharge upon the carbon anti-cathode, in forming a brightly luminescent hollow ring, gradually decreasing in diameter as the vacuum is increased, until it centres on a point, as already mentioned.

It may further be remarked that the diameter of the luminescent ring may be increased or diminished, or finally reduced to a point, without altering the degree of vacuum, by moving the anti-cathode away from or towards or finally into the focus of the cathode stream, the appearance of the ring in each of these cases being practically similar to those shown in the figures for a uniform distance with varying vacuum. When the anti-cathode surface is not at right angles to the line of the discharge, the ring, in place of being circular, takes the proper form of a conic section. The holding of a magnet near the tube distorts the ring from a circular shape and moves its position on the carbon.

From these experiments it appears that the diverging cone of cathode rays acts as though it were not of uniform density throughout its section, but, at any rate, in some instances as if it were completely hollow. This fact does not appear to have previously been noted.

Apparent Hollowness of the Convergent Cone of Rays.

The apparent hollowness of the divergent cathode ray being thus established, it was thought desirable to ascertain whether the same condition of affairs exists in the converging beam of rays between the cathode and the focus. Owing to the well-known difficulty of getting any discharge to pass when the distance between the electrodes is less than the thickness of the dark space, and to the disturbing effect which the anti-cathode screen is found to have when brought within the focus of the cathode, especially with high vacua, this question was found much more difficult to decide than that of the hollowness of the divergent cone. However, that the convergent cone also acts under certain circumstances as though it were almost completely hollow, and acts generally as if it had a considerable tendency towards hollowness at low vacua, was also finally fully determined. The lower portions of figs. 5, 6, and 7 show the bright ring appearance upon the carbon anti-cathode at two different degrees of exhaustion, B being higher vacua than B', and with the anti-cathode at the three different distances from the cathode within the focus of the latter, as shown in the upper part of each figure. As will be observed in this case, the degree of vacuum is found not to appreciably affect the dimensions of the figure, though it should be stated that the vacua in each case were comparatively low, as vacua as high as those employed when the anti-cathode was outside the focus gave no results at all. As will be seen, however, the diameter of the luminescent ring is affected by the degree of proximity of the anti-cathode to the cathode, being larger when the distance is small than when it is great; while in every case there is a decided tendency towards hollowness, though usually with some slight internal luminescence and with a bright central spot, while in one case, when the anti cathode was very close to the cathode and the vacuum was comparatively high, the ring is seen completely hollow, and there is no central spot.

A convenient form of tube for showing the apparent hollowness of both the divergent and convergent cone of cathode rays is shown in fig. 8, where the anti-cathode disc B, made of electric light carbon, is supported upon a small carrier which slides upon the bottom of the tube, and is connected to the anode terminal, D, by means of two aluminium wires, each of which have a ring at their extremity through which they respectively pass. As the carbon, under the action of the cathode rays, gives off hydrocarbon vapour, it is necessary, as already mentioned, to try all these experiments with the tube connected to the mercury pump; but with this connection made through a slightly flexible mercury joint it is possible, by inclining and gently tapping the tube, to bring the anti-cathode to any desired position either near or far away from the cathode. For experiments upon the divergent cone, it is not necessary that the anti-cathode screen should be connected to the anode terminal, and, consequently, the sliding aluminium wires inside the tube are not required. They are, however, necessary when observations are to be made on the convergent cone between the cathode and the focus, as the anti-cathode screen when placed within the focus must be connected to the anode, or it appears to get negatively charged, and acts itself as an additional cathode, throwing cathode rays in all directions.

It may here be mentioned that the fatigue of the carbon already alluded to renders necessary some precautions in carrying out the above-mentioned experiments, as otherwise the observer may be misled into thinking that a beam of cathode rays is effectively hollow when this is not the case, owing to the centre of the carbon covered by the beam having been fatigued by some previous experiments. By taking the precaution, however, of deflecting the cathode beam by means of a magnet on to various portions of the carbon screen, such errors may be avoided. It should also be noted that these hollow effects appear only to be obtained with fairly short focus cathodes, such as are usually employed in X-ray focus tubes, that is to say, with cathodes whose diameter is large as compared with their radius of curvature, so that the rays converge and diverge rapidly to and from the focus. With comparatively flat, long, focus cathodes, the cones do not show any signs of being hollow, and produce a uniformly luminescent spot upon the carbon of larger or smaller diameter, according to the conditions of vacuum and the position of the screen.

For instance, while cathodes 1·125 inches diameter and 0·708 inch radius of curvature gave in the manner described distinctly hollow convergent and divergent cones, a cathode 1 inch diameter and 1·5 inches radius of curvature gave convergent and divergent cones that appeared to be uniformly solid under all conditions.

(To be continued).

THE QUALITATIVE SEPARATION OF ARSENIC, ANTIMONY, AND TIN.*

By S. G. RAWSON, D.Sc., F.I.C.,
Lecturer in Chemistry, Technical College, Huddersfield.

To any originality in the process which I propose describing I can lay no claim, the principles involved depending upon a combination of certain well-known methods. The suggested separation of these metals is based primarily upon the use of oxalic acid as originally published by Clarke in his paper (Chemical News, xxi., p. 124) upon the quantitative estimation of these metals, a process which to me never seems to have come into the prominence which it so thoroughly deserves. I have but little faith in the methods now employed, especially in those for the separation of antimony and tin. The former metal is frequently evolved either as the hydride or deposited as a black stain upon platinum; the tin being thrown down upon zinc; this deposit is then scraped off, dissolved in acid, and the solution treated with mercuric chloride. That other people share in my disbelief in this method is shown by the fact that, in so far as my knowledge goes, I have never heard in any examination of more than two of those bodies being given for qualitative determination in one and the same substance. Even under these favourable conditions, it is seldom that the mixture contains only a small percentage of one of the constituents; the amounts more usually approximate to equality, the difficulties of separation being thereby much reduced. The method I would suggest is as follows:—The sulphides of the metals are washed upon the filter-paper, and the whole or part of the residue is placed in a test-tube and boiled with 2 or 3 c.c. of concentrated hydrochloric acid, to which a drop or two of nitric acid is added, and again boiled. A yellow residue after the treatment with hydrochloric acid gives a preliminary clue as to the presence of arsenic, this sulphide being slightly, if at all, attacked by the acid. A saturated solution of oxalic acid is added in quantity sufficient to fill two-thirds of the test-tube; the whole is boiled, and crystals of oxalic acid are added until a hot concentrated solution of oxalic acid is obtained. A stream of sulphuretted hydrogen is passed, the whole of the arsenic and antimony being precipitated as sulphides, which are filtered off, the tin remaining in solution. To the filtrate ammonia is added until distinctly alkaline. If a precipitate should then appear, which will not be the case unless a large amount of tin be present, add ammonium sulphide drop by drop until the precipitate re-dissolves: this it will do very readily. Acidulate with acetic acid; a heavy white precipitate, turning brown, indicates tin as a mixture of oxide and sulphide. It may be here noted that the treatment of ordinary ammonium sulphide with acetic acid produces a precipitate of sulphur, but the appearance of the precipitates formed in the two cases is quite distinct and cannot be mistaken. Turning again to the residual sulphides of arsenic and antimony, these may be treated either with ammonium carbonate in the well-known way, or, and preferably I think, as follows:—Dissolve in hydrochloric acid with two or three drops of nitric acid, boil, and place the solution in a Marsh apparatus. The evolved hydrides are then passed through a solution of silver nitrate, and the antimonide of silver formed filtered off. To the filtrate add a few drops of silver nitrate, and then very cautiously ammonium hydrate until the yellow precipitate of silver arsenite appears. The silver antimonide precipitate is washed, boiled with tartaric acid and filtered, a little hydrochloric acid is added, and sulphuretted hydrogen passed through the filtrate, orange-red antimony sulphide being thrown down. To both of these precipitates the ordinary reduction and sublimation tests can be applied. The above method gives thoroughly good results, and with amounts of the respective sulphides varying within wide limits, and does not require that tinkering with bits of platinum foil and of zinc which is both unreliable and unpleasant.

THE USE OF ALUMINUM FOR CONDENSERS.*

By T. H. NORTON.

In connection with the extended use of aluminum in this laboratory for various forms of apparatus, water-baths, air-baths, Bunsen burners, hot water filtering funnels, &c., it seemed desirable to study the availability of the metal for condensation processes.

For this purpose a condenser was constructed as follows:—The outer jacket was of glass; the inner tube was of aluminum and possessed the following dimensions—length 122 c.m., external diameter 1 c.m., inner diameter 8½ m.m., weight per metre 29 grms. At a distance of 15 c.m. from the end, the tube was bent at right angles. This permitted of connection with a distilling flask, without allowing the condensing vapours to come in contact with any substance but aluminum. It might be mentioned here that in order to bend an aluminum tube of these dimensions satisfactorily, it is necessary to fill it with molten lead, and further, that several distillations with water are requisite in order to remove completely slight traces of lead adherent to the surface of the aluminum, after this operation.

The method of testing the condenser was to distil a measured quantity of a liquid from the glass flask, used as a still, collect the distillate in glass, evaporate it from weighed platinum dishes, and note the weight of the ignited residue, thus ascertaining whether there was any appreciable attack on the aluminum. Nothing was attempted beyond the ordinary precautions for preventing dust from contaminating the distillates.

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* A Paper read before the Society of Chemical Industry (Yorkshire Section), January 25th, 1897.

* Contributions from the Chemical Laboratory of the University of Cincinnati. From the *Journal of the American Chemical Society*, xix., No. 2.

The liquids first employed were organic. In each case 500 c.c. were distilled, and the weights of the residue left on evaporating the distillate noted. The following results were obtained :—

Liquid.	Residue from 500 c.c.
Ethyl alcohol (specific gravity 0·809)	0·001 grm.
Benzene	0·0016 ,,
Nitrobenzene	0·0004 ,,
Chloroform	0·0002 ,,
Ethyl ether	0·0000
Acetone	0·0001 ,,

In all these cases it was evident that very rapid distillation could be carried on with an exceedingly short tube, on account of the high conductive power of the aluminum. The residues obtained showed that there was practically no attack upon the aluminum.

The deportment of the metal towards steam was next studied, and here it was deemed wise to establish in all cases comparative experiments with glass and block tin. The glass condenser tube used for this purpose was 84 c.m. long and had an inner diameter of 16 m.m.; the tin condenser tube was 305 c.m. long and had an inner diameter of 21 m.m. With the exception of differences in the superficial surface for condensation, other conditions were essentially identical. Three series of distillations were carried on with the three following samples of water :—

A. Hydrant water (Ohio river water), containing much impurity.
B. Hydrant water (Ohio river water), containing less impurity.
C. Distilled water.

In all cases 500 c.c. were employed. The following residues were obtained :—

	Aluminum.	Block tin.	Glass.
A.	0·0112	0·006	0·0118 grm.
B.	0·0032	0·0028	0·0091 ,,
C.	0·0035	0·005	0·008 ,,

A check determination on the amount of dust collecting in the platinum dish during the time for evaporation, showed it to be 0·0002 grm. after ignition.

These results would show that as far as purity of the product is concerned, aluminum possesses about the same advantages over glass as tin, in connection with the distillation of water. In lightness and conductivity it exhibits marked superiority to the tin.

For use with neutral organic liquids it is well adapted, more especially in the distillation of low boiling substances, such as ether. Here, also, the high thermal conductivity, as well as the absence of brittleness, are factors in its favour as compared with glass.

Mr. R. W. Hochstetter rendered valuable assistance in the determination of the above data.

SOIL FERMENTS IMPORTANT IN AGRICULTURE.*

By HARVEY W. WILEY,
Chief of the Division of Chemistry, Department of Agriculture, Washington, D.C.

Introductory.—Soil ferments important in agriculture are those which help to make the soil from original rocks and those which are active in preparing the food of plants for absorption and assimilation. The old idea that the soil is an inert mass of mineral matter has given way to the new conception of the soil as a living organism. The parts of the soil which are not endowed with life at the present time have their highest significance as the environment of the living organisms which they contain, and which they may help to nourish. The plant which forms the growing crop receives its nourishment through the media of the air and soil; but this nourishment must undergo a process of digestion, similar to that suffered by the food which nourishes animals, before it becomes available as plant-food. Indeed, the purely mineral, inorganic foods of plants are probably not always absorbed as such, and must undergo a decomposition before they are assimilated. A striking instance of this is shown in the case of silica, an important plant-food and a type of inert mineral matter. Silica is highly insoluble, and apparently the least suited of the mineral constituents of the earth to enter the vital organism of the plant. Yet not only do we find it in the tissues of the mature plant, but also, strange to say, in the greatest abundance in those parts of the plant organism—viz., the leaves—most remote from the sources of supply. It is evident from this that the highly insoluble silica of the soil must undergo a complete solution in order to be carried by the juices of the plant through the network of cellular tissues, to be finally re-deposited in the leaf.

The part which soil ferments have played in the formation of arable soil from the original rocks is not thoroughly appreciated. The naked rocks of high mountains comprise mineralogical types of the most varied nature, viz., granite, porphyry, gneiss, mica schist, volcanic rocks and limestones of all varieties, and all these have been found to be covered with a nitrifying ferment which is doubtless extremely active in producing incipient decay. At the high altitudes in which these observations have been made, the activity of bacteria is necessarily limited by the low temperature to which they are subjected during the greater part of the year. During the winter season their life is suspended, but is not extinguished, since they have been found living and ready to resume all their activity after an indefinite sleep, perhaps of thousands of years, on the ice of the glaciers, where the temperature never rises above the freezing-point. When the activity of these ferments in the most unfavourable conditions is recognised, it is easily seen how much more active they become when brought down to lower levels, where they are nourished by the favouring conditions which exist, especially during the summer, in cultivated soils. In fact, the importance of the action of these bodies on the mineral particles of which the soil is largely composed has never been fully recognised, and there is no doubt whatever of the great significance of their decomposing action in the liberation of plant-food locked up in undecomposed mineral structures. In this case the activity of the bacteria is not limited to the surface of rock masses, but permeates every particle of soil, and thus becomes effective over a vastly extended surface.

When the extreme minuteness of these organisms, and of the phenomena which they produce, is considered, there may be a tendency to despise their importance; but by reason of the fact that their activity is never ceasing, and of the widest application, it must be placed among the geologic causes to which the crust of the earth owes a part of its actual physiognomy, and to which the formation of the deposits of the comminuted elements constituting arable soil is due.

But the action of these ferments has not stopped with the aid they have given to soil formation. It is highly probable that they assist in a most marked manner in the final dissolution of the soil particles, and the setting free of the plant-foods which they contain. It is quite certain that in the primary decay of bare rocks, especially at high altitudes, the nitrifying organism plays a highly important part, preparing the surface of the rock for the first growth of lichens and other low vegetable organisms, from which the first traces of humus are formed. The discovery that the nitrifying organism can subsist upon a purely mineral food is one of the chief supports of the idea that they were especially active in the very beginning

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* Abstract of a Lecture delivered before the Chemical Section of the Franklin Institute, February 16th, 1897.

of soil formation. It has been shown that these bacteria can be developed by absorbing from the ambient atmosphere traces of ammonia and other bodies which may be present in the air. There is thus discovered in the very first products of the attrition of rocks the characteristic element of vegetable soil, viz., humus, the proportion of which increases rapidly with the processes of disintegration, until finally the decaying mass is capable of sustaining chlorophyll-containing plants. Not only upon the surface of exposed rocks have these organisms been discovered, but they are found to extend also to a considerable distance in the anterior. They not only play an important part by direct action upon the mineral matters which the rocks contain, but later on, through the production of nitric acid, greatly favour the final solution of the soil particles.

Kinds of Organisms in the Soil.—The nitrifying organisms in the soil exist in common with hundreds of others, many of which are doubtless active upou the soil particles. The organisms to which particular attention is called in this address, in addition to those which help to dissolve the soil particles already mentioned, are those which are active in preparing organic foods for absorption and assimilation by plants, and those which act upon free atmospheric nitrogen and bring it into a shape suited to plant-nutrition.

In general these are called the nitrifying ferments, and their action is uniformly favourable to vegetable growth. Attention should also be given to another class of organisms found in the soil, whose activity is inimical to plant growth or hurtful in some other way. This class comprises the denitrifying organisms, and those of a pathogenic nature which may exist in the soil, and by their activity cause disease in man and beast.

The Nitrifying Ferments.—The micro-organisms of most importance to agriculture, and those to which attention is particularly called in this article, are the bacteria which act upon nitrogenous matters and oxidise them to nitric acid, or which exert a reducing effect on nitric acid, bringing it to lower forms of oxidation, or even to free nitrogen. These organisms belong to many different species, and act in very many different ways. The general group to which they belong is known as nitro-bacteria. The classification of these organisms by genera and species would prove of little interest to the readers of this article. In general it may be said that there are three distinct genera, comprising, in the first place, those organisms which form ammonia or carbonate of ammonia from organic nitrogenous compounds, such as albumen; in the second place, the organisms which transform carbonate of ammonia into nitrous acid; and in the third place, those which transform nitrous into nitric acid. Each genus is necessary in the complete transformation of proteid matter into nitric acid, in which latter form alone nitrogen is chiefly available for plant-food.

Production of Ammonia.—The bacteria which are especially active in the formation of ammonia are found constantly in surface soils and in the air and rain-waters. By the activity of these organisms in the decomposition of proteid matter, large quantities of ammonium carbonate are produced. The organic carbon which is present in a compound is acted upon during the oxidation of the proteid, and carbon dioxide and certain organic acids are formed. The organic sulphur which is present is converted into sulphuric acid, and the hydrogen partly into water and partly into ammonia. This oxidation is accomplished by bacteria, and, to a less extent, by moulds and yeasts. The table shown on the screen contains the names of the common soil bacteria which ammonise proteid matters. The column headed "per cent" shows the amount of proteid matter changed into ammonia by the several organisms in twenty days, at a temperature of 30°. Of all the bacteria which have been studied, the species *mycoides* has the highest ammonising power, being capable of changing nearly half of the proteid into ammoniacal nitrogen in the time named. In soils where the environment does not permit of the development of the nitrifying ferments, the change stops with ammonia. Such conditions are found in the vegetable soils of swamps, which are extremely acid. In such soils ammonia is quite freely produced, while the nitrous and nitric organisms are absent.

In the analysis of a swamp soil, which had been shown by a bacterial culture to contain no nitrifying ferments, 0·03698 per cent of nitrogen was found as ammonia, and only a trace as nitric acid. In another vegetable soil, which contained nitrifying organisms, 0·0336 per cent of ammoniacal and 0·0474 per cent nitric nitrogen were present. Of the moulds, several have been found capable of producing considerable quantities of ammonia. Among these *Cephalothecium roseum* converted over 30 per cent of proteid into ammoniacal nitrogen in five days, and *Aspergillus terricola* was only a little less active.

The yeasts are still less active, but a large number of them produces ammonia in small quantities.

In general, it may be said that in cultivated soils which have a neutral or alkaline reaction, bacteria are almost the sole ammonia makers, while in vegetable soils of a marked acid reaction, as in swamps and forests, the moulds are the chief producers of ammonia.

In the oxidation of albumen by the *Bacillus mycoides* the carbon is oxidised to carbon dioxide, the sulphur to sulphuric acid, and the hydrogen to water and to ammonia.

The reaction may be expressed by the formula—

$$\underset{\text{Albumen.}}{C_{72}H_{112}N_{18}SO_{22}} = \underset{\text{Water.}}{29H_2O} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{72CO_2} + \underset{\substack{\text{Sulphur}\\\text{trioxide.}}}{SO_3} + \underset{\text{Ammonia.}}{18NH_3}$$

The *Bacillus mycoides*, under certain conditions, can form ammonia also from nitrates. In the absence of oxygen it reduces nitrates to ammonia in presence of an organic substance like sugar. In this action it is anærobic, while in the ordinary process of converting proteid matter into ammonia the action takes place in the absence of oxygen. This is a curious instance of a reverse action produced by the same organism in a different environment, showing, as it does, an oxidising action in the presence of oxygen, and a reducing action in its absence. Some idea of the character of the *Bacillus mycoides*, and the methods of its culture, can be gained by a study of the photographs which will now be projected upon the screen.

Production of Nitrous Acid.—The next step in the process of nitrification is the conversion of ammonia or its compounds into nitrous acid. With a moderate store of ammonia the oxidation into nitrous acid takes place, as a rule, without any of the nitrogen being lost in a free state or being volatilised as ammonia compounds. When, however, there is a large excess of ammonium carbonate, a considerable loss of nitrogen may take place. The practical deduction to be drawn from this fact is apparent. Nitrogenous fertilisers should be applied only in moderate quantities, so as not to increase the stock of material beyond the power of the active ferments to handle it.

The nitrous ferment is by far the largest and most vigorous of the nitrifying organisms. It is from three to four times as large as the nitric ferment, and under a high power of the microscope appears as minute globules, slightly oblate. These globules are multiplied by fission, and the divided parts develop rapidly to perfect organisms of full size. In most cases the organisms appear as distinct globules, but many are congregated into masses where the distinctive cell structure seems to be lost. (A photograph of the nitrous organism was shown upon the screen).

Conversion of Nitrous into Nitric Acid.—The last step in the process of nitrification consists in the oxidation of nitrous to nitric acid. As a rule, plants absorb nitrogenous food only as nitric acid, but it cannot be said that the nitrogen may not be used by the plant in other forms. Some experiments seem to show that ammonia and its compounds and humus may be directly absorbed by plants, but if this be true it must be only in very limited quantities. The final step, therefore, in nitrification is necessary to secure this valuable food in its most highly available state. The nitrifying organisms are much smaller than their nitrous cousins, and of the same general shape, but more globular.

It must not be supposed that these steps in the preparation of a nitrogenous food are performed with entire distinctness. The impression might be obtained that the ammoniacal ferment exerted its activity, converting the whole of the nitrogenous supply into ammonia, and that in this state only the nitrous ferment would become active and convert the whole product into nitrous acid, which finally, under the influence of the nitric ferment, would form nitric acid. In point of fact, however, in arable soils and under favourable conditions, the steps of nitrification may be almost synchronous. In the case of a growing crop, a chemical examination or repeated chemical examinations might find only traces of ammonia and nitrous and nitric acids. As each particle of ammonia is formed, it is converted without delay into nitrous acid, and then at once into nitric acid. The nitric acid formed is absorbed by the growing plant, and thus it might seem that the activity of the ferments present in the soil had been reduced to a minimum, when in point of fact they were exercising their functions with maximum vigour. The separate stages of nitrification mentioned above can only be secured in the laboratory by a skilled bacteriologist patiently working to separate the different genera of nitrifying organisms until he procures them in an absolutely pure form. As may be supposed, this is very difficult to accomplish.

(A photograph of the nitric organism was shown upon the screen).

(To be continued).

RECOVERY OF WASTE PLATINUM CHLORIDE.

By H. W. WILEY.

Aluminum turnings, freed of oil, have been used in this laboratory for some time for many purposes. Immediately after the publication of the paper of Wislicenus and Kaufmann (*Ber. d. Chem. Ges.*, xxviii., 1323) on the various applications of aluminum amalgam in the laboratory, a large quantity of these turnings was procured from the Pittsburg Reduction Co. Considerable difficulty was encountered in attempting to use these turnings in the manner described in the manner cited above. Mr. McElroy prepared the amalgam by washing aluminum clippings with ether to remove oil, treating with dilute caustic soda till free evolution of gas took place, and then washing with water to remove the alkali. The solution of corrosive sublimate was made in alcohol (chosen because the most convenient solvent), diluted with water, and poured over the aluminum. When the evolution of gas was seen to take place from every piece of aluminum in sight, the mercuric chloride solution was decanted and the aluminum washed chloride-free with water. The treatment with soda and mercuric chloride was then repeated. Finally, the turnings were washed free of water with strong alcohol. The washed amalgam in fresh portions of "absolute" alcohol kept up a steady evolution of gas, long after the time all water should have been removed. A portion was removed from the alcohol, washed with ether, and placed in petroleum ether, where the evolution of gas became quite strong. The containing flask was loosely stoppered and stood aside over night. In the morning the petroleum ether was gone.

A fresh portion of amalgam from 200 grms. of aluminum was prepared and treated as before, except that the washing with alcohol was more thorough. The alcohol was removed with ether, and the amalgam finally washed with kerosene. It was then covered with kerosene and stood aside. In about half an hour the evolution of gas became quite violent and the containing bottle hot. On cooling under the tap the generation of gas slackened, but on standing increased again as the mixture warmed up.

The kerosene was such as is used for lamps. It gave a black zone of lead sulphide when treated with the lead acetate test. It is very likely Lima oil. As is well known, in the Frasch process of purifying, the oil is passed through copper oxide, which it converts into copper sulphide. As for every atom of sulphur removed an atom of oxygen must go into the oil, probably the action of the aluminum consisted in appropriating this oxygen. Neither bright sodium or sodium amalgam had any special action on the kerosene used. The action of the amalgam on strong alcohol has been confirmed by Hillyer (*Am. Chem. Journ.*, xviii., 621). We have been able to use these turnings, amalgamated with mercuric chloride, for the reduction of nitrates to ammonia for analytical and other purposes, and it is probable that a speedy and accurate analytical process may be elaborated on this line. We have, however, found the most successful use of the turnings in the recovery of platinum waste. This method of recovery is due to Mr. K. P. McElroy, and has been worked out by him in detail, and has been successfully used for some time in the recovery of platinum chloride waste from potash analyses. The method is as follows:—

The waste platinum from potash determinations is collected and to the hot water solution of platinum potassium chloride is added aluminum in the form of clippings or turnings. In a few minutes a platinum-aluminum couple is formed and reduction goes on vigorously. The addition of hydrochloric acid is not necessary, but is advisable for promoting the settling of the platinum formed. After the reduction is complete, more hydrochloric acid is added to dissolve the excess of aluminum. When this is done the platinum will be found to settle, and the supernatant liquid will be clear. The supernatant liquid contains but little suspended platinum, but it is passed through a large folded filter. If it does not come through clear, as is sometimes the case, return it a few times. As but little platinum gets on the filter, the same filter is used over and over again for successive filtrations, until enough platinum accumulates to make its recovery worth while. When the clear liquid is all decanted, add water to the spongy platinum, shake, allow to settle, and decant. Repeat this until the supernatant liquid is free of chloride. The spongy platinum is then covered with strong nitric acid and heated for the purpose of removing copper. Aluminum often contains a little copper, which of course remains with the platinum. When the copper is all dissolved, the copper nitrate and the excess of nitric acid are removed by washing with water by decantation as before, till the supernatant liquid is acid free when tested with Congo paper. The resulting platinum black is dissolved with aqua regia, made by mixing five parts of hydrochloric acid with one part of nitric, added in amount sufficient to dissolve all of the platinum present. The solution thus obtained is transferred to a porcelain dish and evaporated on a steam-bath till a portion taken out with a rod solidifies on cooling. The residue is diluted with water and hydrochloric acid and re-evaporated. If, on adding water to the syrupy mass formed by this evaporation, nitrous vapours are evolved, add plenty of water and re-evaporate. Repeat this evaporation with water till the nitrous vapours are no longer evolved on dilution. Finally, dilute sufficiently to filter and add water until the colour of a platinum chloride solution of known content is matched.—*Journal of the American Chemical Society*, xix., No. 3.

NOTICES OF BOOKS.

The Electric Furnace. ("Le Four Electrique"). By Henri Moissan, Membre de l'Institut. Paris: G. Steinheil. 1897. Pp. 385.

(First Notice).

M. Moissan was led, he tells us, to the invention of the electric furnace by the necessity of having an extremely high temperature to enable him to carry on his experiments on the crystallisation of carbon from its solution in molten iron; this can be achieved at about 1000°, but as he aimed at working on fairly large quantities of material, he found the ordinary methods employed inadequate.

The book is divided into four chapters. The first deals with the different patterns of furnaces used, and their application to the study of the fusion and volatilisation of a certain number of refractory bodies. Chapter II. comprises the study of three varieties of carbon, viz., amorphous carbon, graphite, and diamond. In Chapter III. we have the preparation of several *simple* bodies by means of the electric furnace, and the experiments carried out on chromium, manganese, molybdenum, tungsten, uranium, vanadium, zirconium, titanium, silicon, and aluminium; while in the fourth and last chapter we find described the research on a new series of *binary* compounds, such as carbides, silicides, and borides. The preparation of carbide of calcium, in particular, has been the subject of a distinct research, and is described in detail.

The highest temperatures hitherto attained industrially range between 1700° and 1800°. The invention of the oxy-hydrogen blowpipe by MM. Sainte-Claire Deville and Debray rendered great services to chemistry, but the highest temperature obtained by its means was not more than 2000°. Other workers, before M. Moissan, had used the intense heat developed by the electric arc, notably Despretz, Siemens, Huntingdon, Cowles, and others; but there were objections to all their furnaces, though they were suitable to the purposes for which they were devised.

The author of this work insists that his furnace is not an industrial one, but is meant solely for research; his primary object being to concentrate as much heat as possible into the smallest possible space. His early experiments were carried out by means of a small Gramme dynamo, giving a current of 35 to 40 ampères at a pressure of 55 volts. But as the work proceeded, this was found to be insufficient, and by the courtesy of the directors of some of the large electric lighting companies, M. Moissan was enabled to avail himself of much more powerful currents; on a few occasions using as much as 300 h.-p. at one time.

M. Moissan's first furnace was made of quicklime, and was exhibited at the Académie des Sciences in December, 1892. It consisted of two well-dressed bricks of lime placed one on the other, the lower one containing a small cavity which served as a crucible, with two grooves from it to the outside, to hold the electrodes. The upper brick was slightly hollowed out over the cavity in the lower one, and as the surface is soon melted it becomes, so to say, polished, and acts as a reflector, increasing the heat in the cavity below. The cavity could also be used to hold a small carbon crucible containing the substance to be melted. The great point of difference between this furnace and all previous models is that, in this new one, the material under treatment does not come in contact with the electric arc—that is to say, with the vapour of carbon. Another great convenience is that the electrodes are movable, thus affording great facilities for striking and regulating the arc. The dimensions of the bricks first used were as follows:—The upper, 18 c.m. × 15 c.m. × 5 c.m. thick; the lower, 18 c.m. × 15 c.m. × 8 c.m. thick. This was large enough for working with a current of 100 to 125 ampères and 50 or 60 volts; by increasing the length to 22 c.m. or 25 c.m., one can use a current of 450 ampères and 75 volts.

Very great care had to be exercised in the manufacture of the electrodes, so as to, as far as possible, avoid all chance of impurities.

To demonstrate the facility with which quicklime can be volatilised, no crucible need be employed, the bricks themselves supplying the material for the experiment. As soon as the arc is established there is a strong smell of hydrocyanic acid, the small quantity of water remaining in the electrodes forming, with the carbon, acetylene; this gas in the presence of nitrogen, under the powerful action of the arc, accomplishing the synthesis of hydrocyanic acid, as discovered by Berthelot. This, however, does not continue long. The regulation of the arc must be carefully attended to, as the furnace is cold at first, but, on warming, the carbons can be separated until they are 2 c.m. or 2½ c.m. apart. With a current of 400 ampères and 80 volts, the flames issuing from the grooves holding the electrodes are accompanied, after five or six minutes, by torrents of white smoke, produced by the volatilisation of the lime, and this can easily be condensed on any cold surface. With a current of 800 ampères and 110 volts more than 100 grms. of lime can be volatilised in five minutes; this bears testimony to the enormous power of the furnace. On removing the cover at the end of the experiment, it can be seen that the lime in the cavity is actually melted, and by allowing the cover to cool gradually, veritable stalactites are formed.

For some experiments, carbonate of lime is preferable for making the body of the furnace; it possesses greater solidity or compactness than quicklime, and is easily obtained in large blocks.

When using such enormous currents as 1200 to 2000 ampères and 100 volts, lime bricks are speedily put *hors de combat*, and proper manipulation becomes out of the question; in such a case the cavity in the brick is enlarged and lined with alternate plates of magnesia and carbon, the magnesia being next to the lime, and the carbon on the inside. By such an arrangement the carbon and lime, which would otherwise form carbides of lime, are kept apart, and as magnesia is not reducible by carbon, the furnace remains uninjured.

Another modification of the electric furnace consists in inserting a pair of carbon tubes through the lower brick in such a manner that they are at right angles to the electrodes and about 1 c.m. below the arc; by their means the gases inevitably driven off by the intense heat of the arc find a ready exit, and the experiment can be continued for several hours instead of minutes. The tubes and the electrodes are of course kept from contact with the lime or chalk by means of a protective layer of magnesia, and it is noticed that the ends of the carbon tubes exposed to this extreme temperature are entirely converted into graphite. By inclining the tube to an angle of 30° the furnace can be employed to produce the most refractory metals in quantity; thus in an hour 2 kilogrammes of chromium were reduced from oxide and run into an ingot.

A further modification, or rather extension, of the furnace consists in arranging several arcs in parallel; by this means a greater *quantity* of heat can be obtained and large quantities of metals produced without necessarily going to a great extreme of temperature; but, if required, a large and continuous stream of highly refractory metal can be obtained at a melting-point of considerably over 3000°. M. Violle has put the highest attainable temperature at 3500°.

Journal of Agriculture, published by the Department of Agriculture, Cape of Good Hope. March 18, 1897. Cape Town: Townshend, Taylor, and Snashall.

No. 6 of this journal has just reached us; it contains several interesting articles on subjects connected with agricultural and farming work, fruit growing, forestry, &c.

Some interesting remarks are to be found in a short article entitled "Bacteriology and the Plague," in which reference is made also to the work of certain French *savants* in the Transvaal who are engaged in the study of the rinderpest.

The great difficulty to be contended with in serious epidemics of this kind, is to provide at short notice, and keep up an efficient supply of anti-toxic serum. Its preparation is naturally a long and cautious process, as each individual animal can only yield at intervals a limited quantity of serum without feeling ill effects. Long before the present epidemic, the bacteriological treatment of disease had been developed by the Government of India on a much greater scale than that attempted by any European Government. A year and a half ago, in the Presidency of Bengal alone, 42,445 persons were inoculated for cholera, without a single mishap, or injury to health.

Traité Elémentaire de Chimie à l'Usage des Candidats au Certificat d'Aptitude des Sciences Physiques, et Naturelles et des Candidats aux Baccalauréats Scientifiques. Paris: Georges Carré and C. Naud. 1896.

Chimie Minérale. Par A. Haller, Correspondant de l'Institut, Directeur de l'Institut Chimique de Nancy, and P. Th. Müller, Maitre de Conference a l'Institut Chimique de Nancy. Pp. 336.

Chimie Organique. (By the same Authors).

The work on Mineral Chemistry is a good and useful exposition of chemical principles and the elementary laws of chemical science. There is a catalogue of the elements in which argon and helium duly figure, but neodymium and praseodymium are not recognised as separate elements. The laws of Dalton, of Gay-Lussac, the hypothesis of Avogadro and Ampère, are fully expounded; also the determination of molecular and atomic weights are given, followed by an outline of crystallography.

The principles of thermo-chemistry are introduced after the halogens.

Oxygen, sulphur, selenium, and tellurium are made to rank as the second family of the "metalloids." For the recognition of ozone the authors recommend the use of thallium paper in the first place, but Hurter's reagent is not omitted. Mineral waters are here divided into eight classes—the acidulous, the alkaline, the sulphuretted, the chlorides, bromides, and iodides, the sulphate, the iron waters, and the arsenical.

The descriptions of the several elements are followed by a sketch of the periodic classification, here ascribed solely to Mendeleeff. An abstract of qualitative analysis concludes the work.

The authors have accomplished their task ably as far as its limited scope would permit.

In the work on Organic Chemistry, the authors, in their introductory remarks, draw the accepted distinction between organic compounds and organised bodies. They classify organic matter as containing two elements only, such as benzene, or three elements, such as alcohol, or acetic acid, or, again, four elements, as is the case with urea and indigo. As a supplement follow artificial compounds into which a number of extraneous elements have been introduced.

At the end of the work we find an account of products of unknown constitution, such as biliary products, gelatins, albumenoids, syntonines, peptones, enzymes, milk, blood, blood-pigments, &c. We do not find any special mention of the "toxines."

Within its scope this work fulfils the reasonable expectation of the student.

The Principles of Mathematical Chemistry. The Energetics of Chemical Phenomena. By Dr. Georg Helm, Professor in the Royal Technical High School, Dresden. Authorised Translation from the German, by J. Livingston R. Morgan, Ph.D. (Leipzig), Instructor in The Brooklyn Polytechnic Institute. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1897. Pp. viii.—228, 12mo., cloth.

Dr. Helm's well-known "Grundzüge der mathematischen Chemie," published in 1894, is now offered to students in an English dress.

The translation follows the text as closely as possible, and Dr. Morgan has "aimed at clearness rather than literary style;" yet the involved sentences peculiar to German only occasionally appear through the translation.

The work is divided into four parts. Part I. dealing with the measurement of chemical energy, mechanical energy, and the volume energy of gases. Part II. is devoted to entropy, and discusses the thermodynamics of perfect gases, the entropy of gases and gas mixtures, the relations between heat and volume energy, as well as electrical energy. Part III. treats of chemical intensity, concluding with a chapter on the velocity of a chemical reaction. Part IV. considers the degrees of freedom of chemical phenomena, such as the rule and equilibrium of phases.

Students of chemistry who have the habit of dealing with subjects on a mathematical basis will find this volume of great service, throwing much light on the recent developments of the science. It is not a book for beginners, but one which advanced classes should take up with great profit. The author frequently refers to Wilhelm Ostwald's writings, to which Helm's book forms a good guide.

The labours of Willard Gibbs in this direction are more than once gracefully acknowledged by the author. An index closes the volume. H. C. B.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 16, April 20, 1897.

Determination of the Surface, the Bulk, and the Chemical Composition of the Human Body.—Ch. Bouchard.—The disassimilation is proportional to the weight of the body, or rather to the weight of fixed albumen, and the functional or respiratory consumption is proportional to the surface of the body. The products of nutrition, *i.e.*, the chemical products (urea, carbonic acid, and water), and the dynamic products (calories) depend on the quantity of fixed albumen and the intensity of its activity.

Details of the Method followed in precise Cryoscopic Researches.—F. N. Raoult.—The author has succeeded in measuring the reductions of the freezing point with an approximation of 0·0665°. By this means he has made a methodical study of the influence of superfusion upon the congelation-point of aqueous solution.

On the Physiological Action of the X Rays.—W. Crookes.—I can entirely corroborate the observations of the learned author of the paper just read (memoir by M. Sorel, *Comptes Rendus*, Session of April 12, p. 826). I believe, nevertheless, that the X rays act upon different persons with a different intensity. In particular, I have worked for a long time with tubes producing rays of this kind, and I have perhaps been exposed to their action for a longer time than most experimentalists, but without undergoing any effects either upon the face or the hands. On the other hand, I have observed very marked physiological effects, analogous to those which have been just spoken of, produced upon persons who had been exposed to the X rays. I am therefore inclined to think that the very energetic action sometimes observed with these rays depends, up to a certain point, on the idiosyncrasy of the experimentalist.

Comparison of the Absorption by Crystallised Media, of Luminous Rays, and X Rays.—V. Agafonoff.—On studying my proofs I was surprised to find that there exists a general opposition between the absorption for the luminous rays and for the Röntgen rays. The sulphates very transparent for the ultra-violet rays are extremely opaque for the X rays. The inverse holds good for the majority of crystalline organic compounds. The nitrates absorb the luminous rays more than the sulphates and less than organic bodies; the X rays, on the contrary, less than the sulphates and more than organic bodies.

Black Light.—M. Perrigot.—Black light plays no part in the explanation of phenomena connected with facts the law of which is perfectly known.

Separation of Chlorine and Bromine.—H. Baubigny and P. Rivals.

Separation of Nickel from Cobalt and Iron, and of Cobalt from Aluminium.—E. Piñerua.—(See p. 193).

On Cholesterine.—Ch. Cloëz.—Cholesterine can combine with a single atom of bromine to form a body, $C_{26}H_{44}OBr$, less soluble in cold carbon disulphide than is cholesterine itself and its dibromide.

MISCELLANEOUS.

Royal Institution.—The Annual Meeting of the Members of the Royal Institution of Great Britain was held on Saturday afternoon, May 1st, at the house of the Institution in Albemarle Street, Sir James Crichton-Browne, M.D., F.R.S, Treasurer and Vice-President, presiding. The Annual Report of the Committee of Visitors for the year 1896, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. Fifty-eight new Members were elected in 1896. Sixty-four Lectures and nineteen Evening Discourses were delivered in 1896. The books and pamphlets presented in 1896 amounted to about 274 volumes, making, with 621 volumes (including periodicals bound) purchased by the Managers, a total of 895 volumes added to the Library in the year. Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year. The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland, K.G., D.C.L., LL.D.

Treasurer—Sir James Crichton-Browne, M.D., LL.D., F.R.S.

Secretary—Sir Frederick Bramwell, Bart., D.C.L., LL.D., F.R.S., M. Inst. C.E.

Managers—Sir Frederick Abel, Bart., K.C.B., D.C.L., LL.D., F.R.S.; The Right Hon. Arthur James Balfour, M.P., D.C.L., LL.D., F.R.S.; John Wolfe Barry, Esq., C.B., F.R.S., M.Inst.C.E.; William Crookes, Esq., F.R.S.; Edward Frankland, Esq., D.C.L., LL.D., F.R.S.; Charles Hawksley, Esq., M. Inst. C.E.; Donald William Charles Hood, M.D., F.R.C.P.; Victor Horsley, Esq., M.B., F.R.S., F.R.C.S.; William Huggins, Esq., D.C.L., LL D., F.R.S.; The Right Hon. Lord Lister, M.D., D.C.L. LL.D., Pres. R.S.; Ludwig Mond, Esq., Ph.D., F.R.S.; Arthur William Rücker, Esq., M.A., D.Sc., F.R.S.; Basil Woodd Smith, Esq., F.R.A.S., F.S.A.; The Hon. Sir James Stirling, M.A., LL.D.; Sir Henry Thompson, F.R.C.S., F.R.A.S.

Visitors—Sir James Blyth, Bart.; William Arthur Brailey, M.D., M.R.C.S.; Edward Dent, Esq.; John Ambrose Fleming, Esq., M.A., D.Sc., F.R.S.; Edward Kraftmeier, Esq.; Sir Francis Laking, M.D.; Hugh Leonard, Esq., M. Inst. C.E.; Sir Philip Magnus, J.P.; T. Lambert Mears, Esq., M.A., LL.D.; Lachlan Mackintosh Rate, Esq., M.A.; Thomas Tyrer, Esq., F.C.S., F.I.C.; Roger William Wallace, Esq., Q.C.; John Westlake, Esq., Q.C., LL.D.; His Honour Judge Frederick Meadows White, Q.C.; James Wimshurst, Esq.

University of London.—The following Examiners for the year 1897-8 were elected at the Meeting of the Senate, held April 28th, 1897:—Mathematics and Natural Philosophy—E. W. Hobson, Sc.D., F.R.S., and Joseph Larmor, D.Sc., M.A., F.R.S. Experimental Philosophy—Prof. G. F. FitzGerald, M.A., F.R.S., and Prof. Silvanus Thompson, D.Sc., B.A., F.R.S. Chemistry—Prof. Wyndham R. Dunstan, M.A., F.R.S., and Prof. William Ramsay, Ph.D., F.R.S. Geology and Physical Geography—Prof. T. G. Bonney, Sc.D., LL.D., M.A., F.R.S., and Prof. Charles Lapworth, LLD., F.R.S. Materia Medica and Pharmaceutical Chemistry—Sidney Phillips, M.D., and W. Hale White, M.D. Forensic Medicine—Prof. J. Dixon Mann, M.D., and Thomas Stevenson, M.D.

Speed of Esterification, as compared with Theory. Robert B. Warder (*J. Phys. Chem.*, i., 149).—The author shows that the rate of esterification of alcohol and the three chloracetic acids, as determined by Lichty (*Tech. Quart.*, viii., 99), does not conform to the requirements of the laws of mass-action in the form applicable to a reversible reaction of the second order, and he suggests four possible causes of the deviations.—*Journ. Amer. Chem. Soc.*

On the Volatility of Ferric Chloride.—Henry P. Talbot (*Am. Chem. J.*, xix., 52-59).—The experimental data show that no loss of ferric chloride occurs, when its solutions (whether neutral or acidified with hydrochloric acid) are evaporated to dryness on the water-bath or upon the hot plate, provided in the latter case they are not too strongly overheated. The residues so obtained were subjected to the temperature usually employed to dehydrate silicic acid (130° C.) for two hours, but suffered no loss of iron. Prolonged heating of these residues over a free flame occasioned but a slight loss (0·4 per cent) of the iron present. Concentrated acid solutions of the chloride, when boiled in a distilling flask, allowed ferric chloride to pass into the receiver only when a slight separation of the solid had taken place on the side of the flask, which, in the acid atmosphere, was volatilised by the overheating of the glass. When ferric chloride solutions are evaporated with exposure to the air, a loss of chlorine ensues, and the basic ferric salt formed prevents loss of the iron as chloride. The presence of ammonium chloride with the ferric chloride occasioned no loss of the latter, even at 130° C. The residues, when heated over a free flame, suffered a loss of iron, as would be expected. The presence of aqua regia with the ferric chloride solution tends to occasion a slight loss of iron during evaporation. The maximum loss was 0·6 per cent of the iron present, but in other cases very little or no loss could be detected. Vogel's experiments (*N. Rep. Pharm.*, xviii., 157) were repeated, and it was found that a slight volatilisation of iron seems to take place from an ethereal solution at the temperatures of the laboratory, but, on the other hand, the presence of ether or its vapour does not promote the volatilisation of the ferric chloride from its boiling, concentrated, aqueous solutions.—*Journ. Amer. Chemical Soc.*

Pottery and Glass Trades Benevolent Institution.—By way of celebrating the Diamond Jubilee of the reign of Queen Victoria, and of benefitting the funds of this Institution, entertainments have been organised by the Board of Management. On Wednesday, May 12th, there will be a Conversazione and Dance at the Galleries of the Royal Institute of Painters in Water Colours, Prince's Hall, Piccadilly, on which occasion Sir Henry Doulton and Miss Doulton will receive the guests. On Wednesday, July 7th, a Dinner will be held in the Prince's Hall, Hotel Cecil, Salisbury Street, Strand, in aid of the Diamond Jubilee Celebration Fund, when William Woodall, Esq., M.P., for Hanley, will preside. The Board will be pleased to receive subscriptions, and the names of ladies or gentlemen who will kindly consent to act as Stewards. Tickets and further information may be obtained from the Secretary, Mr. A. J. Prickett, 6, Thavies Inn, Holborn Circus, E.C.

The Imperial Hygienic Laboratories of Japan.—Soon after Japan had, in 1869-70, made the treaties now in force with foreign countries, medicines were imported in large quantities, and, in order to protect the public against quackery, the Department of Education established a sub-department or Medical Bureau to examine and report on the quality of all medicines imported. This department has gradually grown, and so increased its scope that it now undertakes the analysis and examination of all kinds and sorts of substances. During the year 1895 the total number of bottles, cans, bags, and other packages examined, amounted to 1,122,733, of which 63,277 were reported to be unfit for use: these figures give an idea of the enormous amount of work done, and it is interesting to note that for some years past the work has been entirely done by the Japanese themselves.

Sixty-ninth Meeting of the German Society of Science and Arts at Brunswick, Sept. 20th to 25th, 1897.—At the meeting of this Society in September next there will be a sitting devoted to the question of the constitution of camphor, and it is requested that any papers or notes which any members of the profession desire to contribute may be sent in by the middle of May, so that they can be included in the official programme which is to be issued at the beginning of July. It is intended to devote Wednesday, the 22nd of September, to a general meeting of all who are interested in the subject of Photography as applied to scientific investigations; and Prof. H. W. Vogel, of Charlottenburg, has promised to deliver the introductory address. There will also be an exhibition of scientific photographs organised by Prof. Max Müller; contributions of papers and photographs are requested from all workers on the subject.

MEETINGS FOR THE WEEK.

Monday, 10th.—Society of Arts, 8. (Cantor Lectures). "Design in Lettering," by Lewis Foreman Day.

Tuesday, 11th.—Royal Institution, 3. "Volcanoes," by Dr. Tempest Anderson, B.Sc.

— Society of Arts, 8. "A Half Century of Line Engraving, 1780-1830," by George Clulow.

Wednesday, 12th.—Society of Arts, 8. "Motor Traffic—Technical Considerations," by Sir David Salomons.

Thursday, 13th.—Royal Institution, 3. "Liquid Air as an Agent of Research," by Prof. Dewar, F.R.S., &c.

Friday, 14th.—Royal Institution, 9. "Explosion—Flames," by Prof. Harold Dixon, F.R.S.

— Physical, 5. "Instrument for Comparing Thermometers with a Standard," by W. Watson. "Experiment in Surface Tension," by A. S. Ackerman. "Effect of Temperature on the Magnetic and Electric Properties of Iron," by D. K. Morris. "Formation of Mercury Films by Electric Osmosis," by Rollo Appleyard.

Saturday, 15th.—Royal Institution, 3. "The Greek Theatre according to Recent Discoveries," by the Rev. J. P. Mahaffy, D.D.

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ON THE FERGUSONITE METALS.

I. On Philippium.

By M. MARC DELAFONTAINE.

After long-continued work on the Gadolinite and Samarskite earths, I came to the conclusion—published in 1878 and 1880—that the yellow oxide erbia discovered by Mosander in 1843 contained two yellow earths, which I called *terbia* and *philippia*. Later on the individuality of the latter was denied by two English chemists. But M. Marignac mentioned it at the close of his elaborate paper on the Samarskite Earths (May, 1880), and Mr. W. Crookes, who first rejected it, mentions it among some of his fractional products of yttria.

The lack of time and insufficient means have long prevented my completing the work, by which I expected to justify my conclusions. The investigation of the Fergusonite earths, though incomplete, enable me to show that the characteristics of philippium are such as to deserve the attention of those who are discussing the Periodic Law and the necessary modifications to M. Mendeleeff's classification of elements.

My results in regard to the other Fergusonite metals will be the subject of a second paper, now nearly finished.

Occurrence.—Philippium has been found in Gadolinites, Samarskite, and the mineral from Bluffton (Slano county, Texas), described and analysed as Fergusonite by MM. Hidden and Mackintosh. I secured several pounds of that Fergusonite from Mr. English, mineralogist, in New York; it has proved to be the best material for the extraction of philippium.

Extraction.—500 grms. of the powdered ore were treated at a time, in a large leaden dish, with three times their weight of strong hydrofluoric acid. The reaction is attended with much heat and a great effervescence,—hence the necessity of having the lead vessel not more than half full of the mixture. When the bubbling has subsided, a moderate heat is applied as long as the stirred mass gives off bubbles. An equal volume of water is added; the acid fluorides dissolve, and the earthy fluorides remain as a sediment, coloured green by uranium. The supernatant fluid is poured out, and several times replaced by water. The insoluble fluorides are then transferred into a large platinum dish, and decomposed by sulphuric acid. The solution of the resulting sulphates containing uranium in the uranous form, it is then time to oxidise the latter with some hydrogen peroxide, or, better, some sodium dioxide, which at once turns the liquid yellow.

Oxalic acid throws down the earthy oxalates; iron and uranium remain dissolved. After ignition of the oxalates the earths are left as a moderately dark yellow powder, completely and readily soluble in nitric acid. The mixed salts show an absorption spectrum, the lack of intensity of which indicates a very small proportion of didymium, and not much more of erbium. The pink colour of the solution is, however, much stronger than we might expect from so small a proportion of the absorbing nitrates. The same fact was noticed before by M. Marignac and myself on other occasions.

Philippium may be separated from that mixture of nitrates by different methods, all based upon the fact that its basic energy is less than that of its congeners. Fractional precipitations, by dilute ammonia or by potassium bioxalate, have been resorted to. I give preference to the fractional decomposition of the nitrates by heat. In that way philippium is separated first, then a pale-coloured earth without an absorption spectrum, followed by the erbia earths, and finally terbia and yttria.

The mass of nitrates is heated in a flat-bottomed dish; it foams much for a while, then comes to a quiet fusion and turns red. After some minutes of that quiet decomposition, the dish is allowed to cool. The solid residue is a beautiful orange-red glass, which water dissolves in part only, leaving a dark yellow gelatinous basic salt.

The same process is repeated on the parts taken up by water as long as a coloured residue is left. It sometimes happens that the glass-like mass re-dissolves entirely in water, and makes an opalescent or milky yellowish liquid with a decided greenish fluorescence. That may be corrected by the addition of dilute ammonia, followed by a digestion of several hours in a warm place; I find it preferable to evaporate the whole liquid again, and decompose it at a somewhat higher temperature. The subsalts thus obtained were sorted according to their colour, and subjected to new series of decompositions, until a bright orange-yellow basic nitrate was obtained, which dissolved slowly in moderately dilute nitric acid, and thus gave a deep orange-red transparent solution. Sometimes the solution is entirely colourless, at once.

Characteristics.—There are two series of philippium compounds—the philippous and the philippic ones, corresponding to a white and to an orange oxide. The salts of the first series are colourless, quite stable, and generally crystallise well; they correspond to the lanthanum and yttrium salts. Their solutions do not seem to give an absorption-spectrum; truly they sometimes faintly show the erbium lines and bands under a thickness of 5 or 6 c.m.; but that is evidently due to a very small proportion of erbium metals, which it is very hard to get rid of entirely.

Potassium-philippous sulphate is soluble in a saturated solution of potassic sulphate. The *formiate* crystallises very slowly from a syrupy solution, in fibro-radiated masses. By ignition, the *oxalate* dried at 130° C. yields about 51·5 per cent of orange-coloured oxide. The crystallised *nitrate* is colourless; when heated it melts, and decomposes into a reddish glass, not entirely soluble in water, but very apt to make a colloidal solution which passes very slowly through the filter.

Philippic oxide has a deep orange-red colour, most intense in the oxide made from the calcination of the nitrate or the acetate. Its moist hydrate is light yellow. When air-dried it is in small and somewhat darker lumps; by calcination it turns dark red. With moderately dilute cold nitric acid, the latter makes a yellow solution; in strong acid it dissoves with effervescence and heat, and gives the colourless philippous nitrate. With hydrochloric acid, philippic oxide evolves chlorine, and gives the protosalt. Other acids dissolve it by boiling with some alcohol.

Equivalent.—Although philippium shows a very close resemblance to yttrium and cerium, the constitution of its compounds remains to be established by crystallography or otherwise.

SO_3(=80) combines with about 96 of philippous oxide, which makes Pp 80, or 120, or 160, according to whether the oxide is PpO, Pp_2O_3, or even PpO_2.

Relationship to Other Elements.—Philippium is more closely allied to cerium and terbium than to any other of the yttrium and cerium metals. It is to yttrium what cerium is to lanthanum. Its equivalent, the colour of its subnitrates and that of the philippic salts, the solubility of its formiate, separate philippium from terbium. These characteristics, and the solubility of potassium-philippo sulphate in potassium sulphate solutions, distinguish it from the two ceriums of M. Brauner and M. Schützenberger. A heated mixture of cerium nitrate with that of the Fergusonite earths (left after the removal of Pp) does not behave at all like the original nitrates; the residue of cerium subnitrates does not resemble the corresponding compound of philippium. Terbium nitrate melts into a colourless glass which after partial decomposition is not yellow, and leaves no yellow residue after washing.

Chicago, April 24, 1897.

ON THE SEPARATION OF THORIA FROM ZIRCONIA.

By M. MARC DELAFONTAINE.

Mr. Glazer's paper on the Separation of Thoria and Zirconia, in recent numbers of the Chemical News, prompts me to describe here the method which I have applied for years to similar cases, with accurate results. The fusion of the mineral with potassium bisulphate does not work well in the case of mixtures containing titanic acid with zirconia. I proceed as follows:—

The powdered mixture (ore or oxides) is fused in a platinum crucible with twice its weight of acid potassium fluoride ($KHFl_2$). The zirconia is separated as potassium fluozirconate, K_2ZrFl_6, from the solidified mass by means of boiling water containing a few drops of HFl.

The insoluble fluorides decomposed by sulphuric acid, and ignited below a dull red heat, will leave thorium, cerium, and other earths, as sulphates. Silica, if present, escapes as silicon fluoride. The sulphates are dissolved in water and precipitated by oxalic acid, the oxalates being treated by a saturated hot solution of ammonium oxalate; the thorium salt is dissolved and cerium left. The ignited oxalates left the oxides in good condition for further work. Zirconia is thrown down from its fluo-salt by ammonium hydrate.

Titanium, if present in the original mixture, is found as fluotitanate soluble in hot water. Hydrogen peroxide would separate it from the zirconia.

Chicago, April 24, 1897.

SOIL FERMENTS IMPORTANT IN AGRICULTURE.*

By HARVEY W. WILEY,
Chief of the Division of Chemistry, Department of Agriculture, Washington, D.C.

(Concluded from p. 224).

Ferments Oxidising Free Nitrogen.—In the preceding paragraphs the attention of the reader has been briefly called to the action of those species of ferments which attack nitrogen in some of its forms of combination. Since nitrogenous food is the most expensive form of nutriment which the plant consumes, it is a matter of grave importance to agriculture to know the full extent of the supply of this costly substance. It is evident that the continued action of nitrifying ferments finally tends to exhaust the stores of this substance which have been provided in the soil. The quantities of oxidised nitrogen produced by electric discharges in the air and by other meteorological phenomena, and which are brought to the soil in rain waters, are of considerable magnitude, but lack much of supplying the ordinary wastage to which the stores of soil nitrogen are subjected. Even with the happiest combination of circumstances, it is not difficult to see in what way the available stores of nitrogen could be diminished to a point threatening the proper sustenance of plants, and thus diminishing the necessary supplies of human food. The examination of the drainage waters which come from a fertile field in full cultivation, is sufficient to convince the most sceptical of the fact that the growing crop does not by any means absorb all of the products of the activity of the nitrifying ferments. Nitric acid and its compounds, the nitrates, are exceedingly soluble in water, and for this reason any unappropriated stores of them in the soil are easily removed by heavy downpours of rain. Happily the living vegetable organism has the property of withholding nitric acid from solution, either by some property of its tissues or more probably by some preliminary combination which the nitric acid undergoes in the plant itself. This is easily shown by a simple experiment. If fresh and still living plants be subjected to the solvent action of water, very little nitric acid will be found to pass into solution. If, however, the plants be killed before the experiment is made, by being exposed for some time in an atmosphere of chloroform, the nitric acid which they contain is easily extracted by water.

The losses, therefore, which an arable soil sustains in its content of nitrogenous matter must be supplied either by the addition of nitrogenous fertilisers or by some action of the soil whereby the nitrogen which pervades it may be oxidised and fixed in a form suited to the nourishment of plants. The discussion in regard to the possibility of fixing nitrogen in the soil has been carried on with great vigour during the last two decades. The proof, however, is now overwhelming that such fixation does take place. It would not be proper here to enter into a discussion of the processes by which this fixation is determined, and, in fact, they are not definitely known. One thing, however, is certain, viz., that it is accomplished by means of micro-organisms or ferments similar, perhaps, in their nature to those already mentioned, but capable of absorbing, assimilating, and oxidising free nitrogen.

Methods of Oxidising Free Nitrogen.—At the present time it is sufficiently well known that this operation takes place in two ways. In the first place, there are found to exist on the rootlets of certain plants, chiefly of the leguminous family, colonies of bacteria whose function is known by the effects which they produce. In such plants in a state of maturity, as was mentioned above, are found larger quantities of organic nitrogen than could possibly have been derived from the soil in which they were grown or from the fertilisers with which they were supplied. Cultural experiments in sterilised soils, with careful exclusion of all sources of organic nitrogen, have proved beyond question that this gain in nitrogen is found only in such plants as are infected by the organism mentioned. The logical conclusion is therefore inevitable that these organisms, in their symbiotic development with the plant rootlets, assimilate and oxidise the free nitrogen of the air and present it to the plant in a form suited to absorption. Attempts have been made to inoculate the rootlets of other families of plants with these organisms, but so far without any pronounced success. There are, however, certain orders of low vegetable life, such as cryptogams, for instance, which seem to share to a certain degree the faculty of the leguminous plants in acting as a host for the nitrifying organisms mentioned. The observation above recorded becomes a sufficient explanation of the fact that the fertility of fields is increased by the cultivation of leguminous plants, which would not be possible except they possess some such property as that which has already been described.

Another order of organisms has also been discovered which is capable of oxidising free nitrogen when cultivated in an environment from which organic nitrogen is rigidly excluded. It seems probable, therefore, even in soils which bear crops not capable of developing nitrifying organisms on their rootlets, that the actual stores of available nitrogen may be increased. This fact explains the observation which has frequently been made that in fields which are not cultivated, but which remain in grass, there may be found an actual increase in the total amount of nitrogen which is available for plant growth. As will be seen further along, the soil is also infested with an organism which is capable of destroying nitric acid and returning the nitrogen which it contains to the air in a free state. It seems almost certain that in every complete decomposition of a nitrogenous organism a part of the

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* Abstract of a Lecture delivered before the Chemical Section of the Franklin Institute, February 16th, 1897.

nitrogen which it contains escapes in the free state. Were it not, therefore, for the fact that this free nitrogen can be again oxidised and made available for plant growth, the total stores of organic nitrogen in existence would be gradually diminished, and the time would ultimately come when their total amount would not be sufficient to sustain a plant life abundant enough to supply the food of the animal kingdom. Thus the Earth itself, even without becoming too cold for the existence of the life which is now found upon it, might reach a state when plant and animal life would become practically impossible by reason of the deficit of nitrogenous foods.

Much less is known concerning the character and activity of the organisms that oxidise free nitrogen than of those which feed upon organic nitrogen. It cannot be doubted, however, that these scarcely known ferments are of the greatest importance to agriculture, and the further study of their nature and the proper methods of increasing their activity cannot fail to result in the greatest advantage to the practical farmer. (Photographs showing the occurrence of the nitrifying tubercules of leguminous and other plants were shown upon the screen).

Fertilising Ferments.—Two years ago I used the following words in a Report published by the Department of Agriculture:—

"When a soil is practically free from albumenoid bodies, and contains but little humus, the attempt to develop a more vigorous nitrifying ferment would be of little utility. Even in a soil containing a considerable degree of humus, it may be found that its nitrogen content has been so far reduced as to leave nothing practically available for the activity of nitrification. In such cases the only rational method of procedure is in the application of fertilisers containing nitrogen. In other cases, where the lack of fertility is due to the extinction or attenuation of the nitrifying ferment, remunerative results may be obtained by some process of seeding similar to that described above. It is entirely within the range of possibility that there may be developed in the laboratory species of nitrifying organisms which are particularly adapted for action on different nitrogenous bodies. For instance, the organism which is found most effective in the oxidation of albumenoid matter may not be well suited to convert amides or the inert nitrogen of humus into nitric acid. We have already seen the day when the butter-maker sends to a laboratory for a ferment best suited to the ripening of his cream. It may not be long until the farmer may apply to his laboratory for particular nitrifying ferments to be applied to such special purposes as are mentioned above. Because of the extreme minuteness of these organisms, the too practical agronomist may laugh at the idea of producing fertility thereby; and this idea, indeed, would be of no value were it not for the wonderful facility of propagation which an organism of this kind has when exposed to a favourable environment." It is true that the pure cultures which the laboratory would afford would be of little avail if limited to their own activity, and it is only in the possibility of their almost illimitable development that their fertilising effects may be secured."

It is of interest in this connection to recall the fact that a few months ago the realisation of the prophecy above made was accomplished. There is now made, and offered for sale to farmers, a nitrifying ferment called nitragin, which is prepared from the tubercules of certain leguminous plants. It is found that this material is of use only when applied to crops similar to those from which it is made, while it does not act upon other crops, especially those of a non-leguminous nature. For instance, if the farmer wish to fertilise his clover-field with a nitrifying ferment prepared in this way, he must get one which is prepared from clover. If it be a field of peas or beans, on the other hand, he must secure a ferment prepared from these vegetables. This process may seem ridiculous to those who do not carefully consider all of its aspects; but in a little phial, no bigger than a goose-quill, can be easily contained the seeds of ferments which, by proper multiplication, will produce an active nitrification over a large area. In the preparation of the ferment it is best to mix it with fine, moderately moist soil. After thorough mixing, this soil is then sowed over the land as one would sow wheat or oats. By the process of fission the organisms which are thus introduced into the soil rapidly multiply, and if they find the rootlets of plants suitable to their environment they at once attach themselves thereto, where new tubercules, similar to the ones you saw upon the screen, are formed. It is too early yet to speak of the commercial success which will attend this method of fertilisation, but there is no doubt of the fact that when a field which contains an abundance of nitrogenous matter becomes practically sterilised, this matter may be rendered more available by the introduction of proper nitrifying organisms, and it is also certain that when those crops, such as the Leguminosæ, which are suited to the development of the colonies of tubercules upon the rootlets, are seeded with the proper organisms, the number of tubercules is increased, their activity favoured, and the assimilation of atmospheric nitrogen hastened. (Photographs were exhibited upon the screen to show the influence of inoculating different plants with different ferments developed on radical tubercules).

Ferments Inimical to Agriculture.—It has been noticed by many observers that when nitric acid is subjected to certain fermentative processes it becomes decomposed and gradually disappears. In studying the causes which lead to this decomposition, it is found that it is due to the action of a micro-organism or ferment, which, by reason of the result of its functional activity, is called a denitrifying organism. While it is true that in numbers and activity this denitrifying organism does not equal its nitrifying relation, yet it is a matter of no inconsiderable importance to know fully the laws which govern its existence. As in the case of the bacteria which are found in ripening cream, where some produce evil and some good effects, so it is with those in the soil. The favouring organisms, whose functional activity prepares nitrogen in a form suited for plant food, are accompanied by others, doubtless nearly related to them, whose functional activity tends to destroy the work which the first have accomplished. It thus happens that in the fermentation of nitrogenous bodies there is danger of losing, as has already been said, a part of the nitrogen, which may either escape as gaseous oxides unsuited for the sustenance of plants, or even as free nitrogen. The object, at least the practical object, of the investigation of these denitrifying organisms, should be to discover some process by which their multiplication could be prevented and their activity diminished. At the present time all that is known is that in ordinary circumstances these organisms are not developed in sufficient numbers to prove very destructive. It has already been mentioned, however, that in case of a very great excess of organic nitrogenous matter a considerable quantity of the nitrogen therein contained may, through the action of these organisms, be lost. The practical lesson taught here is to apply nitrogenous foods in a moderate manner and avoid every unnecessary excess.

In the case of nitrifying ferments, it has been seen that nitric acid and carbon dioxide are some of the final products of bacterial activity. In the denitrifying process, on the other hand, free hydrogen and free nitrogen are the results of the final activity of the micro-organisms. In these tubes which I show you, which are partly filled with gas, the evolution of the gaseous material has been secured by introducing into the sterilised solution containing a nitrate, a denitrifying ferment obtained from a soil taken in proximity to a stable. Experience has shown that stable manures of all kinds contain these denitrifying ferments, and that these are capable of causing considerable waste of nitrogen, unless care is taken in their use. The results of such experiments as these show conclusively that it would be a useless extravagance to use a fertiliser containing nitric acid, such as Chili saltpetre, in connection with stable manures.

Pathogenic Ferments.—There are also other forms of ferments in the soil of an objectionable nature which are not related to the nitrifying organisms. It has been observed in France that, in localities where animals are interred which have died of charbon, the germs of this infectious malady persist in the soils for many years, and that, especially when cereal crops are cultivated upon such soils, there is great danger of contaminating healthy cattle with the same disease. In one case it was observed that many sheep which were pastured in a field in which, two years before, a single animal which had died of charbon was buried, were infected with the disease and died. In like manner, it is entirely probable that the germs of hog cholera may be preserved in the soil for many years, to finally again be brought into an activity which may prove most disastrous for the owners of swine. Every effort should be made by agronomists to avoid infecting the soil by carcasses which are dead from any zymotic disease. Cremation is the only safe method of disposing of such infected carcasses. The investigations of scientists have shown that there are many diseases of an infectious nature due to these germs, and that these germs may preserve their vitality in the soil. Among others may be mentioned yellow fever and tetanus, and the microbe producing the bubonic plague, which retains its vitality in the soil, and thus escapes entire eradication.

Use of Sewage as Fertiliser.—For the reasons given above, the agronomist, who also has at heart the health and welfare of man and beast, can hardly look with favour upon any of the plans which have been proposed for the use of sewage from large cities for irrigation purposes. There is scarcely a time in any large city when some infectious disease, due to the activity of germs, does not exist, and the sewage is liable at all times to be contaminated therewith. In view of the fact that the vitality of the germs mentioned above may be continued for a long time in the soil, it is fair to conclude that it is of the utmost importance to avoid the contamination of the soil, where it is to be used for agricultural purposes, with any of the dejecta which may come from those infected with any zymotic disease whatever.

Supplying Lost Nitrogen.—It is evident that if no process of supplying the loss of nitrogen existed, the soil would soon lose its power of furnishing food and raiment for man. The philosopher who studies the system of Nature sees in the far future the advent of a time when the environment of man on the Earth will be too harsh for his present organisation. The slow cooling of the Sun, and consequently of the Earth, is the principal cause of this misfortune. But added to this must be considered the gradual disappearance of carbon dioxide and organic nitrogen, two of the essential components of the environment which makes plant-life possible. Diminishing heat and light, disappearing carbon dioxide and organic nitrogen, are, little by little, making the struggle for existence harder.

Nitrogen is lost not only by the action of the denitrifying organisms, but also by the solution of nitrates and their loss in drainage waters. From the sea this loss is restored in part by fish and sea-weeds. This is a practical illustration of the text, "Cast thy bread upon the waters, and it shall return after many days." The organisms that oxidise atmospheric nitrogen supply another part.

Fortunately, living organisms adapt themselves to changes in their environment, and life, therefore, will still be possible when the present conditions of existence shall have disappeared.

A careful study of the causes which produce a waste of nitrogen and those which restore the loss, gives the pleasing assurance that the present kind of man will not die of nitrogen hunger. Some of the best producers of proteids flourish at high latitudes.

When the last man of the present race, with a stature diminished by long ages of hopeless labour, and with features pinched from hunger and cold, shall have been driven to the equator by the advancing armies of ice, his last look will be at the mocking disc of the Sun, denying him warmth, and his last mouthful of food will contain the proteids of oatmeal.

(The lecture was fully illustrated with experimental cultures of soil microbes and by means of lantern slides).—*Journal of the Franklin Institute*, cxliii., p. 293.

CONTRIBUTION TO THE STUDY OF HYPONITROUS ACID.*

By **A. HAUTZSCH** and **A. L. KAUFMANN.**

In taking up the study of hyponitrous acid, discovered by Maumené, and afterwards worked on by Divers, Zorn, and Van der Plaats, we had two considerations in view: firstly, the relations existing between hyponitrous acid and the so-called dinitrogenised compounds, expressed by the formula $HON = NOH$, and by the name *dinitric acid*, proposed by Wislicenus; and secondly, the relations existing between this acid and nitramide, $NH_2.NO_2$, discovered by Thiele, and considered by him to be a structural isomer of hyponitrous acid, which was then unknown in the free state.

We have perfected Zorn's method of preparing this acid, in such a manner as to always ensure satisfactory results, and finally we have succeeded in obtaining free nitrous acid in the solid state. Further, we have prepared hyponitrite of ammonium, which was up till recently hardly known, and have isolated in the solid state the benzylic ether of hyponitrous acid. The free acid, the salts, and its ether have been submitted to searching enquiry as to their chemical and physical properties, and compared as far as was possible with the *nitramide* isomer.

Formation of Hyponitrites.

In the series of the intermediate products of reduction, between nitric acid and ammonia, hyponitrous acid will be found between nitrous acid and hydroxylamine:—

$$HNO_3,\ HNO_2,\ (HNO)_2,\ N_3HO,\ NH_3.$$

It follows, then, that hyponitrous acid can be obtained either by the reduction of the preceding or the oxidation of the following compound in the series.

a. *Methods of Reduction.* — Sodium amalgam, either directly (Divers, Chemical News, xxiii., p. 206; Zorn, *Berichte d. Ch. Ges.*, x., p. 1306) or indirectly, has been principally used as the reducing agent; that is to say, by submitting to electrolysis aqueous solutions of nitrite of soda, with the mercury as the negative pole (Zorn, *Berichte*, xii., p. 1509).

However, the resulting amounts indicated by Zorn have never been obtained by the different chemists who have studied this reaction; but Tanatar (*Berichte*, xxvi., p. 163) succeeded in obtaining twice as much as Divers by using a liquid sodium amalgam.

The assertions of some writers that it would be possible to obtain hyponitrite of soda by treating nitrite of soda with ferrous hydrate (Zorn, *Ibid.*, xv., pp. 1007 and 1288) or by melting nitrite of soda with scrap sheet-iron (Mencke, Chem. News, xlix., p. 45) have not been confirmed. Similarly, we have not been able to prepare hyponitrites by the reduction of nitrites in an aqueous solution, by means of aluminium amalgam, as described by H. Wislicenus and L. Kaufmann (*Berichte*, xxviii., p. 1323).

b. *Methods of Oxidation.*—Hyponitrous acid can be prepared by the oxidation of hydroxylamine and its derivatives. The formation of hyponitrous acid, observed by Thum, by the action of hydroxylamine on some metallic oxides,

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* *Moniteur Scientifique*, vol. xi., p. 336, May, 1897.

—mercuric oxide, cupric oxide, and oxide of silver,—is based on the direct oxidation of hydroxylamine:—

$$2NH_2OH + 2HgO = 2Hg + H_2O + N_2O_2H_2.$$

The quantities obtained by this method are not so insignificant as stated by Thum. It was by thus treating, with an excess of mercuric oxide, an alkaline solution of hydroxylamine, prepared from 5 grms. of sulphate of hydroxylamine and an excess of caustic potash, that we obtained—after eliminating the mercury, neutralising with nitric acid, and precipitating with nitrite of silver—0·5 grm. of hyponitrite of silver. This quantity represents 10 per cent of the weight of the sulphate of hydroxylamine, and about 5 per cent of the theoretical returns.

The splitting up of benzo-sulphydroxamic acid (obtained by the action of hydroxylamine on sulpho-chlorated benzine) by alkalis, into benzo-sulphuric acid and hyponitrous acid, lately observed by Piloty (*Berichte*, xxix., p. 1560), and represented by the equation—

$$2C_6H_5SO_2NHOH + 2KOH = \\ = 2C_6H_7SO_2K + N_2O_2H_2 + 2H_2O,$$

can also be considered as an oxidation of hydroxylamine. This method of preparing hyponitrous acid gives fairly satisfactory results.

The action of nitrous acid on hydroxylamine also gives rise to the formation of hyponitrous acid,—

$$HONH_2 + ONOH = HON + NOH + H_2O.$$

According to Wislicenus (*Ibid.*, xxvi., p. 771) this reaction might be considered as a condensation. Neither the action of nitrite of soda on sulphate of hydroxylamine (Wislicenus) or that of nitrite of silver on chlorhydrate of hydroxylamine (Kratschmer, *Thèse*, 1895, p. 9) give satisfactory results. The method proposed by Tanatar (*Berichte*, xxvi., p. 763)—reaction in the presence of certain bases—seems to be the one giving the best results.

We have endeavoured to make hyponitrite of soda, and potash, by passing a current of dry nitric oxide through a liquid sodic or potassic amalgam. But the result was *nil;* there was no reaction. Equally unfruitful were the attempts of P. Schatzmann to combine protoxide of nitrogen with caustic potash under pressure, or at a high temperature. The only products of this experiment were ammonia and nitrite of potash, but no hyponitrite of potash.

Preparation of Hyponitrite of Silver.

As in our experiments we had need of large quantities of hyponitrite of silver, which serves as the starting-point for the preparation of free hyponitrous acid, we endeavoured to improve the then best known among the methods of preparing hyponitrite of silver, viz., that based on the reduction of nitrite of soda by sodium amalgam. We have found from experience that the return is considerably increased — 1. When working at a low temperature; 2. When the nitrite of silver is present in great excess with regard to the nascent hydrogen; 3. When the reaction is carried on in alkaline solution, hyponitrous acid being unstable except in strongly alkaline solutions. Influenced by these facts, we propose the following method for the preparation of hyponitrite of silver:—

To a properly cooled solution of 20 grms. of pure nitrite of soda add 10 grms. of caustic soda in 200 c.c. of water; a liquid amalgam, obtained by dissolving 16 grms. of sodium in 2800 grms. of mercury is slowly added, drop by drop. During the operation, which should last about three-quarters of an hour, the mixture should be strongly and continually agitated. After having separated the mercury, the liquid, cooled to 0°, is heated with diluted nitric acid until it gives but a very slight alkaline reaction. To eliminate the hydroxylamine, which is always formed in this reduction, mercuric oxide is added, the mixture being still constantly stirred, until the last portion of oxide added no longer changes colour. The liquid is rapidly filtered with a filter-pump, a small quantity of mercuric oxide being first placed in the filter. The filtrate is then neutralised with nitric acid, and precipitated with nitrate of silver. The yellow precipitate obtained is washed with warm water, first on the filter, then by decantation in an Erlenmeyer flask, re-dissolved in very dilute nitric acid, and cooled down to 0°. The solution is then rapidly filtered and precipitated by ammonia; by repeating this we obtain perfectly pure hyponitrite of silver. This can be dried either over a water-bath or in an exsiccator after being washed with alcohol and ether.

Analyses of the substance thus obtained have given the following results:—

	I. Grms.	II. Grms.
Substance used	0·2019	0·3308
Ag by titration	0·1573	0·2580

	Found.			Theory.
	I.	II.		
Ag ..	77·91%	78·00%	AgNO ..	78·26%

The salt prepared as described above possesses all the properties of hyponitrite of silver. But, contrary to the statement of Van der Plaats, it does not detonate at 150°. In spite of all our efforts we have been unable to explode it. It is also worthy of note that this silver salt keeps its yellow colour in diffused light; but in direct sunlight it quickly assumes a yellowish green colour, and when moistened the surface becomes black.

The amount of hyponitrite of silver obtained, starting with 20 grms. of nitrite of soda, is from 2 to 3 grms., or 6 to 7 per cent of the theoretical quantity. These figures correspond to the maximum returns indicated by Zorn, but they have not been obtained by any other experimenters who have used Zorn's method.

It is best not to attempt the reduction on more than 20 grms. of nitrite of silver at a time. But the rough products resulting from several reductions can all be purified together. In one or two days one can easily prepare 20 grms. of pure hyponitrite of silver. We therefore believe that the method we have just described is the simplest and the least expensive.

(To be continued).

SOME EXPERIMENTS WITH CATHODE RAYS.*

By A. C. C. SWINTON.

(Continued from p. 221).

The Rays cross at the Focus with no Rotation.

In order to investigate the cathode rays in a focus tube still further, and more especially in order to discover whether the various rays from the cathode cross one another at the focus, or diverge again without crossing, and also in order to discover whether there is any twist or rotation of the rays, similar to what has been observed in the case of rays focussed by magnetism,† a tube was constructed similar to that used in the previous experiments, with a carbon anticathode which was also the anode, fixed at the opposite side of the focus from the cathode, with the focus about equally distant between it and the cathode. The peculiarity of this tube consisted in the fact that a sector of the aluminium cathode, equal to one-eighth of the total area of the cathode, had been entirely removed, as shown at C, fig. 9. It was expected that on using this tube, with the proper degree of vacuum to form a well-defined ring on the anti-cathode screen, that a portion of the ring, corresponding with the amount of the cathode cut away, would be found wanting; and that by the position of this gap in the ring it would be possible to ascertain whether the rays crossed at the focus, and whether there was any rotation. What

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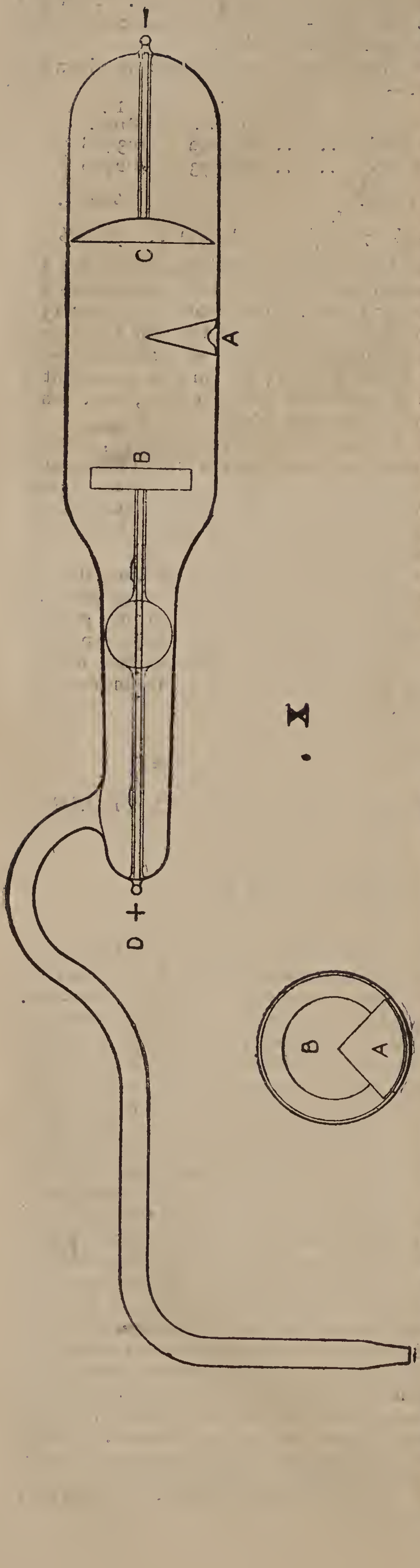
* A Paper read before the Royal Society, March 11, 1897.

† See experiments by K. Birkeland, *Electrical Review*, June 12, 1896.



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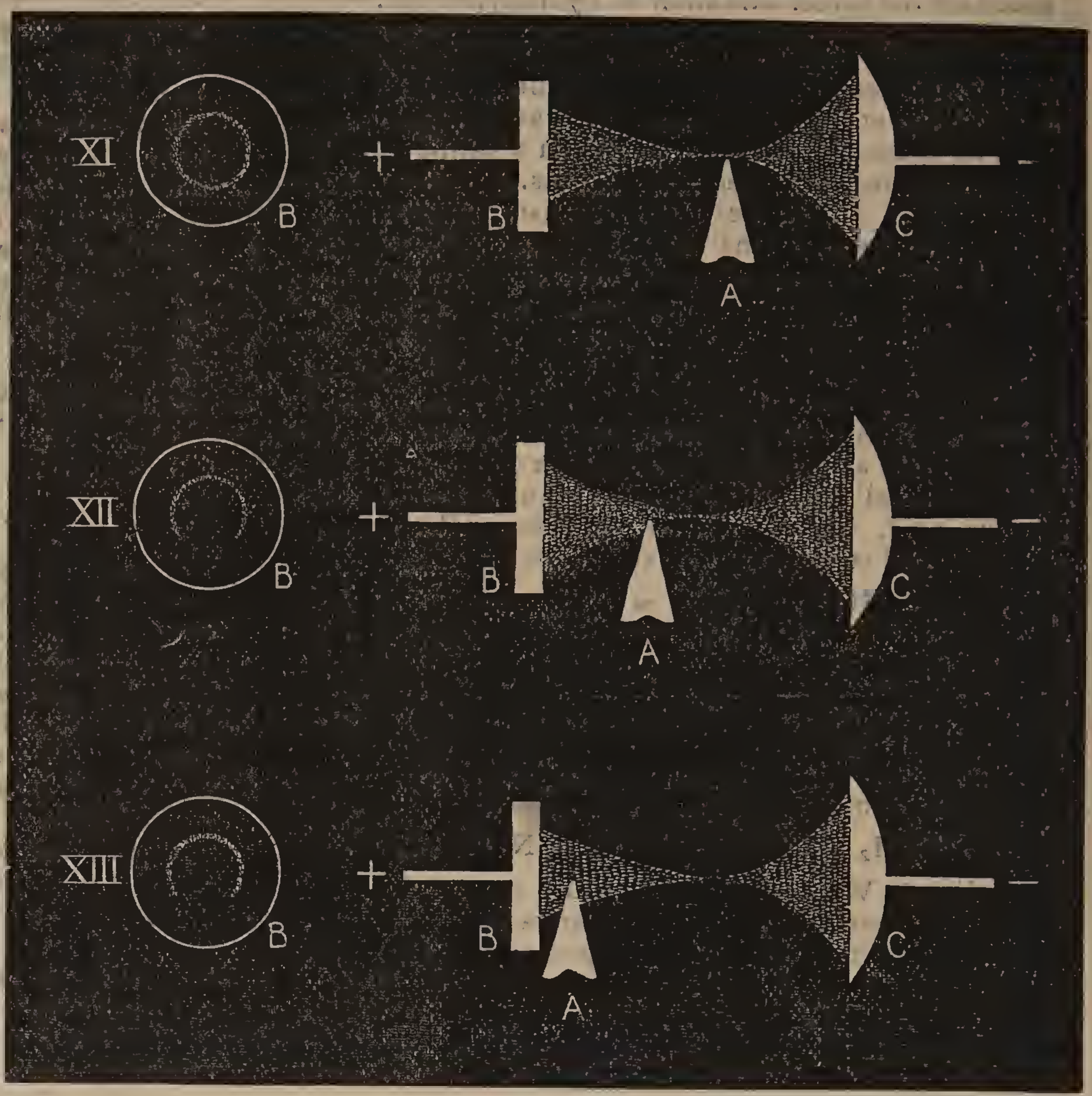

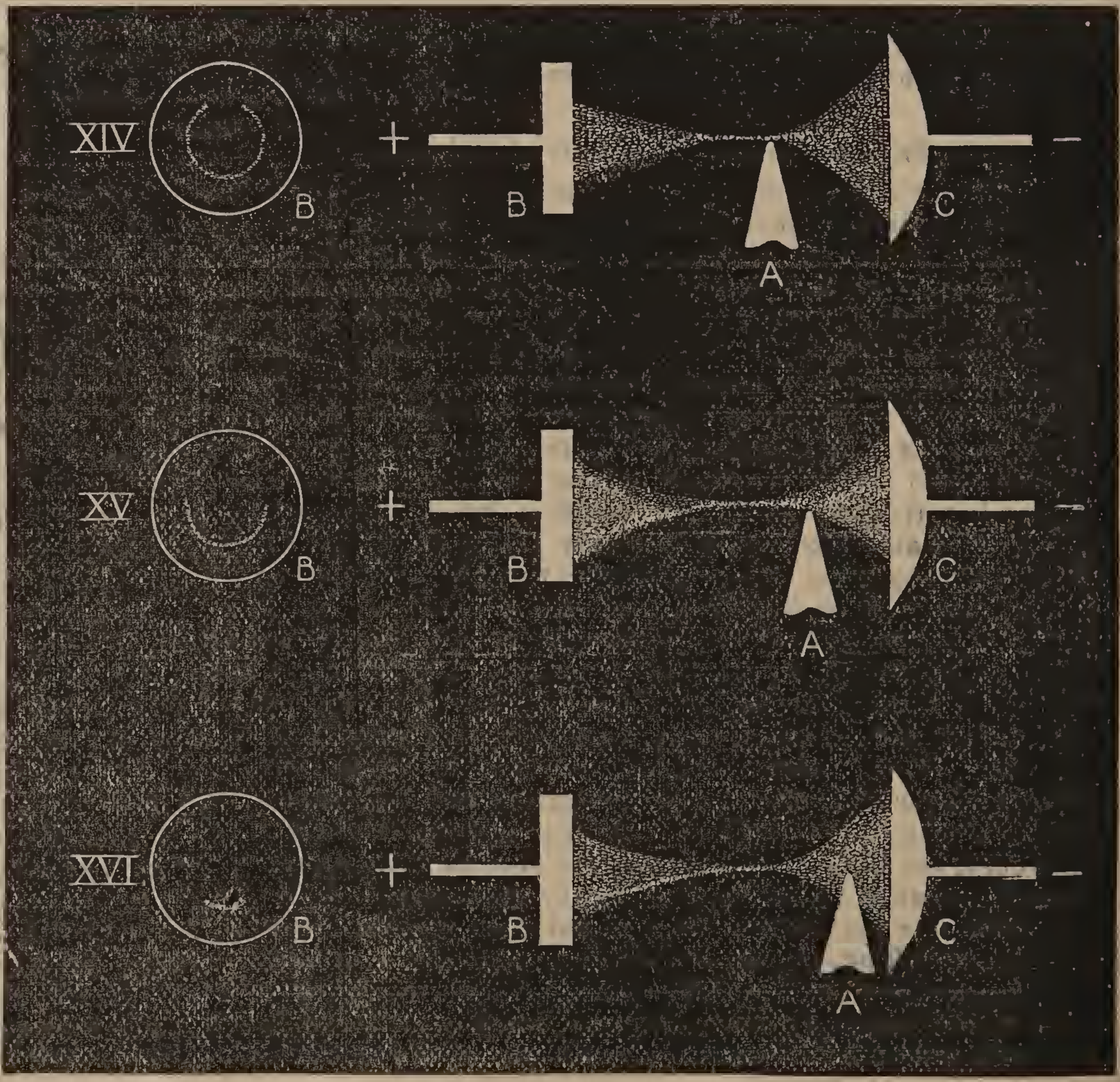

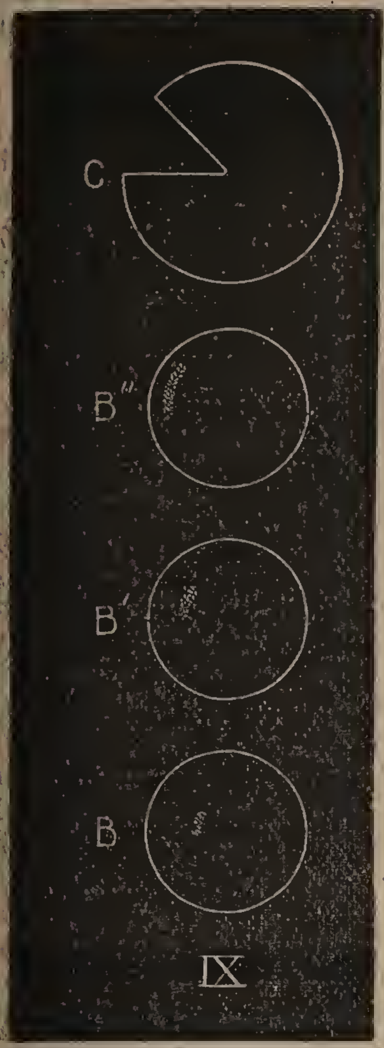

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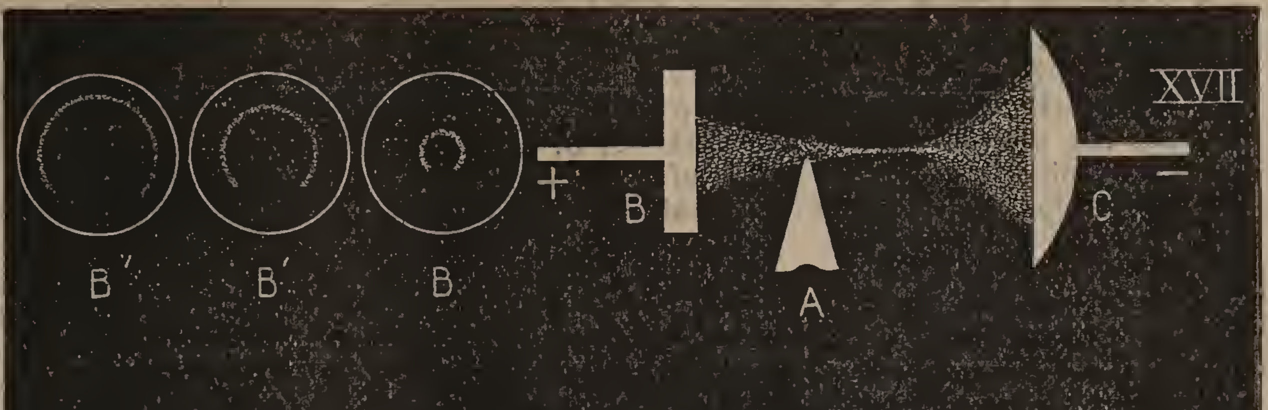

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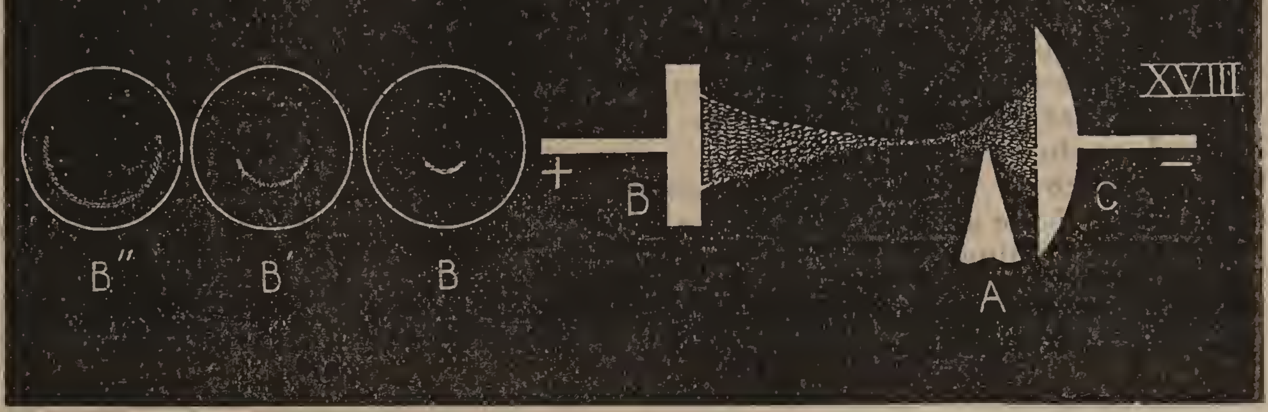

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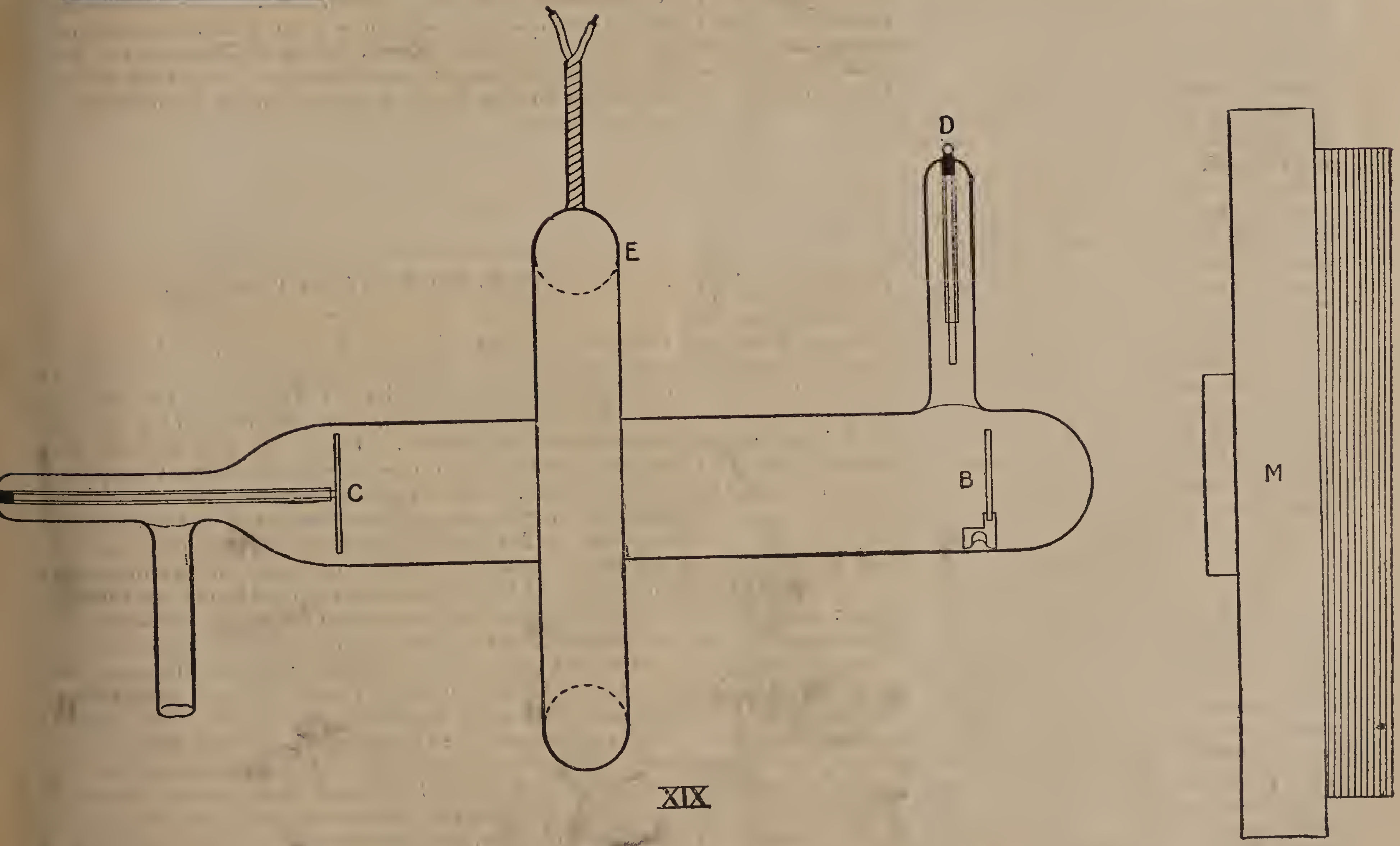


XIX

actually was observed is shown for three different conditions of vacuum in fig. 9, B being for the highest, and B'' for the lowest vacuum. As will be seen, the expected gap in the ring was obtained, but with the unexpected addition that the dimensions of this gap, instead of being only one-eighth of the circumference of the ring, was seven-eighths of the circumference. In fact, the amount of ring shown corresponded not with the seven-eighths of the remaining cathode surface, but with the one-eighth of the cathode that had been removed. The portion of ring that did appear was of a length corresponding exactly to the arc of the removed sector of the cathode, according to its greater or lesser nearness to the centre with different conditions of vacuum; and as the portion of ring was in each case exactly in line with the portion of cathode that had been cut away, it would appear that there is no rotation of the cathode beam as a whole, that the rays do cross at the focus; and, further, that when the hollow convergent cone is, as it were, split in this manner, some unexplained action, similar in effect to the existence of a circular surface tension, causes the gap to widen out and the remaining portion of the ring-shaped section of the cone to contract correspondingly, without, however, altering its diameter.

In order to further investigate the matter another tube was made, as shown in fig. 10, in which the concave cathode was complete; but the interior of the tube was furnished with a small movable piece of aluminium, A, which by shaking could be moved up and down the tube between the cathode, C, and anti-cathode, B, and which, while not quite reaching the centre of the tube, would fill up very nearly one-quarter of the circular sectional area of the latter.

With this arrangement of tube, with the aluminium obstacle placed just at the focus, as shown in fig. 11, the point of the obstacle just missing the cathode rays, a complete ring was formed on the carbon anti-cathode. On moving the obstacle slightly into the divergent cone, exactly one-quarter of the ring on the anti-cathode failed to appear, as shown in fig. 12, and on the obstacle being further moved in the same direction the result was not altered, as shown in fig. 13.

As in each of the latter two cases there was no displacement of the gap in the ring, the above showed that there is no rotation of the divergent cathode cone.

Experiments were next tried with the aluminium obstacle, moved so that its point just entered the converging cone of cathode rays, when a small portion of the ring was cut out; but on the opposite side, as shown in fig. 14, this confirming the previous experiments, which showed that the rays cross one another's paths at the focus without rotation. Upon moving the aluminium obstacle a little nearer to the cathode, so that its point entered still further into the convergent cathode beam, one-half of the ring disappeared, as in fig. 15, while when the obstacle—which, it should be remembered, blocked only one-quarter of the circular area of the tube—was brought close up to the cathode, only about one-quarter of the ring remained, as in fig. 16.

Further experiments were tried with the aluminium obstacle both in the divergent and convergent cones, but with the tube exhausted to different degrees of vacuum, the result being as shown in figs. 17 and 18, in which in each case B shows the highest vacuum and B″ the lowest, from which it will be observed that when the obstacle was in the divergent cone a portion of the ring was cut off exactly proportional to the angle subtended by the sides of the obstacle; while when the obstacle was placed in the convergent cone, a much larger proportion of the ring was cut off in each case, this being much more marked with a high vacuum when the diameter of the ring was small than with a low vacuum when the diameter of the ring was large.

Convergent and Divergent Cones produced by Magnetic Focussing.

In order to discover whether the apparent hollowness of the convergent and divergent cones of cathode rays as above observed, when the focussing was performed by means of a spherical cathode, was in any way due to the concave form of the cathode or to the fact that the rays were converging or diverging, experiments were tried with a tube having a flat aluminium cathode, the rays being caused to converge to a focus by means of a powerful electro-magnet in the manner described by the writer in his paper on "The Effects of a Strong Magnetic Field upon Electric Discharges *in vacuo*" (*Roy. Soc. Proc.*, 1896, vol. lx., p. 179).

The arrangement is shown in fig. 19, the carbon anti-cathode screen, B, being movable, and not connected to the anode D, which was contained in an annex to the tube. By increasing or decreasing the power of an electro-magnet, M, by moving it nearer to or further away from the tube, and by moving the anti-cathode screen up and down the tube, the cathode rays could be focussed on the anti-cathode screen so as to form a circle of any desired size, the focus, which appears to be exactly on the pole of the magnet, being, of course, always beyond the anti-cathode.

In order similarly to investigate a divergent cone of cathode rays magnetically produced, a circular coil of wire, E, was employed instead of the magnet in the manner recently described by Professor Fleming (*Electrician*, January 1, 1897). This coil, which had 72 turns of No. 18 S.W.G. size wire, was supplied with 20 to 25 ampères of current from a storage battery. It focussed the cathode rays at a point exactly central to its own plane, from which they again diverged on to the anti-cathode screen.

With convergent and divergent cones of rays produced magnetically in the above manner, there was no difficulty in showing that, under suitable conditions, these cones acted as if they were hollow, giving bright rings of varying sizes, sometimes with and sometimes without bright central spots, upon the carbon anti-cathode screen exactly similar in appearance to those obtained with the concave cathode.

Further observations were as follows:—

In some instances, two concentric hollow rings were observed, especially with a low vacuum when the magnet was suddenly turned on or off. The rings are probably not simultaneous, but successive, but this cannot be detected with the unaided eye.

With a high vacuum, and the magnet so arranged as to focus the rays accurately upon the carbon, a small bright spot appears at first; as the vacuum goes down this point becomes larger and fainter, but still solid. Suddenly it becomes hollow and brighter, then, as the vacuum falls still further, the ring becomes solid again, though larger and more faint than before, finally it disappears. After this stage it can be reproduced momentarily, without alteration to the vacuum, by switching the magnet on and off suddenly, when it is usually hollow, but sometimes solid.

(To be continued).

SEPARATION OF CHLORINE AND BROMINE.

By H. BAUBIGNY and P. RIVALS.

Determinations of chlorine, bromine, and iodine in mixtures of haloid salts have been always considered as operations of great difficulty. They were, in fact, possible only by indirect methods, generally inaccurate and not admitting of any control. If we can now separate with accuracy iodine from the two other elements, the procedures given, even in the last few years, for determining chlorine in presence of bromine, or inversely. are still imperfect. This fact has led us to our present researches. We shall consider at first the case of a mixture of chlorides and bromides, where the problems are to bring the chlorine and the bromine to the state of alkaline salts, or, secondly, to the state of silver salts.

Alkaline Salts.—The modern methods of separating the halogens are founded in general upon the different properties of their hydracids in presence of different oxidising agents, the effects of which differ also with the conditions of the experiment. As oxidisers we have employed successively lead and manganese peroxides, oxygenated water, the chromates, permanganate, ammonium persulphate, the arseniates, &c., most frequently in presence of a small quantity of sulphuric or acetic acid, or of a salt easily decomposed, such as ferric or aluminic sulphate. But in any case we must meet the necessity of having a solution so dilute that the oxidation may be limited to one of the hydracids. Of all these oxidising agents, those which are the most soluble are evidently the most perfect, or at least the most regular, in their action; and of these, permanganate is one of the most energetic. Peon de St. Gilles has shown that if we treat a mixture of alkaline haloid salts in a neutral or alkaline liquid with an excess of permanganate, all the iodine—and the iodine alone—is oxidised, so that the iodide is entirely converted into iodate, whilst the alkaline chlorides and bromides are not affected even at 100°. But if the permanganate does not act upon potassium or sodium bromides, nothing proves that it must be the same for those of all metals. Indeed, we have found that if the solution of neutral copper chloride is not attacked by permanganate in the cold, that of the bromide of the same metal is decomposed with liberation of bromine.

The phenomenon of oxidation is not of the same order as for the alkaline iodides, but it permits us to separate bromine and chlorine; for in an alkaline chloride or bromide the addition of neutral copper sulphate, in virtue of the law of distribution, determines the formation of copper chloride or bromide. If, then, we further add a little permanganate, the bromine, if present, is displaced. In these latter conditions it is easy to demonstrate that the reaction is quantitative.

To this end, having prepared standard solutions of alkaline chloride and bromide, we operated with these liquors, at first separately, and then in mixing them in known proportions. In our experiments the quantities of salts varied from 0·120 to 0·400 grm., and for these weights we have taken from 4 to 8 grms. copper sulphate, and from 0·350 to 0·400 grm. permanganate. We commence by dissolving the sulphate, $CuSO_4+5H_2O$, with the alkaline salt, and in the cold liquid the crystals of permanganate. The vessel is then set in a vacuum at the ordinary temperature (15—18°) over fragments of potassa. The next day the dry residue, if taken up in a little water, gives off no odour. We then complete the solution by adding enough sulphurous acid to reduce MnO_2 and what remains of the permanganate, and in the liquid we precipitate the chlorine or bromine by silver nitrate, very strong in nitric acid to prevent the reduction of a little nitrate by the excess of sulphurous acid, which is destroyed if heated in presence of nitric acid.

We collect the bromide or chloride until the liquid is cold—for silver chloride is especially soluble in boiling water, even if neutral.

The following are some of the results obtained:—

Value in silver salt of KBr used.	AgBr recovered.
0·192 grm.	0·0005 grm.
0·384 ,,	0·0006 ,,

Value in silver salt of the NaCl used.	AgCl recovered.
0·2922 grm.	0·586 grm.
0·2917 ,,	0·5858 ,,

On the subject of experiments with chloride, we must add that for each of them the dry residue has been re-moistened and re-dried twice *in vacuo*, so as to exaggerate the decomposition of the chlorides if such were capable of being produced; the action may therefore be regarded as nul.

Lastly, for mixtures of chlorides and bromides experiment showed—

Value in silver salt—		
Per NaCl used. Grm.	Per KBr used. Grm.	Salt of silver recovered. Grm.
0·5844	0·192	0·5854
0·0731	0·576	0·0730

—*Comptes Rendus*, cxxiv., No. 16.

Some New γ-Cetonic Acids.—T. Klobb.—The alcoylphenacetylcyanacetic ethers, are easily saponified in the cold by alkalis, but if warmed they quickly give off ammonia. By this means nitrogen-free acids are obtained, of which one only—ethylphenacetylacetic acid—had up to now been prepared. Several others have been now made, and their properties are described in this paper.—*Bull. de la Soc. Chim. de Paris.*

NOTICES OF BOOKS.

The Electric Furnace. ("Le Four Electrique"). By Henri Moissan, Membre de l'Institut. Paris: G. Steinheil. 1897. Pp. 385.

(Second Notice).

The first application of the electric furnace, after it had passed from the experimental stage, was to the study of the crystallisation of the metallic oxides, then the volatilisation of several simple bodies. For the first of the above-named experiments a furnace of quicklime was used, and when working on small quantities of material, and only using about four horse-power, the carbons were purified by being first submitted to the action of chlorine at a high temperature, and then cooled in a current of nitrogen. But when using such currents as were furnished by thirty to thirty-five horse-power, the electrodes had to be prepared and purified with the minutest care, small amounts of impurities exercising great influence on the results. A great variety of substances were experimented on, such as chalk, lime, strontia, baryta, magnesia, alumina, &c. It is impossible to operate on a small quantity of alumina in contact with lime, as a liquid aluminate of lime is immediately formed; in this case a carbon crucible is used. By adding a very small quantity of sesquioxide of chromium to the alumina, a mass of small crystals of veritable rubies is formed. These, however, are not so fine as those prepared by MM. Frémy and Verneuil. The author has not followed up this matter.

The oxides of the iron group stable at high temperatures form masses bristling with small crystals.

M. Dufau has, by using the electric furnace, noted the existence of a chromite of lime, Cr_2O_3,CaO; a tetrachromite of barium, $4Cr_2O_3,BaO$; a cobaltite of magnesium, CoO_3Mg; and a nickelite of barium, $2NiO_2,BaO$.

The ordinary metals are easily volatilised and condensed, as well as even such refractory ones as platinum and uranium.

The experiments to try and volatilise boron were not successful, as boride of carbon was immediately formed; this is easily melted, and on cooling forms definite crystals.

An early conclusion arrived at by the author is, that at such high temperatures as those obtained by means of his furnace, the bodies hitherto considered as most refractory are easily volatilised, and those looked upon as being the most stable in mineral chemistry are destroyed either by dissociation or volatilisation. There remains only a series of new compounds, perfectly crystallised and of exceptional stability, which are able to resist the action of this extreme amount of heat. These are borides, silicides, and—above all—the metallic carbides.

Carbon is, of all the simple bodies, the one which forms the most curious allotropic varieties. Its contradictory properties, its different specific heats, &c., have long been matters for earnest thought and study. The study of amorphous carbon ranges over a wide field, and we will do no more than mention the fact *en passant.* Graphite, before the researches of M. Berthelot, included all varieties of carbon capable of leaving a mark when rubbed on paper; molybdenite was thus easily confounded with graphite. Berthelot defined graphite as "every variety of carbon capable of forming by oxidation a graphitic oxide." This property definitely established the classification of the varieties of carbon into three groups—diamond, graphite, and amorphous carbon. M. Moissan has, in his researches, shown the possibility of bringing all kinds of carbon, diamond or amorphous, into the graphitic state. The discovery of graphite in a meteorite from the Cañon Diablo led the author to examine other meteorites, to find out if they also contained carbon, and, if so, in what form. In some, such as the meteoric iron from Kendal County, Texas, none was found; that from Newstead, in Roxburghshire, contained amorphous carbon and graphite; déesite, from Chili, contained a small quantity of graphite; and of three samples of iron from Ovifak, all contained amorphous carbon, two contained graphite, but none contained diamond, either black or transparent.

A few of the graphites which can be prepared in the laboratory are here passed in review. Diamond heated in the electric arc is converted into graphite; wood charcoal, properly purified, is, at a temperature of about 2200°, converted into graphite in ten minutes. There are many other methods for producing it at densities varying from 2·10 to 2·25.

The study of the solubility of carbon in metals at high temperatures led to the research on the action of boron and silicon on liquid carbide of iron, and it is shown that these chemical reactions are as clear and well-defined as those in aqueous solutions, as performed in the laboratory at ordinary temperatures. A sample of cast-iron was taken, containing 3·18 per cent of carbon and 0·5 per cent of slag. To 10 grms. of this was added 2·3 grms. of boron. After heating, it was allowed to cool, when the slag on the surface was found to contain all the original slag and most of the boron, while the carbon in the iron was reduced to 0·27 per cent, the boron present amounting to 8 or 9 per cent.

Silicon has a similar action of replacing a part of the carbon, the carbon expelled being found on cooling, on the top of the metal in the form of graphite.

To obtain pressure in the manufacture of graphite in molten iron, recourse was had to the plan of suddenly cooling the whole mass in cold water; this has the effect of strongly compressing the carbon dissolved in the iron, and after cooling, dissolving the iron, &c., crystals of graphite, of a beautiful shining black colour, were formed, bearing a close resemblance in general appearance to specimens of graphite found in the blue ground from Kimberley; its density is 2·16, and it burns in oxygen at about 660°.

All the samples of graphite hitherto examined have been found to contain hydrogen. This might be due to three reasons: it may be a physical phenomenon, or condensation of hydrogen gas in the graphite—as might be imagined from some experiments made by M. Cailletet, who noticed that hydrogen was absorbed by molten iron; or, again, it might be a chemical phenomenon; an experiment here described, however, shows that hydrogen is not in combination with the graphite.

Having succeeded in making crystallised graphite, it was but natural that M. Moissan should next attempt the artificial production of diamonds. Many workers have already attempted this difficult task, but their results have been contradictory and uncertain. The author fully recognised that, even if he did succeed, the diamonds obtained would, at first at any rate, be merely microscopic.

It is interesting here to note the definition of "diamond"; it is an elementary body, of maximum hardness, 3·5 density, and burns in oxygen at a temperature somewhat above 700°; 1 grm. giving 3·666 grms. of carbonic acid. The principal characteristic of the diamond is its great hardness. Numbers of bodies—carbides, borides, silicides, &c.,—have been produced by means of the electric furnace which will scratch ruby, but only boride of carbon will even slowly scratch a diamond.

By studying the occurrence of diamond, and the character of its associates—zircon, topaz, titanic iron, &c.,—which are found in the same matrix and under similar conditions, M. Moissan concluded that the diamond was formed in the interior of the earth under conditions of great heat and enormous pressure. To imitate this he had recourse, as before, to the sudden cooling of a mass of molten iron in which carbon was held in solution; the exterior being suddenly solidified subjected the still liquid interior to very great pressure.

It was not without a certain amount of apprehension that this experiment was performed for the first time; indeed, it seems marvellous that the act of plunging a crucible containing molten iron heated to a temperature of over 3000° into a vessel of cold water did not result in a disastrous explosion; but happily it is not so—the experiment has been performed over 300 times without accident.

CORRESPONDENCE.

ACTION OF ENZYMS UPON STARCHES.

To the Editor of the Chemical News.

Sir,—I have read with much pleasure the interesting review in your issue of April 30th on Dr. Stone's report, especially in regard to the action of enzyms on starches. I notice that Taka-diastase has claimed the attention of Dr. Stone to such an extent that, although this special digestive agent had not been long before his notice when he made his report, he considered it to be of sufficient importance to call for special mention and space. I am not surprised at this keen interest in regard to a preparation possessing diastasic potency to the extent present in Taka-diastase.

As I have experimented with this diastasic ferment and considered its action to a greater extent than has perhaps any one else at present in this country, I venture to place before your readers a few remarks which suggest themselves to me after making numerous tests on different varieties of starch and comparisons with other preparations for which diastasic power is claimed, as also after having had frequent discussions with medical men who have used Taka-diastase practically im amylaceous dyspepsia—a form of dyspepsia which is said to constitute about three-fourths of the indigestion due to deficiency in the quality or quantity of the digestive secretions generally.

When making demonstrations fn this connection before some members of the British Medical Association in the summer of 1895, I was impressed by the interest which was manifested in the treatment of mal-digestion or want of due assimilation of starchy foods. This interest is of comparatively recent growth, as is much of the knowledge in regard to the causes which lead to the production of the condition referred to; in fact, not many years ago there was hardly any serious attempt at differentiation in the diagnosis or treatment of what is called "indigestion." In the minds of many persons who have studied the questions connected with this subject there still exist certain misconceptions which prevent a clear understanding of the difficulties that present themselves. Dr. R. G. Eccles states that "one of the gravest mistakes we have made in the past has been in supposing that the stomach only had to deal with proteids—that within it only albumen, casein, gluten, and the like were disposed of. The fact is that the very first important act performed in the stomach is the digesting of starch. All gluten reaches it enveloped in an insoluble coating like the sugar or gelatin on the outside of a pill. To make way for the digestion of proteids this must be rendered soluble and removed. To do so, starch-digesting has to be the first task of the stomach; following it comes proteid digestion." He refers to the belief once entertained almost universally that conversion of the trifling amount of starch acted on during the process of mastication was all the duty saliva performed, and then states that "Ptyalin was never intended by Nature to do its work in the mouth." The fact is that, under normal conditions, the contents of the stomach may not contain any free hydrochloric ecid until after the expiration of half-an-hour to an hour from the time the food is ingested.

The claim made for Taka-diastase is that it will convert one hundred times its own weight of starch into assimilable material in ten minutes, and, as it is an enzym or unorganised ferment (the action of which might theoretically be regarded as infinite), it might be considered to proceed indefinitely if the products of its conversion were removed as formed. But Sir William Roberts states that diastase is no exception to the rule in physics, that energy in performing work is expended and finally exhausted. Nevertheless Taka-diastase converts over 1500 times its own weight of starch in three hours.

It may be argued that as digestion of starch is not likely to proceed for three hours in the stomach it is not necessary, in considering digestion, to estimate the power of a diastase during this period of time; but we have to bear in mind that, as digestion proceeds, the pylorus relaxes, allowing the passage to the intestine of finely divided particles and of such fluids as may not have been absorbed in the stomach; and as the diastase passing with such material in the early stage of digestion may still be active (as a matter of fact Taka-diastase converts starch even in a slightly acid medium), we have no reason to conclude that the action does not, under such circumstances, proceed in the intestines, where any acid may be expected to be gradually neutralised before the alkaline condition asserts itself.

About two years ago I witnessed many experiments performed by Mr. Takamine (assisted by Mr. E. V. Hitch, of Chicago) in regard to the action of Taka-diastase on different varieties of starch, as also in comparison with other diastases. The tests were almost entirely confined to the action of the diastase from the commencement of the process to the end of from twenty to thirty minutes only (that being considered a satisfactory period in which to make the tests), during which time Taka-diastase was found to be considerably more active than any of the numerous preparations with which comparison was made and for which diastasic potency was claimed. Here I would remark in regard to tests of diastase *in vitro* that there is no reason to consider that conversion to the achromic point, although useful as a means of comparison, must occur before absorption takes place in normal digestion. Sir William Roberts states that "the dextrines, even those coloured by iodine, are highly diffusible," and that complete conversion would require that the material should retrace its steps to some extent in being converted into glycogen.—I am, &c.,

Thomas Christie.

Chepstow Place, W., May 10, 1897.

BENDING ALUMINIUM TUBES.

To the Editor of the Chemical News.

Sir,—In the paper by Mr. T. H. Norton on "The Use of Aluminum for Condensers" (Chemical News, vol. lxxv., p. 221) it is suggested that to bend the aluminium tube it should be filled with lead, which is afterwards melted out. Would not resin or shellac be more easily manipulated, while the traces left in the tube could be readily removed by alcohol or some other solvent? The cycle-makers, in bending steel tubes up to 1 in. diameter, habitually use resin for filling the tube previous to bending.

I should like to ask why American writers usually speak of "alumin*um*." The name "aluminium" has had a long and honourable career, and it seems a pity, as Curran would have said, to knock out one of its *i*'s. The oxide is, and has always been, called alumina; but no one, I believe, has proposed the names "sod*um*" and "potass*um*" because *their* oxides are called soda and potassa.—I am, &c.,

E. G. Bryant.

King's School, Pontefract, May 8, 1897,

Death of Mr. M. Carey Lea.—We regret to hear of the death of Mr. Carey Lea, at Philadelphia. The deceased was well known to the readers of the Chemical News in connection with his researches on the allotropic forms of silver and the photo-sensitive compounds of this metal.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Bulletin de la Société Chimique de Paris.
Series 3, vols. xvii. and xviii., No. 7.

Apparatus for the Estimation of Free Nitrogen in Purified Coal-gas.—G. Arth.—The author has arranged his apparatus in such a manner as to enable him to collect and measure large quantities of nitrogen gas, thereby considerably reducing the effect of *errors of observation.* The apparatus, which appears to give excellent results, may be briefly described as a kind of combination of Crum's nitrometer with Frankland's gas measuring apparatus, but cannot be properly understood without the accompanying diagram.

New Fractionation Apparatus for Use in Industrial Laboratories.—A. Tixier.—This apparatus is an improvement on previous forms, but requires the accompanying diagram.

Cryoscopic Measurements. — A. Ponsot. — The author has made a number of experiments to determine the congelation-point of solutions of cane-sugar of various strengths. The thermometer used was an extremely delicate one, each principal division being equal to 0·5 m.m.; but by very fine subdivision, and using a glass magnifying fifty times, and allowing corrections for pressure and calibration, the final readings, he claims, can be reduced to 1/20,000th of a degree Centigrade.

Ethylisoamylamines.—Aug. Durand.— These were obtained by the action of iodide of ethyl on isoamylamine. By mixing them carefully in certain proportions a pasty mass is formed, composed of the iodides of the primary, secondary, and tertiary bases. This mass is dissolved in water, boiled, and a solution of potash added, then boiled again; the distillate is received in an excess of dilute hydrochloric acid. From this, the secondary base—that is to say, ethylisoamylamine—can be separated in the form of its nitroso-derivative by adding nitrite of soda dissolved in a small quantity of water. This is, after purification, treated in various manners. Several of its compounds are here described, such as chloroplatinate of ethylisoamylamine, chloroaurate of ethylisoamylamine, oxalate of ethylisoamylamine, &c.

Anethol and Homologues of Anethol.—Ch. Moureu and A. Chauvet.—The authors have succeeded, with great ease, in preparing two homologues of anethol, viz., parabutenylanisol and paraisopentenylanisol.

Yellow Colouring-matter derived from Dinitrofluorescine.—F. Reverdin.—A paste is made of 100 grms. of water and 100 grms. of dinitrofluorescine; to this is added, while agitating, 75 c.c. of 21 per cent ammonia. The mixture dissolves at once with an increase of temperature; it then gradually commences to thicken, till after a few hours it forms a solid mass. It is then triturated with 125 c.c. of salt water, filtered; then, after well draining, the product—an ammoniacal salt of the colouring material—is converted into an acid by weak hydrochloric acid. It is filtered, dried, and then digested for some hours at the ordinary temperature with 10 parts of acetone, in which it is completely insoluble, but which frees it from several impurities and by-products which accompany it. After filtering and drying it is converted into a salt of soda easily soluble in water. About 70 grms. of this salt are obtained. The first filtrate contains an orange colouring-matter, which no longer gives the reactions of dinitrofluorescine, but which, by treating with bromine, gives a red colouring-matter, similar to scarlet.

Some Derivatives of Furfurane.—P. Freundler.—Several derivatives of furfurane have not yet been described, in spite of the interest there would be in comparing them with the corresponding benzenic derivatives. Among these are *furfurane-amine* or *furane-amine*. The best method of preparing this body was found to be by the nitrification of furfurane and the reduction of the nitrified derivative. This will be fully described in a future paper, the present one being devoted to the action of the hypobromites and of hydrazin on the pyromucic derivatives.

Distillation of very Dilute Mixtures of Ethylic Alcohol and Water. Application to the Estimation of Alcoholic Solutions containing only 1/3000th to 1/10,000th part.—M. Nicloux and L. Baudeur.—This paper will be inserted in full.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxviii., No. 1.

This issue contains no chemical matter.

NOTES AND QUERIES.

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

Wells' Patent Continuous Cooling Process.—Will some correspondent kindly inform me who are the proprietors of this process. —Enquirer.

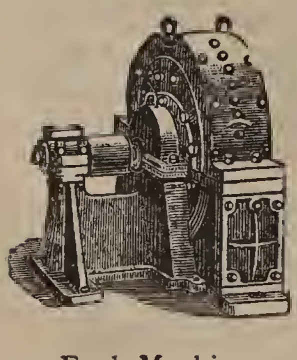
MEETINGS FOR THE WEEK.

Monday, 17th.—Society of Arts, 8. (Cantor Lectures). "Design in Lettering," by Lewis Foreman Day.

Wednesday, 19th.—Society of Arts, 8. "London Water Supply," by Dr. P. F. Frankland, F.R.S.

Thursday, 20th.—Chemical, 8. "Theory of Osmotic Pressure and the Hypothesis of Electrolytic Dissociation;" "Molecular Rotation of Optically Active Salts;" Heats of Neutralisation of Acids and Bases in Dilute Aqueous Solution;" by Holland Crompton, "The Platinum-Silver Alloys—their Solubility in Nitric Acid," by John Spiller. "A Comparative Crystallographical Study of the Normal Selenates of Potassium, Rubidium, and Cæsium," by A. E. Tutton.

— Society of Arts, 4.30. "Kerman and Persian Beluchistan, with special reference to the Journeys of Alexander the Great and Marco Polo," by Capt. P. Molesworth Sykes.



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THE CHEMICAL NEWS.

Vol. LXXV., No. 1956.

ON THE REACTIONS BETWEEN LEAD AND THE OXIDES OF SULPHUR.*

By HENRY C. JENKINS and ERNEST A. SMITH,
Royal College of Science, London.

The authors of this paper draw attention to the fact, previously noticed by one of them, that when molten lead is exposed at high temperatures to the action of a current of sulphur dioxide, both lead sulphide and lead oxide are found in the product.

The paper is the account of a research undertaken with a view to ascertain the precise reaction which takes place under these conditions, as well as to see whether it did not account for some anomalies that are met with whenever a full explanation of the chemistry of lead smelting in the reverberatory furnace has been attempted.

Mr. Hannay had sought (Chemical News, vol. lxx., 1894, pp. 43 to 45) to explain these anomalies by the assumption that a volatile body, PbS_2O_2, had been formed. He based the evidence for the existence of this body, that could not be isolated, on the observation that in some experiments he had conducted, by passing air over heated galena, he only obtained one-half of the lead in the metallic state according to an equation—

$$2PbS + O_2 = Pb + PbS_2O_2.$$

The authors, on repeating this experiment with air and with oxygen, find that the amount of lead that is volatilised in such an operation does not bear any definite ratio to the total amount of lead present, but can be made to vary greatly, and is entirely dependent upon the velocity of the current of air employed. They, therefore, submit that there is now no evidence of any such reaction, the ratio found by Mr. Hannay being the result of some accidental coincidence of experimental conditions.

In continuing the research, the authors found that, on heating a mixture of lead sulphide and lead sulphate in a vacuum, a reaction occurred having sulphur dioxide as one of the products; they also found that the amount of residual lead sulphide and oxide was dependent on the duration of the experiment as well as on the temperatures. They then proceeded to test separately the pairs of bodies supposed to be present, with a view to discover whether secondary or reversed reactions occurred. On heating lead with lead sulphate, they always obtained lead sulphide in the product, in amounts varying with the temperature of the experiment and the length of time that it occupied.

On heating together lead and sulphur dioxide, they found that at moderately elevated temperatures—300° to 400° C.—lead sulphide and sulphuric anhydride are formed in each other's presence, and that this leads to the formation first of lead oxide and then of lead sulphate. The action is represented more or less completely by the equation—

$$Pb + 3SO_2 = PbS + 2SO_3,$$
$$Pb + 2SO_3 = PbSO_4 + SO_2,$$

or more simply—

$$2Pb + 2SO_2 = PbS + PbSO_4,$$

the main condition determining the relative amounts of the products being the temperature at which the experiment is performed under similar conditions.

One of the authors is continuing the investigation of the exact conditions of the equilibrium, as well as its extension to other metals.

The last of these equations occurring in the presence of excess of sulphur dioxide is the exact inverse of one of the main reactions of lead smelting, as stated by Dr. Percy, and in which reaction a supply of air is required to sweep away the sulphur dioxide as soon as it is liberated. The authors submit that, as the new equations quite account for the anomalies to which attention has been drawn, there is now no reason whatever to doubt that the reactions given by Dr. Percy,—

$$Pb + PbSO_4 = 2PbO + SO_2,$$
$$PbS + PbSO_4 = 2Pb + 2SO_2,$$

as well as—

$$PbS + 2PbO = 3Pb + SO_2,$$

do actually take place, and form the basis of the metallurgy of lead.

THE ESTIMATION OF CARBON IN FERRO-CHROME.

By H. BREARLEY and R. L. LEFFLER, F.C.S.

When, three or four years ago, the need to estimate the percentage of carbon in a sample of ferro-chrome arose, the method usually adopted for silica spiegels, and such alloys as are unacted upon by copper solutions,—viz., combustion of the powdered sample with CuO,—was resorted to. The results obtained were low, very low. In a neighbouring laboratory it was customary to grind the ferro-chrome and CuO together, burn, re-grind, and burn again. The tediousness of the method, together with the errors of weighing and re-weighing, would make the method an unreliable one in case the alloy was completely decarbonised. But with such heat as we could get, from an ordinary Bunsen combustion furnace, only about 50 per cent of the contained carbon could be extracted after grinding and re-grinding six or seven times. By substituting lead chromate for copper oxide, and prolonging the heat for two hours or so, much better results were obtained. In fact, by re-grinding and re-burning three or four times, nearly the whole of the carbon was eliminated. But this method would not serve when samples were regularly received.

As many periodicals and text-books as were available were searched for a less tedious and more accurate method. A method by Fresenius and Hintz (Chem. News, lxi., 65)—treatment with chlorine gas and combustion of the carbonaceous residue — stood solitary. Later, Arnold ("Steel Works Anal.," p. 213) published a method which will be referred to later on. Enquiries were made from works' chemists and laboratory instructors as to their respective *modus operandi*, but all either declared their lack of a satisfactory method or preferred to say nothing of the one they had. The following experiments represent the attempts made, at intervals during the last few years, to find an accurate method giving consistent results with as little trouble as possible.

Throughout the ferro-chrome used had been ground to a fine powder in the agate mortar. Leffler shows below that this excessive fineness is sometimes unnecessary.

Of the variable results obtained by simply heating, those were highest which had been most highly heated. This naturally suggested raising the temperature beyond that attainable with the ordinary furnace arrangement. The part of the tube, therefore, containing the porcelain boat was made hotter by means of a bowpipe flame urged by a foot-bellows. The results were higher, more consistent, and more readily obtained.

For clearness sake the method had better be briefly described:—Half to 1 grm. finely-powdered ferro-chrome mixed with 10 grms. lead chromate, which had been previously fused and re-ground to a powder: place in

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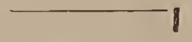
* Abstract of Paper read before the Chemical Society, May 6, 1897.

porcelain boat and burn in porcelain combustion-tube packed with CuO, &c. In principle there is of course nothing new in this method ; it is rather in the matter of accessories and manipulation that the advantage lies.

When the tube is heated by the blowpipe, the mixture in the boat melts and evolves carbon dioxide, sometimes so vigorously as to spirt over the side or strike the roof of the tube. Even if the boat be withdrawn before cooling, the tube will rarely bear re-heating. A few tubes lost this way led to the adoption of glass tubes. No simple tube obtainable would stand the necessary heat, and many varieties—including Schott's Jena glass—were tried. The tubes were covered with asbestos millboard, 1-32nd of an inch or so thick. This plan is adopted with porcelain tubes for ordinary combustions. There is much less danger of fracture on account of sudden heating, and in the case of the best Bohemian glass tubes finally selected it preserved them from bending when sustained at an almost white heat. Over the part which had been strongly heated the surface was pitted with small holes. In places the asbestos was fused into the glass. If the tube was otherwise preserved it invariably cracked on re-heating, on account of this asbestos, so that either the boat had to be changed with the tube at red heat, or a strip of paper had to be wound round the tube before laying over the wetted asbestos. The paper burned, of course, but left a protective covering of ash.

To prevent the boat sticking to the inside of the tube it was covered with a thin piece of millboard and a thicker piece lined the inside, so that the fusion might be removed and the boat preserved. A cover shaped so—



was laid on the top to prevent the spirting melt striking the roof of the tube. It is made to bend over the end of the boat, so that it may not easily be brushed off in passing along the tube. The boat with its fittings is strongly ignited before use.

The lead chromate and sample were mixed by shaking together in a weighing tube. The long shape with wide-stoppered neck is most convenient. A little asbestos on the finger-tip removes the last traces cleanly and effectively.

When the blowpipe has raised the temperature of the tube the gas bubbles through the potash bulb more and more quickly, until the bubbles can scarcely be distinguished. When only half a grm. of the sample is taken, this can be fairly well controlled by judicious heating; but with larger amounts—say from 1 to 1½ grms.—the evolution of gas is beyond control. On unfortunate occasions it is almost vigorous enough to shatter the bulb. After the storm comes the calm. The contents of the boat now greedily absorb oxygen, and unless the supply be quickened the KHO may be pulled back; the soft glass tube will certainly be crushed on to the boat, wrapping it completely round.

The most satisfactory way of showing that the method used was a reliable one was to repeat assays with varying weights of the ferro-chrome.

Two pieces of apparatus, shown in figs. 1 and 2, were used to control the rush of evolved gases. Fig. 1 was used most largely, because it was to hand and already fitted up. It is indeed Stead's "Gas Sampler," and is fully described in Mawson and Swan's Catalogue. One of the lower taps should be replaced by a larger one. Fig. 2 works automatically.

Let the tube be heated by the furnace in the ordinary way, then heat the locality of the boat with the blowpipe. The reaction runs the length of the boat like a train of gunpowder. The "controller" being attached as shown, and the mercury arranged as though a sample of gas was being taken, J and K are opened. With the hand on L, the potash bulb is watched. As the bubbling becomes more and more rapid the O is shut off, the tap (L) suitably turned, and the rush accommodated in G. (A plug of asbestos fibre should have been pushed in after the boat, to prevent a cloud of lead oxide being drawn along the tube and into the "controller"). The oxygen is re-passed, so as to supply the vigorous absorption in the boat and keep a gentle stream through the bulb. When the absorption in the boat is finished, the gases are forced from G by turning the taps and raising H. The connections are swept out by opening M.

There is no reason why a porcelain tube should not be used over and over again if the noted precautions are taken. The best glass tubes only serve three or four times.

The operation is not so long as the description might suggest. With samples powdered and tubes already packed, four samples have been weighed, mixed, boated, and burned in five hours. Such arrangements, partly existing in most metallurgical laboratories, we have used for nearly two years.

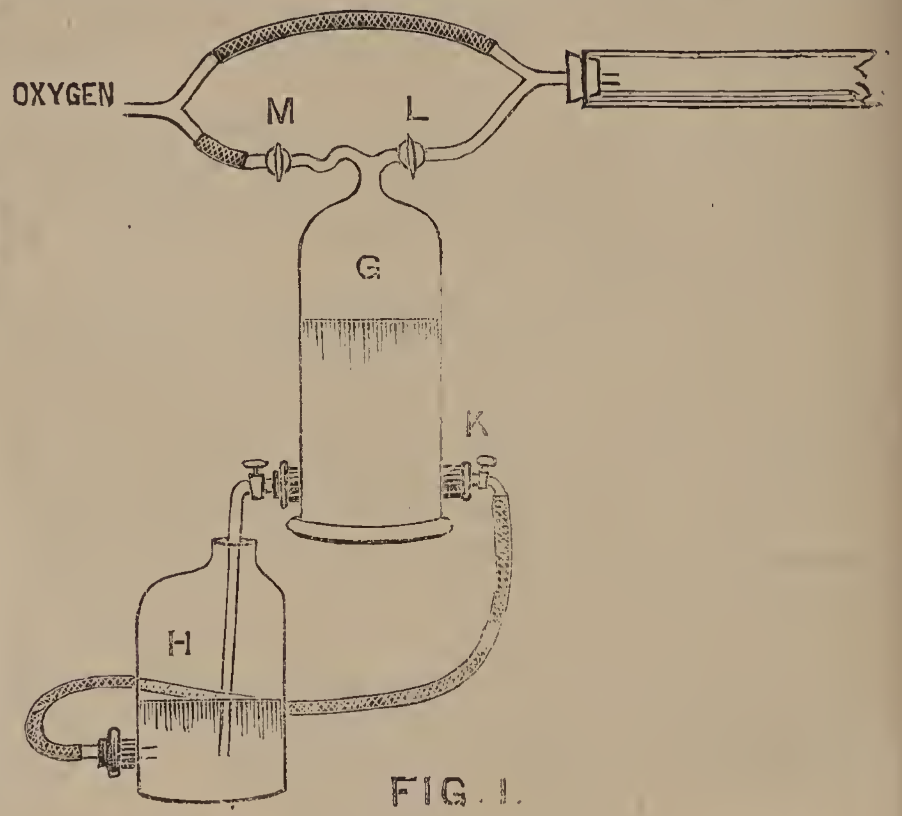


FIG. 1.

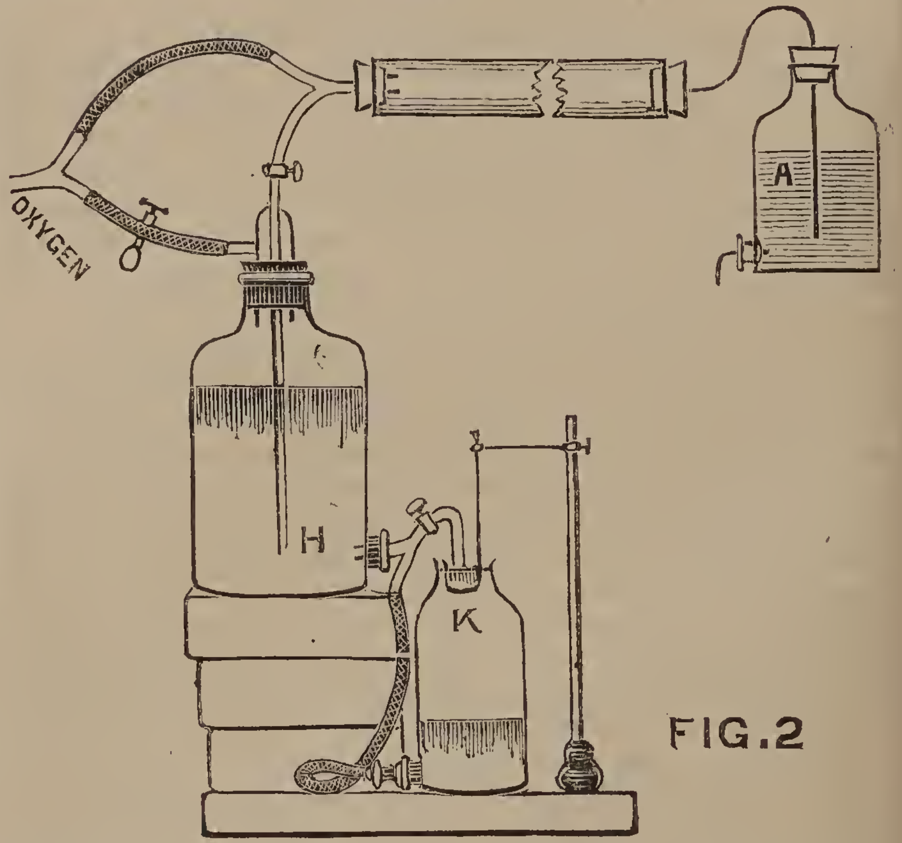


FIG. 2

We are induced to notice fig. 2 as an alternative to fig. 1, in the hope that it may serve some other purpose. Neither are needed in the operations to be described later. It is necessary to note that the combustion tube, &c., is aspirated by an arrangement indicated at A (fully described Chem. News, lxxiv., 225), which ensures constant pressure. The two bottles and tubes figured are in principle precisely the same. The small mercury cup, K, prevents any back rush of air, and serves to make the final adjustment of pressures. The furnace is heated, oxygen passed, and aspirator attached as usual. By means of K, or its in-dipping tube, the aspiration due to the fall of mercury is made, so that gas, from the combustion-tube, is just on the point of being drawn through H. Any increase of pressure in the tube, such as would be caused by the reaction in the boat, causes mercury to flow from K, and provides itself with room in the upper bottle. The gases are re-passed through the combustion-tube by admitting oxygen and running the mercury below the level of H, and then sweeping the whole out by passing successively oxygen and air.

The following assays were made with lead chromate, as described on a sample marked 10,543, which contained 61 per cent of chromium. Those marked with an asterisk were done a year ago when the sample was received. The rest were done for this paper.

	I.	II.	
0·5 grm. taken.	8·80*	8·86*	per cent.
0·75 ,,	8·84	—	,,
1·00 ,,	8·86*	8·83	,,
1·25 ,,	8·90	—	,,
1·50 ,,	8·91	—	,,

When copper oxide is substituted for lead chromate more heat is needed; there is less spirting, and not so violent a reaction. The fusion has the appearance of a piece of gas coke. The general phenomena are similar to those noticed with chromate.

Results on same sample (10,543) are :—

0·75 grm. taken.	8·89 per cent.
1·00 ,,	8·89 ,,
1·25 ,,	8·80 ,,

Other metallic oxides were tried, more from curiosity than from hope of finding more suitable reagents than copper oxide or lead chromate. In 1859 a patent was taken out for the production of malleable iron by heating with zinc oxide, so long as the iron contained appreciable amounts of carbon metallic zinc, distilled over but stopped when the decarbonisation was complete. With this recommendation zinc oxide was tried, but it could not be made to decarbonise the ferro-chrome within reasonable time at such temperature as could be obtained with our blowpipe.

It need not be argued that it would be an advantage if the combustion could be completed at ordinary furnace temperatures, and in a becoming manner, without the use of any rush controlling arrangement. The use of lead peroxide makes this possible. In this operation the boat need not be covered with asbestos on the inside. The charged boat is placed in the *cool* combustion-tube. The taps are burned separately and slowly, so as to gradually liberate the oxygen from the PbO_2. The mixture fuses, and there is the same need to quicken the oxygen to supply the absorption in the boat, but all else goes on with comparative quietness and at ordinary temperatures. Some results on 10,543 with 10 grms. PbO_2 are :—

0·75 grm. taken.	8·87 per cent.
1·00 ,,	8·86 ,,
1·25 ,,	8·87 ,,

This method we prefer no less on account of accuracy than convenience.

Lead protoxide did not give satisfactory results. In all cases a blank combustion had to be made, but with protoxide the blank was very large and very variable. The sample used was made from the peroxide, but gave a much larger blank, which is most likely due to its well-known property of absorbing carbon dioxide from the air. Very much the same things may be said of the fused variety litharge; although, probably a coincidence, two very good results were obtained.

I have only a mere acquaintance with other methods than those described. Volatilisation in a stream of chlorine, and subsequent combustion of the carbonaceous residue, does not seem to have found much favour. This may be partly due to the fact that the apparatus for such an operation is not in frequent use in steel works' laboratories, and whatever virtue the method may have is more than counterbalanced by the inconvenience of putting things out of joint for a day or two.

Professor Arnold's method has been largely worked by Leffler, who also kindly furnishes other useful information.

The method recommended by Prof. Arnold consists in placing the sample, intimately mixed with lead chromate, in a glass combustion tube between asbestos plugs, and subjecting to prolonged heating in a stream of moist oxygen. The method has been repeatedly tried in asbestos-covered tubes; no naked tube obtainable would stand the ordinary furnace heat, and, unfortunately, Prof, Arnold limits himself to "very hard glass" tubes. Samples kept at a bright red heat from two to four and a half hours only yielded about fifty per cent of the total carbon obtainable. (Found, 4·44, 4·57, 4·77, on a sample containing 8·69 per cent C). But if the temperature of this arrangement was raised by the blowpipe, an additional amount of carbon, bringing the results up to the known percentage, was obtained. Occasionally the oxide of lead formed acted severely on the glass. A current of moist oxygen seemed to have no more effect than a dry one; and, theoretically at least, it seems to be a disadvantage in this way. The oxide of lead formed by the reaction between the reduced lead and oxygen might conceivably be—and in some cases, indeed, was—carried to the far end of the tube. These traces, if dry, may absorb no appreciable amount of CO_2; but the hydrate of lead protoxide, made possible by the deposited moisture, very readily absorbs that gas.

It is generally stated that the ferro-chrome used should be in the finest possible state of division. Grinding in the agate mortar is a painful job, and the ease with which some of the reagents mentioned above decomposed the ferro-chrome suggested that this state of "impalpable flour" was sometimes unnecessary. A sample was therefore prepared in three states of division.

1. Passing through wire sieve of 30 meshes to the inch but not through 60.
2. Through 60 but not 90.
3. Through a 90.

The sample contained 8·69 per cent C.

Sample through—	Per cent of carbon with—		
	$PbCrO_4$.	CuO.	PbO_2.
30 not 60	3·76	1·02	7·58
60 ,, 90	8·60	8·68	8 67

In the 30, with $PbCrO_4$ and CuO, the grains of the ferro-chrome were distinctly visible after the combustion; the CuO, too, was not even fritted. With this comparative coarseness of sample, the reaction was noticeably less violent. It was not considered necessary to make assays on the 90 after obtaining such accurate results as are shown with 60. Of course, the assays with $PbCrO_4$ and CuO were blasted, and all of them carried out as previously mentioned. The following are examples showing that the carbon percentage is very variable :—

C.	Cu.
5·82	89·46
8·40	60·02
9·20	60·73
9·39	61·84
10·18	60·25
11·22	67·24

The Laboratory,
Messrs. Thos. Firth and Sons, Lim.,
Sheffield.

CONTRIBUTION TO THE STUDY OF HYPONITROUS ACID.*

By A. HAUTZSCH and A. L. KAUFMANN.

(Continued from p. 233).

Free Hyponitrous Acid.

Hyponitrous acid was first obtained in the free state in aqueous solution by Van der Plaats (*Berichte*, vol. x., p. 1507). It has also been studied by Thum (Wiener, *Monatsh.*, vol. xiv., p. 294). About the same time as we did, Tanatar obtained it in an oily state, probably still containing water. To obtain this acid in the solid state it is necessary to proceed as follows:—A current of hydrochloric acid gas, dried with the greatest care, is passed through ether absolutely free from water. To this etherised hydrochloric acid, perfectly dry hyponitrite of silver is added little by little. The solution must be kept cool, and special precautions must be taken to prevent the access of moisture. Hyponitrite of silver is added until the last portion added no longer loses its colour; that is to say, until the etherised solution no longer contains any free hydrochloric acid. This solution is then rapidly filtered on a dry filter, and placed in an exsiccator *in vacuo*. Moisture and acid fumes must be guarded against with the utmost care, and for this reason a crucible containing solid caustic potash should be placed in the exsiccator. The evaporation of the ether can be accelerated by passing through the etherised solution a current of air which has been first passed through two wash bottles—the first containing a solution of caustic potash, the second sulphuric acid—and then through a tube containing phosphoric anhydride. It is advisable to keep the exsiccator in a refrigerating mixture; the ether then evaporates, leaving the hyponitrous acid in the form of white scales.

Hyponitrous acid is very explosive. When absolutely dry it decomposes spontaneously; the decomposition is accelerated by the presence of acid fumes, but retarded by cold. Simply touching it with a glass rod is enough to cause its decomposition. Contact with solid caustic potash is sufficient to cause sudden decomposition accompanied by ignition.

Hyponitrous acid is not only very soluble in water, but it also dissolves with great readiness in alcohol, ether, chloroform, and benzene.

We have not been able to carry out the analysis of this acid. So long as there is any ether present, the crystals can be preserved for some time, but as soon as they become quite dry, they detonate even at 6° without any apparent cause.

We have, however, been able to show, by qualitative reactions, that the substance obtained was really hyponitrous acid. We placed some of the crystals on a plate of porous porcelain, and the moment they became dry they were slid off into a watch-glass containing iced water. The solution gave, on the addition of nitrate of silver, the characteristic hyponitrite of silver. The aqueous residue obtained by the decomposition of the crystals also gives the same reaction.

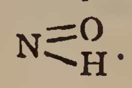
The water formed by the decomposition of hyponitrous acid, according to the following equation,—

$$HON,NOH = H_2O + N_2O,$$

dissolves a portion of the acid, and thus saves it from decomposition.

In aqueous solution, hyponitrous acid is much more stable than in the anhydrous state. Although, as will be shown further on, the acid does decompose rapidly enough when in aqueous solution at 25°, it is still sufficiently stable at 0° to enable one to determine its molecular weight by the cryoscopic method.

Determination of the Molecular Weight.—For this operation we used pure water, whose freezing-point had been determined in Beckmann's apparatus, and with it we prepared a one-sixth normal solution of hydrochloric acid, by passing through it a current of hydrochloric acid gas and diluting to the proper point. 200 c.c. of this solution, which contained 0·1217 grm. of HCl, lowered the freezing-point by 0·625° (mean of five experiments). Without removing the Beckmann apparatus from the freezing mixture, we added a solution of hyponitrite in excess. The one-sixth normal solution thus obtained (0·1035 grm. in 20 c.c. of water) produced a lowering of the freezing-point of only 0·167° (mean of three observations). The lowering of the congelation-point produced by equivalent quantities of hydrochloric acid and hyponitrous acid, are in the proportion of 1 to 3·8. As at this degree of dilution (the molecular quantity in 6000 litres of water) hydrochloric acid is completely dissociated, and has a molecular weight of 18·4, and a number of ions = 2; the substitution of $H_2N_2O_2$ for $HCl = (2H + 2Cl)$ ought to result in the reduction of the number of molecules to one quarter. This is only possible if the hyponitrous acid, very much diluted (molecular quantity in 3000 litres of water), does not appreciably dissociate itself into its ions; that is to say, if it is a very weak acid, that which our experiments on its conductivity fully confirm. We have then:—Molecular weight: found, 59; theory, $H_2N_2O_2$, 62. This result proves that, under the conditions we have just indicated, hyponitrous acid does not exist in the state of a simple molecule—



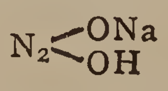
$$N{<}^{=O}_{-H}.$$

Action of Alkalis.—If hyponitrous acid closely resembles carbonic acid by its ready dissociability, the analogy between these two acids is shown in a still more striking manner in their titration by means of alkaline solutions, using phenolphthalein as indicator. Thus, as Thum as already shown, the titration indicates only half the amount of acid present. The following experiment leaves no doubt on the subject:—

To 20 c.c. of a decinormal solution of hydrochloric acid hyponitrite of silver was added in excess. The hyponitrous acid liberated was immediately neutralised at 0° by a titrated solution of baryta, using phenolphthalein as indicator.

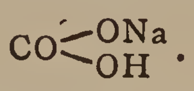
		Theory.	
		BaN_2O_2.	$BaH.N_2O_2$.
Solution of baryta used,	5 c.c. 50	10 c.c. 9	3 c.c. 45

Monosodic hyponitrite, like monosodic carbonate, is neutral to phenolphthalein. Thus, this analogy exists:—



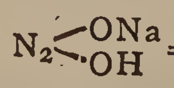
$$N_2{<}^{ONa}_{OH}$$

and



$$CO{<}^{ONa}_{OH}.$$

Further, acid hyponitrite is not stable in aqueous solution. If, in a solution of hyponitrous acid titrated with an alkaline solution until the red colouration of phenolphthalein shows, we cause the colour to disappear by adding a drop of hydrochloric acid, and let it stand, the red colouration will reappear. The acid hyponitrite of soda decomposes very slowly into protoxide of nitrogen and caustic soda, according to the equation—



$$N_2{<}^{ONa}_{OH} = N_2O + NaOH.$$

We can follow this decomposition by determining the increase of the alkalinity of the solution. Thus, for example, in one experiment 43 per cent of the amount of hyponitrous acid which was originally present in the solution in the state of an acid salt was decomposed after eighteen hours at the ordinary temperature.

Reactions of Hyponitrous Acid.—Contrary to the assertion of Van der Plaats, solutions of hyponitrous acid do not decompose iodate of potassium, liberating iodine (Thum). We found that on adding to a freshly prepared solution of free hyponitrous acid a solution of potassic

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* *Moniteur Scientifique*, vol. xi., p. 336, May, 1897.

iodide and starch, slightly acidulated with acetic acid, the blue colour does not appear at first, but after the lapse of some time the liquid becomes blue, and the colour continues to become more and more intense. A further remarkable thing is, that on adding hyponitrite of silver to cold concentrated sulphuric acid, and adding a little diphenylamine, a very intense blue colouration is produced. With a solution of ferrous sulphate a brown ring is obtained. These reactions are characteristic of nitrous and nitric acids. We shall refer to them again later on, when discussing the decomposition of hyponitrous acid.

Hyponitrite of Ammonia, H_4NOH,NHO.—This salt was hitherto unknown. Zorn observed that the solution obtained by the reaction of hyponitrite of silver on a solution of chloride of ammonium, which should contain hyponitrite of ammonium, decomposed very rapidly at the ordinary temperature, with evolution of gas. However, it is possible to isolate an ammoniacal salt by passing a current of well-dried ammonia gas through an etheric solution of hyponitrous acid, as already described. After a very short time the salt is precipitated in the form of a white mass. It is filtered rapidly, washed with ether, and dried on plates of porous porcelain.

Hyponitrite of ammonium melts about 64° to 65°, decomposing with violence. It is easily soluble in water, giving an alkaline reaction. But it has not been recovered either from its aqueous or alcoholic solutions, even when working *in vacuo*. The solutions leave no residue whatever on evaporation. Jackson's assertion (*Berichte*, vol. xxvii., R., p. 562) that hyponitrite of ammonium could be obtained in beautiful crystals by the reaction of hyponitrite of silver on an alcoholic solution of sulphide of ammonium is evidently founded on an error. In the solid state this substance decomposes slowly at ordinary temperatures into ammonia, water, and protoxide of nitrogen, and therefore cannot be brought to a constant weight. It is for this reason that exact analytical results cannot be obtained. The ammonia has been estimated by decomposing the freshly-prepared and rapidly weighed salt (taking no note of the loss of weight) by caustic potash, absorbing the gas in a normal solution of sulphuric acid, and titrating the excess of acid. Three estimations carried out on three portions of one and the same sample gave the following results:—

	Grm.		Per cent.	
I.	0·0560	of hyponitrite of ammonia gave	20·34	NH_3.
II.	0·0947	,, ,, ,,	20·10	,,
III.	0·0631	,, ,, ,,	19·94	,,

Theory:—

$NH_4HN_2O_2$ .. .. 25·52 per cent

$(NH_4)_2N_2O_2$ .. .. 35·42 ,,

We did not continue our experiments on the estimation of the protoxide of nitrogen by decomposing the salt in the eudiometer with concentrated sulphuric acid. Our first attempt resulted in a violent explosion, which blew the apparatus all to pieces.

The spontaneous decomposition of hyponitrite of ammonia was studied by determining the loss of weight that the salt sustained when left in the exsiccator *in vacuo*. The following are some of the results obtained:—

Time. Hours.	Weight. Grm.	Loss of weight. Per cent.
0	0·1057	—
87	0·0214	79·75
119	0·0169	84·0
167	0·0136	87·13

This decomposition of acid hyponitrite of ammonia resembles that of bicarbonate of ammonia, only the latter is more stable. We have not succeeded in preparing the neutral hyponitrite of ammonia, even when passing a current of ammonia through hyponitrous acid for a considerable time. Here, again, the analogy existing between hyponitrous acid and carbonic acid is evident; for, as is well known, the neutral carbonate of ammonia is rapidly transformed into acid carbonate when exposed to the air.

(To be continued).

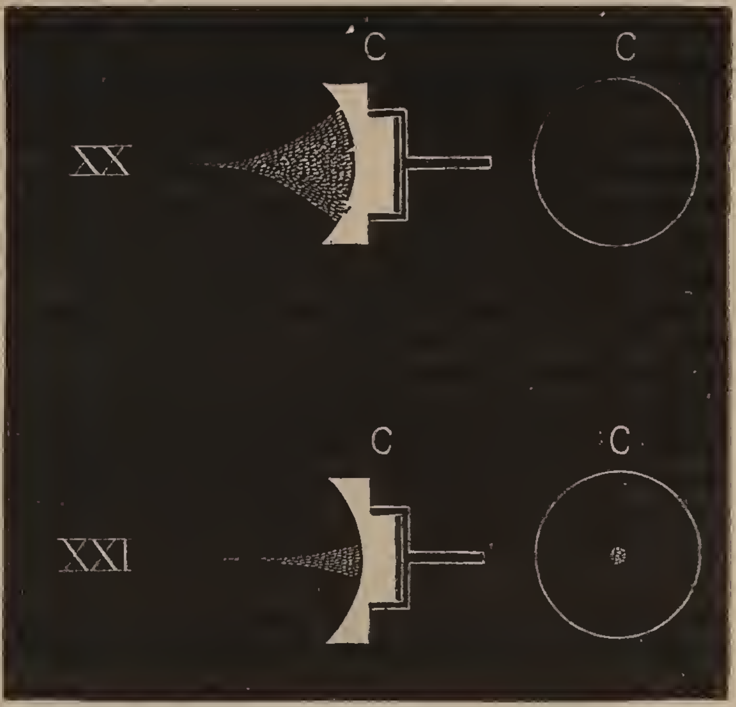
SOME EXPERIMENTS WITH CATHODE RAYS.*

By A. C. C. SWINTON.

(Concluded from p. 236).

The Convergent Cone at Higher Vacuo.

As has been mentioned, the carbon anti-cathode screen was found useless for investigating the convergent cone of cathode rays at anything but a very low vacuum, by the reason of the well-known difficulty in getting any discharge to pass when the distance between the electrodes is less than the thickness of the dark space, and for the further reason that if the anti-cathode screen was not connected to the anode, it became itself negatively charged and acted as an additional cathode when brought into the space between the cathode and the focus.



Under these circumstances it was thought that possibly some additional information might be obtained with regard to the form of the convergent cone at high vacua, by making the concave cathode itself of carbon. A tube was therefore constructed having a concave carbon cathode, the diameter of which was 1 inch, and the radius of curvature 0·75 inch. The appearance of the cathode with this tube is shown for a fairly high vacuum in fig. 20, in which the cathode itself is shown in section, so as to let the form of the discharge be better seen. As will be observed under this condition of vacuum, which was too high to show any divergent cone, the cone of convergent rays appears to be contracted in diameter at its base, and to come off from the central portion of the cathode only, the remaining surface of the cathode being apparently inactive. This was found to be still more the case at higher vacua, as will be seen from fig. 21, which shows in a similar manner the form of the cathode discharge in a tube exhausted to a very high vacuum. In this case, as will be observed, the whole of the cathode rays appear to come off from a very small spot in the centre of the cathode. Further, that this small spot is, at any rate, the source of most, if not all, activity, was evident from the fact that it became luminescent exactly in the same manner, but in a less degree, than had previously been

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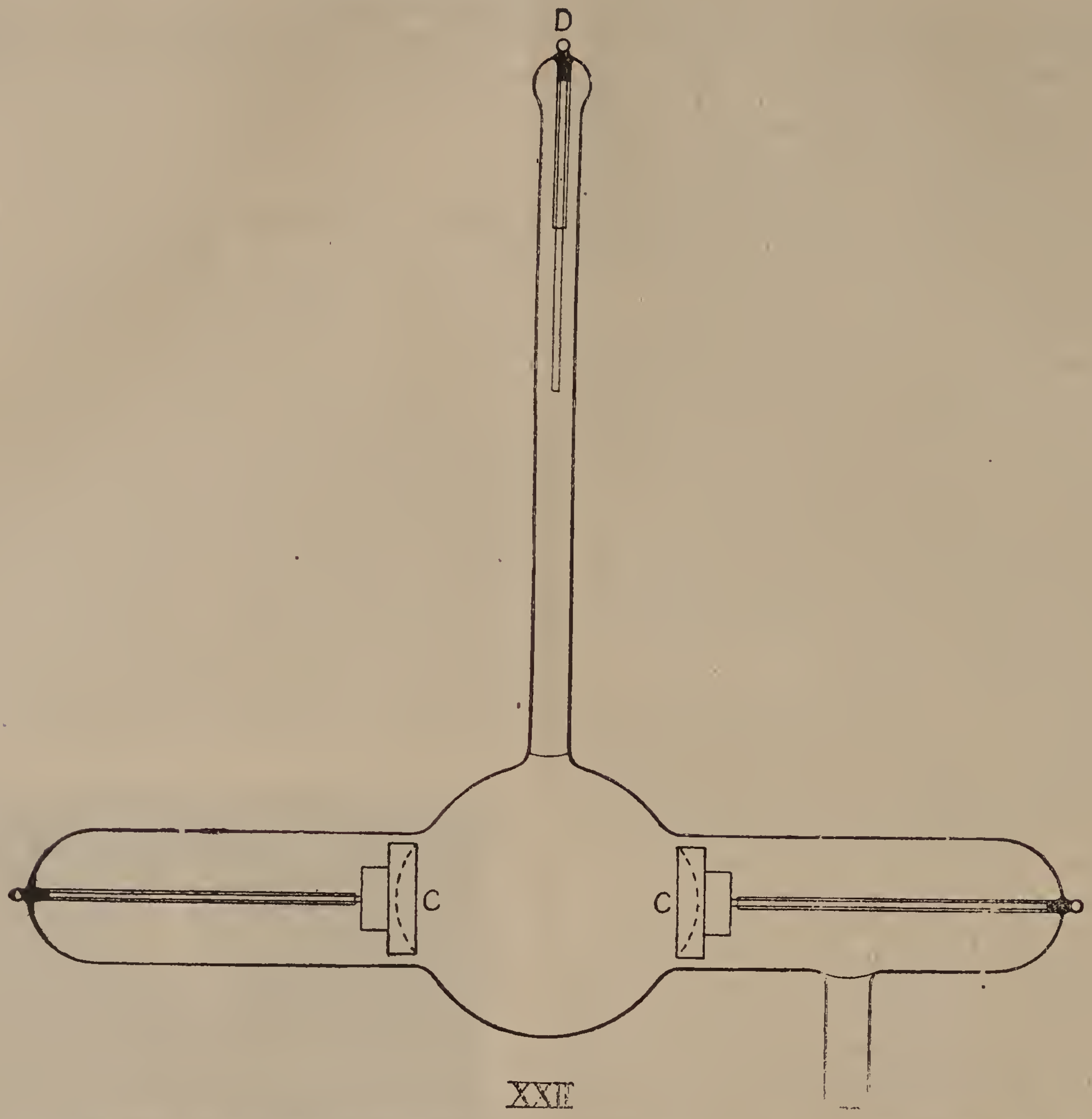
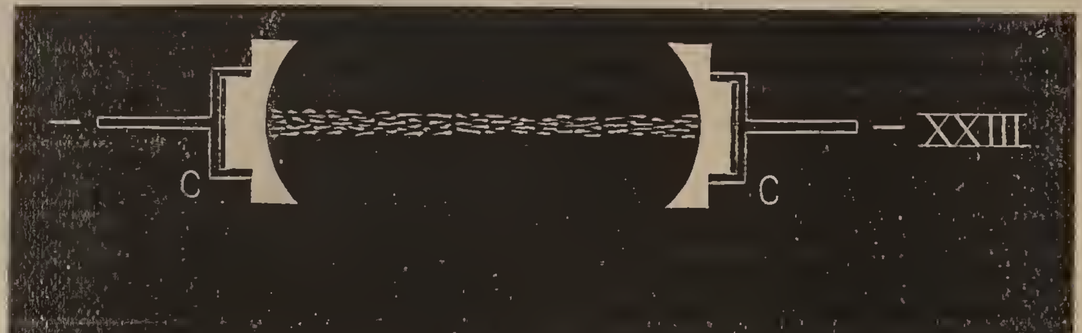
* A Paper read before the Royal Society, March 11, 1897.



XXII



XXIII

XXIV

observed with a carbon surface upon which cathode rays were concentrated. Whether this surface luminescence of the cathode carbon at the point where the cathode rays leave it is due to the violent tearing away of particles of carbon, or to some other cause, it is difficult to say, but the fact that at high vacua the cathode rays come off entirely, or at any rate almost entirely, from only a very small portion of the centre of the cathode, explains the observed fact that within limits large cathodes have no advantage over small cathodes in X-ray tubes.

During the carrying out of the above experiments with a carbon cathode, very bright sparks were occasionally seen coming off the cathode and passing through the focus, and it was consequently thought that possibly by placing two concave carbon cathodes facing one another, such particles, by being caused to rebound backwards and forwards continuously between the two, might render the form of cathode stream visible at very high vacua when the stream itself becomes otherwise invisible.

With this view a tube was made as shown in fig. 22, in which two concave carbon cathodes, C C, similar to those employed in the last experiment, were placed exactly opposite one another, so that a prolongation of the focus of either one would pass through the centre of the other. The anode, D, was placed in an annex, as shown in the illustration, and the two cathodes were connected together by means of a wire outside the tube. At a very high exhaustion this tube gave very beautiful effects, and showed clearly the form of the cathode discharge at a degree of exhaustion when it is usually in itself quite invisible. Immediately on the current being turned on and the discharge passing, a straight and thin stream of bright golden coloured particles, of apparently incandescent carbon, passed between small luminescent spots at the centres of each cathode, as shown in fig. 23. This did not last for more than a second, when, owing no doubt to the rapid fall of vacuum, the appearance changed to that shown in fig. 24, and the incandescent particles of carbon could be seen passing backwards and forwards along the convergent and divergent cones of cathode rays, which, at the lower vacuum, proceeded from both cathodes, and spluttering in the centre, where the particles going in opposite directions collided. This appearance lasted for some seconds, becoming gradually fainter as the vacuum fell. By re-exhausting the tube with the pump, however, the original appearance shown in fig. 23, as also the appearance shown in fig. 24, could be produced as often as desired. Apparently the particles of carbon become heated to incandescence either by the action of the cathode rays upon them while they are flying through space, or by their friction in passing through the residual gas, and possibly by their mutual collisions, for in the stage shown in fig. 24, when the cathodes themselves show no luminescence, the flying particles appear to be most intensely luminescent when in the centre of the tube. It may be mentioned that after this experiment had been repeated several times, the glass of the tube became perceptibly blackened, which, taken with the fact that a similar tube with cathodes of aluminium showed no stream of bright particles, goes to show that the particles consist of carbon torn off the surfaces of the cathodes.

The Production of X-rays.

The tube, fig. 22, with carbon cathodes was found to produce feeble X-rays, which, when observed with a fluorescent screen, appeared to come either from the fluorescent glass of the bulb or from the travelling particles of carbon.

In order to ascertain whether it is necessary that the cathode rays should fall on solid matter in order to produce X-rays, another tube was constructed, similar in all respects to that shown in fig. 22, with the exception that the two cathodes were made of aluminium.

It was thought that with this tube the opposing streams of cathode rays might possibly produce X-rays at the point where they met. This does not however, appear to be the case, as though this tube, when exhausted to so high an extent that the alternative spark in air leapt fully 8 inches, gave X-rays in considerable quantity, these rays appeared to come entirely from portions of the glass of the tube that were covered with green fluorescence, and not at any rate appreciably from the central point between the two cathodes, where the opposing streams of cathode rays would meet one another.

It seems, therefore, that X-rays can only be produced by cathode rays when these strike solid matter.

In conclusion I wish to mention how much I owe in carrying out these experiments to the assistance of Mr. J. C. M. Stanton and Mr. H. Tyson Wolff, who have made and exhausted all the tubes, and to whom I am also indebted for many valuable suggestions.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending April 30th, 1897.

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

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

London, May 10th, 1897.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined all were recorded as clear, bright, and well filtered.

The rainfall at Oxford during the month was 1·95 inches; the average for 30 years is 1·66 inches, making an excess of 0·29 inch; 0·54 inch fell on the 21st, the rest was fairly evenly distributed throughout the month. We have now had a total excess of 2·02 inches this year on an actual fall of 8·82 inches, or nearly 25 per cent.

Our bacteriological examinations of 234 samples give the following results:—

	Microbes per c.c.
Thames water, unfiltered (mean of 24 samples)	3277
Thames water, from the clear water wells of five Thames-derived supplies (mean of 118 samples)	38
Ditto ditto .. .. highest	335
Ditto ditto .. .. lowest	1
New River, unfiltered (mean of 23 samples) ..	892
New River, filtered (mean of 23 samples) ..	13
River Lea, unfiltered (mean of 23 samples) ..	708
River Lea, from the clear water well of the East London Water Company (mean of 23 samples)	27

These figures give a sufficient proof of the efficiency of the filtering beds and the excellent quality of the water supplied to the Metropolis.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

THE QUANTITATIVE AND QUALITATIVE SEPARATION OF BARIUM, STRONTIUM, AND CALCIUM.*

By S. G. RAWSON, D.Sc., F.I.C.,
Lecturer in Chemistry, Technical College, Huddersfield.

In the quantitative or qualitative separation of barium, strontium, and calcium, there has been always a considerable amount of difficulty due to the remarkable properties of strontium which in so many respects lie almost midway between those of barium and of calcium. Hence though the estimation of both barium and calcium when present together, or of strontium when alone, presents but little trouble, yet if the whole three members of the group be taken the task becomes one of greatly-increased difficulty, it being no easy matter to ensure either the complete precipitation or the entire retention in solution, according to the process to be employed, of the strontium. To attain one or other of these ends many methods have been proposed; among these I may mention the following:— Fresenius recommends in his work the precipitation of the

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* A Paper read before the Society of Chemical Industry (Yorkshire Section), January 25th, 1897. From the *Journal of the Society of Chemical Industry*, vol. xvi., No. 2.

barium as silicofluoride and the subsequent separation of the strontium and calcium by means of prolonged boiling with an enormous excess of ammonium sulphate. The particulars of the remaining processes are taken from the *Journal of the Society of Chemical Industry*. Fresenius and Ruppert (1892, p. 776) have investigated the relative solubilities of strontium and calcium chromates in dilute alcohol; though of value qualitatively they consider that quantitatively the method is lacking in accuracy. McElroy and Biglow (1893, p. 181) suggest the use of aqueous acetone upon these same salts, but seemingly only for qualitative purposes. In this year also (1893, p. 627) Fresenius recommends the separation of calcium as nitrate from the other nitrates by its solubility in ether-alcohol, the results he gives being very accurate. Browning (1894, p. 282) carefully examined the solubility of strontium nitrate in boiling amyl alcohol, in which the salt is almost insoluble; the corresponding calcium nitrate dissolves readily, but to effect a complete separation a second treatment is necessary. Dupasquier (1895, p. 822) points out that calcium is converted into a tartrate by boiling in a liquid containing a soluble tartrate and sulphate, while barium and strontium remain as sulphates. These are estimated indirectly for quantitative purposes. Baubigny (1895, p. 1065) separates the strontium as sulphate in the presence of potassium sulphate, but the precipitation is not complete.

This bibliography, though not complete, includes the most important of the plans suggested. It will be noticed that in almost all of them there arises the difficulty of the slight solubility of the strontium salts in the solvents necessarily employed. Further, it rarely happens that the same method can be used both quantitatively and qualitatively. But the special objections to these methods are due to the fact that either out-of-the-way reagents are employed, or that much and prolonged boiling is necessary to convert the given salts into the required modifications. Both these are hindrances in the way of quantitative analysis, and are most serious detriments to qualitative work.

The principle of the separation upon which I have worked depends entirely upon the behaviour of the nitrates of these three metals towards concentrated nitric acid. The method is also readily applicable to qualitative analysis; the nitrates of barium and of strontium are quite insoluble in this acid, whilst calcium nitrate dissolves very rapidly. That barium nitrate is insoluble appears to be accepted, but there is considerable divergence of opinion as regards the strontium salt; thus, Wurtz (*Am. J. Sci.*, [2], xxv., 377) states that it is sparingly soluble in concentrated nitric acid, whilst Schultz (*Zeit. Ch.*, [2], v., 537) considers it to be insoluble. The experiments by which I sought to settle this initial contradiction were as follows:—The nitric acid used, and which was bought as pure, was re-distilled, the water also being similarly treated. In the case of both the nitric acid and of the water, portions upon evaporation either left no residue or one which it was not possible to weigh. The carbonate was obtained, at different times, from Germany, and as being perfectly pure. I may here mention that it is most difficult to procure pure strontium carbonate. All the material which I obtained invariably contained traces of calcium in amounts varying from 0·25 per cent to even 2 per cent. The presence of this impurity caused me great inconvenience, and at first much loss of time. In order to purify the carbonate a considerable quantity was converted into nitrate and thoroughly stirred with nitric acid, filtered, and the residue dissolved in water and precipitated as carbonate, washed, and dried. In the spectroscope no trace of the calcium lines were now visible. So satisfactory and rapid is this method that I would recommend it strongly as being the most easy and the most safe for the purification of strontium from calcium salts. I may here mention that throughout my experiments I always used the carbonates of the metals partly because of the much greater convenience and certainty in weighing, and also because the carbonates are far more likely to be required for estimation under usual conditions than the nitrates, and therefore it seemed advisable to work upon the more commonly occurring body.

The pure carbonate was treated with dilute nitric acid and evaporated to dryness upon the water-bath. Pure concentrated nitric acid (sp. gr. 1·445) was then added and the mixture kept well stirred for many hours, in some cases three days. The solution was then filtered through filter-paper or glass-wool, and the filtrate evaporated to dryness, taken up with a little hydrochloric acid, and again evaporated. The residue gave, in the spectroscope, no trace of the strontium lines, but consisted of small traces of sodium and iron sulphates derived from the acids employed, and of celluloid matter arising from the filter-paper, when used. Similar experiments were repeated many times, varying the amounts of carbonate and of nitric acid, but only upon one occasion, in one of my earlier experiments, did I distinguish the strontium lines. I had treated some 3 grms. of the carbonate with nitric acid, and upon filtering and evaporating to dryness the residue clearly contained strontium. This was due to the solution of traces of the nitrate, the nitric acid having become diluted by the considerable amount of water formed in the conversion of the carbonate into nitrate. On all subsequent occasions I invariably evaporated the nitrate to dryness upon the water-bath, and then took up with fresh nitric acid. Under these conditions the reaction was only as between the nitrate and nitric acid, and the strontium lines did not again become visible in the filtrate. Hence strontium nitrate is insoluble in concentrated nitric acid. Direct experiments upon barium nitrate showed this salt to be also insoluble, whilst calcium nitrate readily dissolved. As regards the nitric acid, I prefer the specific gravity to be about 1·46 (corresponding to 80 per cent of the acid) or even higher, but for most purposes the ordinary acid of specific gravity 1·42 (containing 70 per cent of HNO_3) will suffice.

The actual quantitative estimation of these elements carry out in the following manner:—The carbonates are evaporated with nitric acid, either in a beaker or in a porcelain dish, preferably the latter, upon the water-bath until the mass is quite dry. Concentrated nitric acid is added in excess, and the mixture kept well stirred. The crystals settle out after each stirring very rapidly, and the clear supernatant liquid is poured through a double filter-paper which has been moistened previously with concentrated nitric acid. The residue may be washed either with the concentrated acid by decantation, a method to which the mass from its crystalline nature readily lends itself, or in the customary way upon the paper.

The filtrate is evaporated either to dryness, taken up with hydrochloric acid, and the calcium precipitated as oxalate, or evaporated down with sulphuric acid, and the residue after ignition weighed as sulphate.

The remaining nitrates are dissolved in water, and the solution made alkaline with ammonium hydrate, acidified with acetic acid, and the barium precipitated as chromate. The filtrate is warmed with hydrochloric acid and alcohol until the chromate is reduced, the chromium precipitated as hydrate and filtered off. The filtrate is evaporated to dryness upon the water-bath with a little sulphuric acid. The residue is treated with dilute alcohol and washed, and the residual strontium sulphate weighed as such. Two out of the different test analyses which I have made give the following results:—

	1.		2.	
	Taken.	Found.	Taken.	Found.
Barium carbonate ..	0·5393	0·5379	0·2127	0·2130
Strontium carbonate	0·2578	0·2584	0·4583	0·4576
Calcium carbonate..	0·5473	0·5470	0·2773	0·2780

For the qualitative separation the above process may be much simplified. The carbonates, after treating with the minimum amount of nitric acid, are boiled down just to dryness; then treated with concentrated nitric acid, the paper having been first moistened with this acid, filtered, and the residue washed by decantation. The filtrate is diluted considerably with water made alkaline with ammonia, and the lime thrown down as oxalate. The residue is dissolved in water (the filter-paper will not disintegrate unless boiling cold water be used), made alkaline with ammonia, acidulated with acetic acid, and the barium precipitated as chromate. To the filtrate is added hydrochloric acid, and it is boiled with a little alcohol, and the chromium precipitated as hydrate, which is filtered off. To the filtrate sulphuric acid is added, and the solution heated; if necessary alcohol is added, the strontium coming down as sulphate. The separation of the chromium as hydrate is not in all cases necessary.

The process can be carried out very rapidly, and, further, is a complete separation of these three metals, and does not rest upon grounds such as the length of time allowed for boiling or standing, or the greater or lesser concentration of solutions.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, May 14th, 1897.

Mr. Shelford Bidwell, President, in the Chair.

Mr. W. Watson described "*An Instrument for comparing Thermometers with a Standard.*"

The thermometers to be compared are inserted together in an enclosed vapour-tube, the temperature of which can be maintained very constant at different parts of the scale. The apparatus is an adaptation of the arrangement devised by Ramsay and Young for vapour densities. It consists of a wide vertical glass tube, with a narrower tube attached at the top. The narrow tube bends downwards and communicates with a closed vessel of considerable volume. A portion of the vertical tube is surrounded by a condensing-jacket, and a manometer tube is inserted near the top. The object of the large vessel is to diminish errors arising from fortuitous changes of pressure resulting from small leakages or "bumping" of the boiling liquid. Electrical heating of the bulb containing the liquid effectually removes the "bumping." The following liquids, used consecutively, give a range of temperature from 20° C. to 120° C.: carbon bisulphide (20°—46°), ethyl alcohol (80°), chlorobenzine (120°). The apparatus, when once started, requires very little attention; from results submitted by the author, the variations do not exceed 0·02° C. per hour. In constructing the various parts, the difficulties of glass-blowing are reduced by making the joints of indiarubber stoppers, attached to the glass with indiarubber solution. Each joint is jacketted with glycerin. If the above liquids are used in the vaporiser, the scales of the thermometers can always be read within the tube; it is only with water that the condensed vapour gives trouble.

Prof. Ayrton thought the apparatus would come into extensive use; it did away with errors arising from differences of length of thermometer stems, it left no question as to the equality of temperature of the two bulbs, and there was no probability of error due to a difference of thermal "lag" in any two thermometers.

Mr. Watson, in replying to a question of Prof. Perry's, said the fact of using indiarubber joints limited the available range of temperature. Working with blown joints, Ramsay and Young had found no difficulty in their vapour-density experiments at higher temperatures.

Prof. Carey Foster read a paper by Mr. D. K. Morris, of Zürich, on "*The Effect of Temperature upon the Magnetic and Electric Properties of Iron.*"

The investigation relates to the measurement of the magnetic permeability, hysteresis, and electrical resistance of iron simultaneously at different temperatures. The specimens are formed into annular rings made from iron strip. The strip is first lapped round with asbestos-paper and mica, and then wound upon itself to the requisite thickness. A platinum wire is included in the mica lappings, for thermometrical purposes. Upon each annular ring are the following windings:—(1) A primary magnetising coil. (2) A secondary coil connected to a ballistic galvanometer. (3) An electrical heating coil. Further, the iron strip is itself connected to a Wheatstone's bridge, for resistance measurements. The coil can be heated to 1050° C. At the higher temperatures, the surrounding air has to be freed from oxygen; this is done by enclosing the coil in a suitable vessel and exhausting with an air-pump. When most of the air has thus been removed, the residual oxygen is absorbed by an electrically heated iron wire. Curves are drawn representing the changes of permeability at the different temperatures, and, at the same temperature, the corresponding hysteresis loops are plotted. The hysteresis diminishes with temperature; it nearly vanishes at about 764° C.

At the suggestion of Prof. Ayrton, it was agreed that the discussion on this paper should be adjourned until the publication of the results. The paper will therefore be printed without delay.

Mr. Rollo Appleyard read a paper on "*The Formation of Mercury Films by an Electrical Process.*"

If a sheet of damp leather, or similar permeable substance, is used as a separating diaphragm between two bodies of mercury, and a current is sent through it, a film of mercury is deposited upon the surface connected to the positive pole; and the film remains on the diaphragm after removal from the apparatus. If the diaphragm is replaced in the apparatus and subjected to a current in the reverse direction, the film vanishes from that surface, and a second film appears on the other side; that is to say, the film is always on the side of the diaphragm connected to the positive pole of the battery, and there is no film on the negative surface. Different diaphragms and films were exhibited—of filter-paper, asbestos-paper, plaster of Paris, &c. A current of about one-fiftieth of an ampère, or more, is necessary. A sheet of tin-foil, included between folds of filter-paper, becomes perforated with pin-holes when the current is passed between the outside surfaces. This happens whether the outside electrodes are mercury or metal plates. If the top electrode should be tin-foil, this also becomes perforated as well as the included sheet. A further experiment was shown, in which a gold coin is placed upon the folds of filter-paper; the current produces a gold discolouration which penetrates the folds. This, it was suggested by the author, may help to account for the formation of metallic lodes and veins as they exist in rocks; and they may partly explain the "inductoscripts" of Mr. F. J. Smith.

Dr. S. P. Thompson said he did not know of any other examples of an *anode* being more active—mechanically—than the *kathode*, except the electric arc. He was surprised that the film should appear on the positive surface.

Mr. Shelford Bidwell thought selenium presented, in some of its actions, an example of the *anode* being thus active.

Prof. Ayrton said that if a vessel containing a substratum of mercury amalgam was filled up with water in which gold crushings were washed, the gold descended into the amalgam. This, however, might be partly due to gravity, and partly to simple electrolysis.

Mr. Appleyard said he had no definite views as to the formation of the films. He believed it to be a secondary effect of electrolysis, aided by electric osmosis. The experiments of Mr. C. K. Falkenstein upon the electric tanning of leather, and the early results of M. Perret, helped the idea of electric osmosis; they were not sufficient, however, to justify that theory without further research. A careful chemical analysis of the deposits left in the folds of filter-paper would be the best guide.

The President proposed votes of thanks to the authors, and the meeting was adjourned until May 28th.

THE ROYAL SOCIETY.

A Conversazione was held at the Royal Society's Rooms at Burlington House, on Wednesday, the 19th of May. The guests and Fellows were received by the President, Lord Lister.

Among the exhibits were some interesting colour-photographs, produced by the Danzac-Chassagne process, the details of which are not known, but the prints (silver) are believed to be treated with a solution containing albumen and certain metallic chlorides, and afterwards with colouring materials—blue, green, and red.

Mr. Campbell Swinton showed a good collection of the various latest forms of X-ray tubes.

In the principal Library, Prof. Roberts-Austen showed his apparatus for micro-photography, and some slides showing the mode of existence of carbon in steel; also a diamond made by himself, by M. Moissan's method—the magnifications vary from 500 to 1000 diameters.

Messrs. C. T. Heycock and F. H. Neville had a curious alloy of silver and zinc, which would have warmed the hearts of the old-time alchemists. At the ordinary temperature it is the colour of silver, but when warmed up to 300° C. and *suddenly cooled* it becomes copper-coloured or bright red, and remains so; if again heated, and cooled slowly, it resumes its original colour. This is not an effect of oxidation, as the phenomenon occurs equally well in hydrogen gas or in vacuo.

Prof. Oliver Lodge exhibited an apparatus, demonstrating Zeeman's discovery of the broadening of spectrum lines by the action of a magnetic field on the source of light. By reason of reversals, the usual appearance of each sodium line is as if it were double; the magnetic field makes it appear triple, or even quadruple.

Perhaps one of the prettiest exhibits is Prof. Silvanus Thompson's model of a Hertz wave transmission, showing the manner in which a wave can be transmitted to and received by a resonator in tune with the oscillator.

At 10 p.m. Prof. Ayrton gave a demonstration with experiments and lantern slides, on "Some Electric and Mechanical Analogues"; and at 11 p.m. Prof. Farmer showed some slides from micro-photographs illustrating nuclear division in animal and vegetable cells.

NOTICES OF BOOKS.

The Electric Furnace. ("Le Four Electrique"). By Henri Moissan, Membre de l'Institut. Paris: G. Steinheil. 1897. Pp. 376.

(Concluding Notice).

The preparation of simple bodies by means of the Electric Furnace forms, as we mentioned previously, the subject-matter of Chapter III. The high temperature now reached renders possible many chemical changes which have hitherto been unattainable. We know, for instance, the laws of decomposition by heat, of carbonate of lime; but until now carbonate of barium has been considered to be undecomposable, simply on account of the limited means at our disposal. It is now shown that carbonate of barium, like chalk, loses its carbonic acid at a very high temperature, and is converted into caustic baryta. Further, certain oxides—such as silica, the alkaline earths, oxides of uranium, vanadium, and zirconium—have now been directly reduced by carbon, yielding the pure metals themselves, or metallic carbides.

Some of these highly refractory substances, though reducible to the metallic state, have not yet been produced in the form of ingots, but persist in remaining in a powdery state, a phenomenon analogous to very finely-divided mercury. Calcium, strontium, and barium are among these; on the other hand, chromium, molybdenum, titanium, uranium, &c., can be produced in ingot form without much difficulty. For the purpose of his research on chromium, M. Moissan prepared 40 kilogrms. of the metal.

The details of the manufacture, the precautions taken in so doing, and the analyses of the samples of ten of these rare and interesting metals are then given.

The general method of procedure will be by now easily understood; but the various and minute details, to be followed in the handling of such large currents, and enormous temperatures, in the production of these chemically speaking *simple* bodies, afford many pages of most interesting matter.

Alumina has always been regarded as irreducible; but if a perfectly transparent crystal of corundum be placed in a carbon crucible, in a carbon tube, and exposed to the heating effect of a current of 1200 ampères and 80 volts, it is volatilised in a few minutes. The crubible, completely converted into graphite, does not contain a trace of ash, but the surface of the tube on either side is covered with a deposit of crystals of graphite and metallic aluminium in spheres up to 2 or 3 m.m. in diameter. The author has made extensive experiments on the various impurities in commercial aluminium, experiments of considerable importance to the manufacturers of this metal: different samples of aluminium, made by different processes, vary considerably, not only in chemical composition but also in mechanical utility, small quantities of impurities having—as is well known to metallurgists—an enormous influence on the physical properties of many metals. Comparative tests were made with several ingots of aluminium, some containing a small proportion of carbon (different analyses have given 0·104, 0·108, and 0·080 per cent of carbon), and the other containing no carbon. The effect of this minute amount of impurity was very striking; the breaking strain of pure aluminium was 11·1 kilos. per square m.m. and the elongation 9 per cent, while the other samples containing carbon had breaking strains of only 6·5 to 8·6 kilos. per square m.m. and elongations of from 3 to 5 per cent.

Chapter IV. deals with the large class of new compounds known as carbides, borides, and silicides. It would not be correct to say that metallic carbides were unknown before the invention of M. Moissan's furnace. It was known that certain metals would dissolve carbon in variable proportions, generally when the metal was in large excess; but the direct preparation of crystallised carbides was impossible with the furnaces then in use. The researches of M. Moissan have enabled him to classify the different simple bodies; the carbides, in fact, from being looked upon as ill-defined compounds, are now shown to possess new properties, so well defined that they serve as a good basis for the classification of the elements into natural groups. The property of decomposing cold water and furnishing absolutely pure acetylene gas is characteristic of the carbides of lime, barium, and strontium, while the carbides of aluminium and glucinum—under similar conditions—will produce pure methane; these are two distinct and new reactions of great importance.

We will not, however, dwell longer on this subject—it has previously been published at some length in these columns, but will close this notice by expressing our admiration for the excellent work done and the great amount of time and labour M. Moissan has devoted to his research.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. ii., No. 4.

Analysis of the Fourth Report of "The Research Committee on Alloys" of the Institution of Mechanical Engineers of London.—This is a long and interesting review of Prof. Roberts-Austen's report to the Institution of Mechanical Engineers and Engineering on February 12, 1897, but it is not suitable for abstraction.

Revue Generale des Sciences Pures et Appliqués. Nos. 7 and 8.

Neither of these numbers contain any original matter of chemical interest.

Bulletin des Travaux de la Société de Pharmacie de Bordeaux. April, 1897.

Detection of Oil of Arachis in Olive Oil.—Prof. Ch. Blarez.—The detection of oil of sesame, cotton-seed oil, &c., in olive oil is not a matter of any great difficulty, but the problem of detecting the presence of oil of arachis is always a matter of delicacy. The author considers that M. Renard's method of detecting this adulterant has the fault of being too long and requiring great experience on the part of the person using it, and he proposes a new and much quicker method, based on the property its potash soaps possess, of being almost insoluble in strong, cold alcohol, in presence of a notable excess of potash. The originality claimed consists in the special procedure followed and the use of very simple apparatus, and may be briefly described as follows:—1. Pour 1 c.c. of the oil under examination into a test-tube 15 c.m. long. 2. Add 15 c.c. of pure 90° alcohol containing 4 or 5 per cent of pure potash. 3. Fit the tube with a vertical condenser. 4. Heat the tube carefully for about twenty minutes; the oil will rapidly saponify and disappear, the alcohol returning into the tube. 5. Remove the condenser, cork the tube and put it in a cool place. In the case of pure oil of arachis the contents of the tube became solid after the lapse of twenty-four hours. With pure olive oil there is no sign of solidification after the lapse of twenty-four, forty-eight, or even seventy-two hours; but with a mixture of the two there is always a flocculent precipitate, in which can be distinguished crystals of arachidate of potash.

MISCELLANEOUS.

Royal Institution.—The Friday Evening Discourse at the Royal Institution next week (May 28th) will be delivered by Prof. H. Moissan (Directeur Laboratoire de Chimie Minerale à l'Ecole Superieure de Pharmacie, Membre de l'Académie des Sciences, Paris), who will lecture in French on "The Isolation of Fluorine" (with experiments). On Friday, June 4th, Mr. W. H. Preece, C.B., F.R.S., will lecture on "Signalling through Space without Wires." On Friday, June 11th, Mr. William Crookes, F.R.S., will deliver the last of the Friday Evening Discourses for the year; his subject will be "Diamonds."

The General Italian Exhibition.—This Exhibition will be held in Turin in 1898. A special section will be devoted to Electricity, and a prize—called the "Galileo Ferraris Prize"—will be given to the most important application of electricity to industrial purposes. The amount already subscribed towards this prize reaches 15,000 francs.

The Rose Polytechnic Institute of Terre Haute, Indiana.—The Calendar of this Institute now before us gives a complete list of the lectures and courses of instruction included in its curriculum. It is, firstly, an Engineering College; this naturally includes scientific training in such subjects as Chemistry, Electricity, Mathematics, &c. The general plan of instruction is based on the principle that laboratory and shop work, field and office practice, should all go hand-in-hand with theory and book work.

The Pennsylvania State College.—We have received the Prospectus and Syllabus of the above-named College, and have much pleasure in noting its growing importance and the extended scope of its teachings. Started in 1859 as the "Farmer's High School," for the purpose of giving a purely agricultural education, it has been so enlarged as to include all those subjects which lie at the foundation of modern industrial pursuits. The several courses of lectures, and of instruction generally, are grouped into seven Schools,—such as the School of Natural Science (biology and chemistry), the School of Mathematics and Physics, the Schools of Mines, Engineering, and so on. The course of chemistry lasts for two years, and includes both mineral and organic chemistry, theoretical and practical. Electricity is of course not neglected, with its many modern applications, while another peculiar feature of the College is its military organisation.

Disinfection with Formic Aldehyd.—In the Sanitary Chronicles of the parish of St. Marylebone, for the month ending March 31st, 1897, Dr. Winter Blyth records some interesting and valuable work done in connection with the disinfecting properties of formic aldehyd, commercially known when dissolved in water as "formalin" or "formol." The antiseptic powers of formic aldehyd are extraordinary; 1 part in 10,000 suffices to preserve milk, soup, and similar articles, for a considerable time, which fact naturally suggested that it might have true disinfecting powers. The aqueous solution called formalin does not give very satisfactory results when exposed in open dishes, as it has the peculiar property of changing into a white solid,—in other words, polymerisation takes place, $CHOH$ changing into $C_3H_3O_3H_3$, the latter substance being a far less efficient disinfectant. Bouse and Boudet, however, found that when the gas is dissolved in a solution of calcium chloride, and afterwards heated under pressure, practically dry formic aldehyd was driven off. The ordinary method of disinfecting a room is to seal and plug up every crack and opening; then open a bottle of compressed sulphurous acid, and leave the room undisturbed for about twelve hours or more. A comparative trial was made with sulphurous acid and formic aldehyd, in two rooms in which were exposed, on bits of linen, four cultures of diphtheria, four of the typhoid bacillus, four of tuberculosis, and four of anthrax; there were also samples of coloured paper and materials placed in the room, to enable the officials to observe the effect, if any, on colours. After nineteen hours the rooms were opened, and the infected pieces of linen were sent to Prof. Macfadyen, who reported as follows:—

	Sulphur gas.	Formic aldehyd.
I. Diphtheria bacillus.	No growth.	No growth.
II. Typhoid bacillus.	Good growth.	No growth.
III. Anthrax bacillus.	Good growth.	No growth.

The tubercle samples could not be properly reported on, as they were found to be contaminated with other micro-organisms. The formic aldehyd room, on being entered, smelled strongly of the gas, but beyond making the eyes smart there was not much inconvenience for a short while; but in the sulphur gas room three attempts, in as many quarters of an hour, were made to open the windows, and in each case Dr. Blyth was compelled to retire, gasping and choking; it was more than an hour before the windows could be opened. As for the colours, both gases showed a trivial bleaching in the case of silk when very carefully compared, but in the dyed papers no alteration whatever could be discerned. In conclusion, Dr. Blyth considers that formic aldehyd gas is superior to sulphurous acid gas as a disinfectant, and he recommends its adoption by the Vestry.

Sophistication of Foods.—We learn from the *Chem. Zeitung* that the Sanitary Department of San Francisco is publishing a black list of the manufacturers and dealers in adulterated food, with the names and addresses of the offenders in full.

Memorial to Professors Gauss and Weber.—We have the pleasure of calling the attention of our readers to the project for erecting, at Göttingen, a monument to the late Professors Gauss and Weber. A sum of 23,520 marks has been already collected for the purpose. Further subscriptions will still be welcomed, as the design of Prof. Harza (of Berlin) is of a somewhat expensive character. The work will be completed within two years. The President of the Committee is Prof. Dr. W. Vogt, and the Treasurer is Siegfried Bonfey.

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.

Filling for Joints.—Can any of your correspondents recommend a good filling for open joints in a laboratory bench?—F. M.

MEETINGS FOR THE WEEK.

MONDAY, 24th.—Society of Arts, 8. (Cantor Lectures). "Design in Lettering," by Lewis Foreman Day.
TUESDAY, 25th.—Royal Institution, 3. "The Heart and its Work," by Dr. Ernest H. Starling.
WEDNESDAY, 26th.—Society of Arts, 8. "Silver and Prices—the Economic Drain of Debtor Nations;" by M. Frewen, B.A.
THURSDAY, 27th.—Royal Institution, 3. "Burke and the Revolution," by Churton Collins, M.A.
FRIDAY, 28th.—Royal Institution, 9. "The Isolation of Fluorine," by Prof. H. Moissan.
—— Physical, 5. "The Perception of Phase Difference by the Two Ears," by Dr. A. A. Gray. "The Isothermals of Isopentane," by Mr. Rose-Innes.
SATURDAY, 29th.—Royal Institution, 3. "Music in England during the Reign of Queen Victoria," by J. A. Fuller Maitland, M.A.

IMPORTANT NOTICE.

Change of Address.

The Printing and Publishing Offices of the CHEMICAL NEWS have been

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THE CHEMICAL NEWS.

VOL. LXXV., No. 1957.

AN ATTEMPT TO CAUSE HELIUM OR ARGON TO PASS THROUGH RED-HOT PALLADIUM, PLATINUM, OR IRON.*

By WILLIAM RAMSAY, F.R.S., and MORRIS W. TRAVERS.

To chronicle experiments which produce no result is a necessity, although not entirely an agreeable one. Whatever the reason of the passage of hydrogen through red-hot iron, and through moderately heated palladium, and platinum—whether it be due to the solubility of the gas in the metal, or to the formation of an easily decomposable compound—neither argon nor helium is able to pass through any one of these metals, even at a fairly high temperature. This would imply their inability to form any compound, however unstable, with these metals, or to dissolve in them at a red heat. Such inactivity is in accordance with their general behaviour, and is still another proof of their inertness.

The experiment was made in the following manner:—A tube of hard, infusible glass was connected at one end with the reservoir of the gas under experiment, helium or argon. Into its other end was corked a tube of platinum, closed with a palladium cap, or, if iron was the metal under experiment, with a tube of thin wrought iron, also closed at the end; the closed end of the interior tube was placed so that it could be raised to a bright red heat by bringing a blowpipe flame to bear on the hard glass tube. The open end of the metal tube was cemented to a glass tube, attached to a Töpler pump, and provided with a Plücker's vacuum tube, so that the spectrum of any gas passing through the metal could be observed. This afforded, at the same time, a most delicate test of the presence of the gas under experiment. The metal tube was exhausted, until green phosphorescence appeared in the vacuum tube, and the gas, helium or argon, was admitted into the space between the glass and the metal tube, at atmospheric pressure. The glass tube was then heated to the highest temperature attainable with a blowpipe—perhaps 900° or 950° C. In no case, whether the metal tube consisted of palladium, platinum, or iron, was there the smallest transpiration of gas, even after half an hour. The phosphorescent vacuum remained in all experiments quite unimpaired.

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[*] A Paper read before the Royal Society, May 14, 1897.

SEPARATIONS WITH ALKALINE ACETATES.

(PRELIMINARY PAPER).

By HARRY BREARLEY.

IT has been previously shown (CHEMICAL NEWS, xxvii., 14; lxxv., 13) that the separation of iron from manganese by means of soda or ammonia acetates is the more imperfect the larger the excess of acetate used. It has also been shown (CHEMICAL NEWS, xl., 273; lxxiv., 16) that for this and other metals the effect of excessive acetate was obviated by the presence of free acetic acid.

The reaction between ferric chloride and soda acetate has been written—

$$6NaC_2H_3O_2,3H_2O+Fe_2Cl_6= \\ =NaCl+Fe_2(C_2H_3O_2)_6+3H_2O;$$

whence it follows that 8 grms. of the crystallised soda acetate ($NaC_2H_3O_2.3H_2O$) would be needed to precipitate 1 grm. of metallic iron existing as ferric chloride. But iron solutions are never precipitated in that state. Pure or carbonated alkali is added; after the free acid is neutralised, the precipitated hydrate continues to be dissolved by the ferric chloride to saturation point. When this is reached, the faint excess, taken up in two or three drops of HCl, marks the point, commonly called "neutralised," to which solutions are usually taken before adding the acetate. Acetate is needed only to precipitate that portion of the ferric chloride not already precipitated as hydrate, and which holds the precipitated hydrate in solution. The amount theoretically required will bear the same ratio to 8 grms. that the final bears to the initial quantity of Fe_2Cl_6 when 1 grm. of metal is operated on. It may be of interest to show experimentally what amount of acetate is necessary to precipitate a solution containing variable quantities of ferric chloride and hydrate. It is certain that many an imperfect separation may be redeemed by using minimum amounts of acetate; and separations, generally considered impossible, effected by further modification in the same direction.

It was decided to answer questions similar to the ones suggested when the iron solutions contained—(*a*) No free acid and no dissolved hydrate; (*b*) half the total soluble hydrate; and, (*c*), total soluble hydrate, *i.e.*, as much hydrate as the solution could be made to dissolve. More or less completely, the same series was gone through with varying amounts of acetic acid and with soda and ammonia salts.

The iron solution chiefly used was made by dissolving 40 grms. of Swedish bar iron in 290 c.c. HCl and oxidising with 50 c.c. HNO_3. There was prepared also a solution of iron in HNO_3 (1·20), and a solution by dissolving in HCl, oxidising with HNO_3, evaporating to dryness, and re-dissolving in HCl. The two latter solutions were intended for comparing with the first at different points, so that the data established might be available whichever method should be used for preparing the iron solution. All three are recommended in one or other of the modern text-books.

The amount of free acid was determined by adding excess of normal soda carbonate to boiling iron solutions, filtering off aliquot part, and determining excess of alkali with standard acid and methyl-orange (Sutton, "Vol. Anal.," 5th ed., p. 89).

Dissolved Hydrate.

For determining the dissolved hydrate, iron solution representing ½ grm. of metal was placed in a flask and normal soda or ammonia carbonate run in from a burette. Towards the end the alkali was added very slowly, and plenty of time allowed for the precipitated hydrate to dissolve. The faint permanent precipitate was dissolved with standard HCl. The total alkali used, less that needed for neutralising the free acid, gives the quantity

TABLE I.

With Soda Carbonate.

Iron solution.	Total alkali. C.c.	Required by free acid.	To precipitate Dissolved hydrate.	 Total hydrate. C.c.	Ratio, total to final Fe_2Cl_6.
Aqua regia..	37·74	14·2	23·54	26·8	8·35
	37·84	14·2	23·64	26·8	
Hydrochloric acid.. ..	33·72	10·35	23·37	26·8	7·93
	33·82	10·35	23·47	26·8	
Nitric acid..	34·0	10·1	24·0	26·8	9·57
	34·0	10·1	24·0	26·8	

With Ammonia Carbonate.

Iron solution.	Total alkali. C.c.	Required by free acid.	Dissolved hydrate.	Total hydrate. C.c.	Ratio, total to final Fe_2Cl_6.
Aqua regia..	37·84	14·2	23·64	26·8	8·48
Hydrochloric	33·93	10·35	23·58	26·8	8·32

TABLE II.

		Soda acetate.				Ammonia acetate.		
	Free acetic	0	5	10	20 c.c.	0	5	10 c.c.
N. H.	Acetate	145 c.c.	150	160	175	150	155	163
	Temp. turbidity	84° C.	90	94	95	86	94	90
H. H.	Acetate	73	75	80	90	78	80	85
	Temp. turbidity	74	80	82	80	80	91	92
T. H.	Acetate	5*	6	12	16	5*	7	10
	Temp. turbidity	?	80—84	80—84	88	?	80	81

needed to form the dissolved hydrate. These solutions, on standing, become gradually turbid, and after standing weeks or months allow the precipitate to settle somewhat, but such a precipitate cannot be separated by ordinary filtration. Completely "neutralised" and perfectly clear solutions will appear slightly turbid by reflected light after standing over night. This additional precaution was taken in determining the dissolved hydrate. Some results are arranged in Table I.

These solutions all contained alkaline salts, due to the neutralisation of the free acid. On this account they do undoubtedly require less alkali. The nitrate is less active in this respect than the chloride, and this may partly explain why more hydrate is dissolved in the nitric than the aqua regia solution, and least of all in the HCl solution. When ammonium chloride representing 10 c.c. strong HCl was added to a solution the alkali required to precipitate the dissolved hydrate fell from 23·57 c.c. to 22·74, and with nitrate representing 10 c.c. HNO_3 (1·42) it fell to 22·87 c.c.

Kessler (CHEM. NEWS, xxvii., 14) states:—"When a hydrochloric acid solution of perchloride of iron is neutralised by means of soda carbonate, so as to cause a permanent precipitate, and the latter is cautiously dissolved by the addition of some HCl, a liquid is obtained which contains fourteen times its equivalent of ferric hydrate in solution, yet it is not precipitated by boiling.* This passage seems to have been misread by Blair ("Chem. Anal. of Iron," p. 108), who makes out that, *theoretically*, half a grm. of soda acetate is sufficient to precipitate 1 grm. of iron, as though fourteen times as much iron exists as dissolved hydrate as exists as chloride. The intended meaning seems to be that the dissolved $Fe_2(HO)_6 = 14\ Fe_2$ (existing as Fe_2Cl_6). Read this way, the two results are broadly confirmatory.

Precipitating the Iron.

The precipitations with acetate were performed in flasks. One grm. of iron taken in all cases, and made, finally, in the cold, up to 480 c.c., so that at boiling-point it would measure 500 c.c. approximately. The temperature at which the heated solution became turbid was observed. In some cases after a faint turbidity the formation of the precipitate was very tardy, and is represented by two observations: *e. g.*, 76—80° C., 20 c.c. of the soda acetate contains 1 grm. $NaC_2H_3O_2 \cdot 3H_2O$ crystals. The ammonia acetate was made by neutralising acetic acid (33 per cent) with ammonia. One and a half c.c. of such a solution contained as much acetic acid as 1 grm. soda acetate crystals, so that they were made of equal value by making 1·5 c.c. of the former up to 20 c.c. The solutions were neutral on the acid side, if I may be allowed to use such contradictory terms.†

An iron solution may be said to be completely precipitated when, the basic acetate having settled, the supernatant solution is colourless and free from iron. This, agreeable to theory, was found to be the case when having no free acid and no dissolved hydrate, 8 grms. of soda acetate crystals were added; 7½ grms. left a faintly coloured supernatant solution. If this faintly coloured solution is passed hot through an asbestos filter, the filtrate is colourless, crystal clear, and when acidified gives no colouration with sulphocyanide. A similar result is obtainable using 7¼ grms. It is this property of an asbestos filter which it is more particularly desirable to observe; for is it not likely that, if only so much acetate is added as will leave a faintly coloured supernatant solution, an associated metal, having similar properties, may remain completely in solution and depend for its complete separation from the last portion of iron on its deportment to the asbestos? A very considerable quantity of iron may be removed from a hot solution in this way; cold solutions pass unaltered.

No great labour was spent, therefore, in determining how much acetate was needed to give a colourless supersolution after the settling of the precipitated acetate, but rather to determining with how little acetate an iron-free filtrate could be obtained. There is, of course, no absolutely unalterable amount. Something depends on how the filter is made, how long the solution is boiled, what amount of alkaline salts, &c. In the instances tabulated the solution was heated until it quite boiled, cheesed until the precipitate settled, and filtered. Where soda acetate is used for precipitating, soda salts have been used throughout, and similarly for ammonia. N.H., H.H., and T.H. mean that the iron solution contained no hydrate, half the total hydrate, and the total hydrate respectively. The table shows the minimum acetate.

The solutions marked with an asterisk became turbid on adding the acetate, but did not leave a clear supersolution unless they were heated. When larger amounts of acetate (10 c.c.) were added, the precipitate settled, without heating, leaving a perfectly colourless supersolution.

The preparation of the large vols. of T.H. solution enabled me to confirm the figures given above for the amount of hydrate soluble in ferric chloride.

A dozen or so precipitations were made of iron solutions to which ammonia salts, containing respectively 10 c.c. HCl and 10 c.c. HNO_3, had been added. Their presence favours the precipitation, the chloride more decidedly so than the nitrate. With the same volume of acetate the temperature of turbidity falls about 10° C.

Precipitating from more dilute solutions did not seem to make much difference. The tendency was to give more perfect separations, but this may be due to the longer digestion of the larger volume between precipitating and boiling points.

The present object is to find with what amounts of acetate, dissolved hydrate, and free acetic acid, the most effective separations may be made of those metals which are at all separable by these means. Attention is specially to be paid to those separations which are of value to the steel works' chemist, and hence separations from iron claim first notice. Qualitative tests, which have indicated at least the partial separation of ferric oxide and alumina, for instance, lend colour to the hope that the completed investigation may not be without value.

The Laboratory, Norfolk Works, Sheffield.

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* The neutralised solutions I obtained, if diluted with about 200 c.c. of water, were partly precipitated by boiling.

† The ammonia acetate was made two months before using. It was then neutral, as when first made. It has been stated that the solution decomposes on keeping, and should be made as required. I believe this is not a general practice, and this point is specially noted in the hope that it may elicit further information.

CONTRIBUTION TO THE STUDY OF HYPONITROUS ACID.*

By A. HAUTZSCH and A. L. KAUFMANN.

(Continued from p. 245).

Hyponitrite of Benzyl, $C_7H_7ON{=}NOC_7H_7$.

THE only ether of hyponitrous acid yet known, hyponitrite of ethyl, was obtained by Zorn in the form of a yellow oil, by treating iodide of ethyl with hyponitrite of silver. In spite of the explosibility of this ether, its vapour density has been determined. It corresponds to the formula $(C_2H_5)2N_2O_2$. The benzylic ether which we have prepared is much more stable.

Pure, dry, hyponitrite of silver is added in excess, to a well-cooled etherised solution of carefully purified iodide of benzyl; the temperature, which will tend to rise, must be kept low. When, after two or three hours, the smell of iodide of benzyl has disappeared, it is filtered, the ether is evaporated off, and we obtain the benzylic ether in a pure state by re-crystallisation in ligroin.

I. 0·1883 grm. of the substance gave 0·4757 grm. CO_2 and 0·1042 grm. H_2O.
II. 0·1147 grm. of the substance gave 0·2905 grm. CO_2 and 0·0639 grm. H_2O.
III. 0·1460 grm. of the substance gave 14·5 c.c. N at 17° C. and 760 m.m. pressure.

	I.	II.	III.	Theory, C_7H_7NO.
C.	68·89%	69·07%	—	69·42%
H.	6·15%	6·19%	—	5·79%
N.	—	—	11·53%	11·57%

The molecular weight of the ether has been determined cryoscopically in acetic solution, by passing—as recommended by Beckmann—a continuous current of dry air over the liquid.

I. 0·1041 grm. of the substance, dissolved in 20 c.c. of glacial acetic acid (sp. gr. = 1·055), lowered the congealing point by 0·081° (mean of six observations).
II. 0·3086 grm. of the substance, dissolved in 20 c.c. of glacial acetic acid, lowered the congealing point by 0·251° (mean of seven observations).

Molecular Weight.

Found.		Theory,
I.	II.	$C_{14}H_{14}N_2O_2$.
236	227	242

Hyponitrite of benzyl is bi-molecular, as is free hyponitrous acid and Zorn's ethylic ether. It is easily soluble in alcohol and ether, but only slightly so in ligroin. The latter precipitates it from its solution in alcohol or ether. It melts at 43° to 45° with decomposition, and detonates when rapidly heated to 60°. Even at the ordinary temperature it volatilises easily. In an experiment made, its loss of weight was 7·5 per cent in seventeen hours.

The decomposition of hyponitrite of benzyl when warmed gives rise to a considerable disengagement of gas. To discover the nature of this gas we dissolved a weighed quantity of the ether, in methylic alcohol, warmed the solution to 50° in a current of carbonic acid, and collected the gas in a nitrometer.

0·1915 grm. gave 17·7 c.c. (at 18° and 751 m.m. pressure) of nitrogen (and not protoxide of nitrogen).

Nitrogen found 10·57 per cent; theory 11·57 per cent. Assuming that the nitrogen is liberated nearly quantitatively, the decomposition of hyponitrite of benzyl is no doubt according to the following equation:—

$$C_6H_5CH_2ON,NOCH_2C_6H_5= \\ =C_6H_5CH_2OH+C_6H_5CHO+N_2.$$

This experiment confirms Zorn's observation relative to the decomposition of the ethylic ether of hyponitrous acid.

Decomposition of Hyponitrous Acid.

It has been generally admitted, up to the present, that hyponitrous acid splits up quantitatively into protoxide of nitrogen and water.

The fact that hyponitrous acid gives a blue colour to iodide of potassium and starch acidulated with acetic acid, then the brown colouration produced by the addition of ferrous sulphate and the blue colouration produced by the additon of a phenylamine to a sulphuric solution of hyponitrous acid, and, again, the observations made on the determination of the conductivity of this acid, which will be described further on,—all these facts go to prove that, by a secondary reaction, hyponitrous acid gives birth to nitrous acid.

Above all we could suppose that, by the inverse of the synthesis of hyponitrous acid achieved by Wislicenus, this acid would split up, under certain conditions, into nitrous acid, and hydroxylamine according to the equation $HON,NOH+H_2O=HONO+NH_2OH$.

In spite of all our efforts we have not been able to prove the presence of hydroxylamine among the products of decomposition of hyponitrous acid. On the other hand, we have shown that hyponitrous acid partially splits up into nitrous acid and ammonia, according to the equation—

$$3N_2O_2H_2=2N_2O_3+2NH_3.$$

This decomposition is easily explained on the supposition that the acid, HON,NOH, becomes first changed into its tautomeric demi-molecular form, O,NH, to which nitrosobenzine corresponds as its ether; after which a molecule of this aldehyd of nitrous acid becomes oxidised, after the manner of true aldehyds, at the expense of another molecule, which is thus reduced to ammonia:—

$$HON,NOH=2HNO$$
$$3HNO=NH_3+N_2O_3.$$

As a secondary reaction, the molecule of ammonia may be oxidised at the expense of the half molecule of nitrous anhydride formed, and may eventually form nitrogen, water, and nitrous or nitric acid, according to the equation $NH_3+N_2O_3=N_3+H_2O+HNO_3$. However, in comparison with the splitting up into protoxide of nitrogen and water, the decomposition we have just mentioned takes place but very slowly in aqueous solution. A freshly prepared solution of hyponitrous acid, boiled in a flask fitted with a vertical condenser, became completely neutral, and did not contain a trace of nitrous acid. But, on the contrary, an exactly similar solution left for several hours at 25° before being boiled, maintained its acid reaction to the end of the operation, and, moreover, contained 2 per cent of free acid. When neutralised and evaporated to dryness, it showed the nitrite reactions very clearly.

Another portion of the same solution was similarly boiled, and then evaporated to dryness with hydrochloric acid. Ammonia could be detected in the residue by means of Nessler's solution.

In another experiment a freshly prepared solution of hyponitrous acid was divided into three portions; the first portion was left intact, the second was treated with caustic potash in excess, while to the third a few drops of hydrochloric acid were added. After the lapse of twenty-four hours, these three solutions were analysed. In the first, which had been hyponitrous acid alone, we proved the presence of nitrous acid by means of diphenylamine. the complete absence of ammonia, and the presence of unaltered hyponitrous acid. The second contained neither nitrous acid nor ammonia, but there was still some hyponitrous acid present. The third contained neither nitrous acid, ammonia, nor hyponitrous acid, but nitric acid. These three experiments confirm the view that hyponitrous acid is most stable in an alkaline solution, and least stable in

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* *Moniteur Scientifique*, vol. xi., p. 336, May, 1897.

an acid solution. The stability of the pure acid in aqueous solution is midway between the two.

We need not be astonished that no ammonia is formed in these last three experiments. The ammonia which might be formed in very small quantities in tte acidulated solution, would be immediately destroyed by the action of the nitrous acid which would be formed simultaneously. We can only detect the presence of ammonia by the very rapid evaporation of strongly acid solutions of hyponitrous acid.

The formation of nitrous acid during the decomposition of hyponitrous acid explains the blue colouration obtained with diphenylamine, and the brown colouration with ferrous sulphate, This reaction equally explains the fact that the determination of the rapidity of the decomposition of hyponitrous acid into protoxide of nitrogen and water has not been found possible.

Before recognising this secondary reaction we quite expected that the relation between the still undecomposed acid (a) and that already decomposed into protoxide of nitrogen and water (x) could be determined at any or every moment by the diminution of the acid titration. By the equation—

$$c = \frac{1}{t} \cdot \log \frac{a}{a-x}$$

we could have measured the speed-constant of the decomposition. With this idea we took, at stated intervals, 10 c.c. samples of a solution of hyponitrous acid, prepared at 0° and kept at 25° in an Ostwald thermostat, These samples were titrated with a 1/16th normal solution of baryta, using phenolphthalein as indicator. But the values of c, calculated according to the above formula, were not even approximately constant, and moreover increased as the experiment went on. This increase in the speed of decompositon can only be attributed to the gradual acceleration of the secondary reaction, which results in the formation of nitrous acid. It is another example of accelerant catalytic action of the ions of hydrogen, for here again the presence of nitrous acid has been definitely proved.

The fact that acid considerably accelerates the decomposition of hyponitrous acid has been shown in a special experiment, by determining the speed of decomposition in the presence of hydrochloric acid. The initial values of c were in this case much greater than those obtained with an aqueous solution of pure hyponitrous acid. But here again we could not obtain a constant by the diminution of the titration of the acid. But if we took as abscissæ the calculated values of

$$c = \frac{1}{t} \cdot \log \frac{a}{a-x},$$

and the corresponding intervals of time as ordinates, we obtained a regular curve which showed that the speed of decomposition increased with the quantity of the substance decomposed. We propose later to make a special study of this phenomenon.

(To be continued).

A NEW AND ACCURATE METHOD FOR THE ESTIMATION OF POTASSIUM.

By H. N. WARREN, Principal, Liverpool Research Laboratory.

The solution containing the alkalis as chlorides, having been previously exhausted of the accompanying group metals, is heated with an excess of platinic chloride, and the whole evaporated to very small bulk in a platinum dish, or other suitable receptacle; to the contents are now added about double the original quantity of a mixture composed of equal parts of amylic alcohol and ether. The precipitate is by these means immediately rendered dense, and can thus be washed once or twice with the utmost facility, using the same mixture. The yellow precipitate thus obtained is next transferred to a small glass beaker, and heated to the boiling point with the addition of about 5 c.c. of formic acid. The solution thus speedily assumes a brownish tint, at which stage a slight excess of ammonia is introduced, and re-boiled, when the whole of the platinum is precipitated in the form of black flocks, which may be readily washed and dried, from the weight of which the percentage of potassium present may be readily calculated.

With a little practice the operation will be found more expeditious, more accurate, and at the same time less troublesome, than the general methods advised for the estimation of potassium.

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ON THE RECOGNITION OF THE YELLOW OF NAPHTHOL S, AND OF ANALOGOUS COLOURING-MATTERS IN WHITE WINES AND LIQUEURS.

By ALBERTO D'AGUIAR and WENCESLAU DA SILVA.

The yellow of naphthol S, like diamond brilliant yellow S, &c., are scarcely extracted from an alkaline solution by means of solvents, such as amylic ether, acetic ether, sulphuric ether. Under these conditions we proceed as follows:—

A portion of the wine is strongly acidified with sulphuric acid, and shaken up with amylic ether, which extracts all the colouring-matter derived from the coal-tar and a part of the natural colouring-matter of the wine. After decantation and filtration the amylic alcohol is agitated with an excess of ammonia, and allowed to remain at rest until it is permanently limpid. The natural colouring-matter of the wine, as also various other matters, are precipitated by the ammonia. The amylic alcohol retains in solution a portion of the coal-tar colour sufficient for its detection by dyeing-tests or by reagents. The amylic solution is shaken up with water and acidulated sulphuric acid; after standing it is evaporated, in contact with a thread of silk, with a few drops of ammonia. The silk is then distinctly dyed, and the residue left by the amylic alcohol is next submitted to the action of sulphuric and hydrochloric acids and ammonia, to allow of a study of the changes produced by these reagents.

We have made these experiments on wines coloured with naphtha yellow S, brilliant yellow S, diamond yellow, turmeric and fustic, as well as on natural wine. The results were positive with the first three, but negative with the last three, notwithstanding the strong colouration of the amyl-alcoholic tinctures.

Bellier's procedure also gave very distinct positive results with the first three tests, but negative with the latter.

These experiments have been repeated on Ermida wine mixed with the other yellow coal-tar colours mentioned in a former paper. The results have been also positive.—*Comptes Rendus*, cxxiv., No. 18, 1897.

Contribution to the Study of Tinctorial Reactions.—A. Reychler.—After describing a number of experiments and verifications of the conditions existing, the author claims that he has not disproved the theory put forward by M. Knecht; but, on the contrary, he has confirmed the ideas held on the constitution and action of saline solutions in respect of dyeing.—*Bulletin de la Société Chimique de Paris.*

SOME PRESENT POSSIBILITIES IN THE ANALYSIS OF IRON AND STEEL.[*]

By C. B. DUDLEY.

To the analytical chemist there are few substances in nature more interesting than a piece of pig-iron, few substances which have received more study, and few which present chemical problems more difficult of solution. The amount of work which has already been done in connection with this very common but very complex substance is something enormous. Indeed, if we add to the study which has already been put on pig-iron itself, the work which has been done on what may perhaps fairly be called its progenitors, viz., the ores, the fuel, the flux, and the refractory materials used in its production, and then consider still farther the labour already expended in the analysis of what we may call the progeny of pig-iron, viz., castings, wrought iron, malleable iron, and the numerous grades and kinds of steel made by the various processes of the present day, we shall surely be safe in saying that more chemical work has been done in connection with pig-iron than with any other substance in nature. Is it too much to affirm that at the present time one-third, possibly one-half, of all the chemical work done in the world is in connection with the iron industry, either in the solution of unworked-out problems, the development of new methods of analysis, or in the routine analyses affecting the interests of producer and consumer.

But the amount of work already done and in daily progress in connection with this substance is not all that may be said in regard to it. The complexity of pig-iron is very great, and consequently the analytical problems presented are far from being easy of solution. It may not be uninteresting to enumerate some of the substances which have already been found in pig-iron. We find, besides the element iron, carbon, phosphorus, silicon, sulphur, manganese, copper, chromium, tungsten, titanium, vanadium, nickel, cobalt, aluminum, potassium, sodium, magnesium, calcium, and lithium. It is fair to say there is apparently well grounded belief that the last five are characteristic of intermingled slag rather than of the metal itself. It is not intended that it should be understood that all of these substances have been found in any one sample of pig-iron, but that all these substances have actually been detected in the analysis of this alloy. Indeed there seems no reason why any element, which either occurs in the metallic condition in nature, or which is reducible to that condition by carbon, and which is not volatile at the temperature of the blast furnace, may not occur in pig-iron, provided of course it will alloy with the metal. Quite a large number of other substances besides those mentioned above have actually been alloyed with some form of iron or steel. Among these may be mentioned zinc, tin, lead, antimony, bismuth, molybdenum, silver, platinum, rhodium, iridium, palladium, and gold. Nor is this all that may confront the analyst who devotes himself to the chemistry of iron and steel. Not less than three elements which usually exist in nature in the gaseous form occur in these metals, and are believed to have important influences on their physical properties. These are oxygen, hydrogen, and nitrogen; while the numerous analyses show the presence of carbon monoxide in both cast-iron, wrought iron, and steel. It seems quite evident that the chemist who hopes to successfully cope with the problems which are involved in even the ultimate analysis of iron and steel in their various forms, must be well equipped with a liberal share of the methods and processes known to mineral chemistry; and, on the other hand, if he attempt the proximate analysis of these substances, or the separation and determination of the various compounds of the elements present, with iron or with each other, he will at least be brought on the border-ground of organic chemistry. Some of the carbon compounds which are characteristic of the brilliant work of the present President of the French Chemical Society, are known to occur in or have already been isolated from pig-iron.

It would lead us too far from our present purpose to do anything more than enumerate the largest number of the elements given above. Suffice it to say that in what follows, we shall confine ourselves to the five first mentioned, viz., carbon, phosphorus, silicon, sulphur, and manganese. And the question which we shall ask ourselves is, what is the present condition of a portion of the analytical methods for the determination of these substances, considering these methods both in regard to their accuracy and speed? One word of precaution. It would be manifestly impossible to comment on all the methods in use for determining these constituents. To enumerate them alone would weary your patience. We shall confine ourselves, therefore, principally to methods which may be, or are, used when the diverse interests of producer and consumer are involved.

Beginning, then, with total carbon in pig-iron, wrought iron, and steel, we deem it safe to say that the method by combustion in oxygen gas, as at present known and worked in many laboratories, leaves very little to be desired, so far as accuracy is concerned, and is sufficiently rapid for most commercial uses. The modification introduced some years ago, of using a solution of the double chloride of copper and ammonium, instead of simple chloride of copper,[*] to release the carbon from the iron, took away from the combustion method one of its greatest difficulties, viz., the long time required to dissolve the metal. This modification, as many will doubtless remember, reduced the time required for solution from two or three days to an hour or less. Indeed, at the present time, if a good stirring machine is used, it is quite possible to dissolve 3 grms. of fairly fine borings of pig-iron, wrought iron, or steel, in 200 c.c. of the proper solvent in from ten to forty minutes. Still further, the studies of the Committee on International Standards for the Analysis of Iron and Steel have further modified the method, and it is believed rendered it much more accurate. Among these modifications may be mentioned the use of an acid instead of a neutral or basic solution of the double salt to dissolve the metal. This point was thoroughly worked out by Blair (*Trans. Am. Inst. Mining Eng.*, xix., 614). Following this came the work done in the laboratory of the Pennsylvania Railroad Company, demonstrating the unreliability of the use of the double chloride of copper and ammonium as a solvent, owing, as appeared later, to the probable presence in all ammonia and its salts obtainable in the market, even those marked "C. P.," of some carbonaceous material, possibly pyridine (*Trans. Am. Inst. Mining Eng.*, xx., 242) derived from the gas liquor used in making the ammonia. The substitution of the potassium for the ammonium salt has apparently completely overcome this difficulty, and this, with the use of oxygen gas instead of lead chromate, in which to burn the carbon, and some modifications of the absorbing and purifying train (*Journ. Amer. Chem. Soc.*, xv., 448), have seemingly placed the dry combustion method for determining carbon in the front rank of successful and accurate analytical processes. The principal known source of error in the method at the present time appears to be in connection with the weighing. The potash bulbs and small calcium chloride tube used in

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[*] Presidential Address delivered at the Troy Meeting of the American Chemical Society, December 29, 1896. From the *Journal of the American Chemical Society*, xix., No. 2.

[*] It is difficult to say positively who first suggested this modification. The first mention in literature that we are able to find is in the *Transactions of the American Institute of Mining Engineers*, iv., 157, by J. B. Pearse. But a private communication from Andrew S. McCreath, states that he made the suggestion while working under Pearse, and that Professor Richter, in the "Leoben Jahrbuch," had previously suggested the use of potassium or sodium chloride with copper chloride, which led him to try the ammonium salt. McCreath's description of the method, as used by himself, is published in the *Transactions of the American Institute of Mining Engineers*, v., 575.

absorbing the carbon dioxide weigh altogether some 50 to 60 grms., and present considerable surface. If now, between the weighing before the combustion and the weighing after the combustion, the interval being an hour or a little more, there is considerable change in the hygroscopic condition of the atmosphere, an error of 0·01 per cent may be easily introduced. If we may trust our experience, it is difficult to make closely agreeing duplicate combustions in showery weather. Blair suggests a method of overcoming this difficulty, consisting in having a second potash bulb and calcium chloride tube of—as nearly as possible—the same size on the opposite end of the balance when weighing.

In regard to the accuracy of the method as at present understood, it may be said that undoubtedly the best test of the accuracy of a method is the recovery of a known amount of any substance added to the material to be analysed. This procedure being manifestly impossible in the case of iron and steel, we are compelled to judge of the accuracy of the combustion method, as applied to these metals, in some other way. For this purpose, however, we have at hand the results obtained by different chemists, using different methods, but working on the same samples. In the course of the work done by the Committee on International Standards for the Analysis of Iron and Steel, the carbon in four samples of steel was determined. First, by using acid double chloride of copper and potassium as solvent, and burning in oxygen gas; Second, by using the same solvent, and burning in chromic acid solution; and Third, by treating the borings direct with bisulphate of potash and heat, conducting the carbon monoxide and sulphur dioxide formed over hot solid chromic acid, which oxidised both gases and retained the sulphur trioxide formed, and finally measuring the volumes of the resulting carbon dioxide in an eudiometer tube. Each method was used by a different chemist. The results obtained are as follows, the letters at the side representing the four samples of steel, the figures at the top representing the chemists, and the figures in the columns the percentages of carbon in the steel samples:—

	1.	2.	3.
A	1·455(*a*)	1·440(*a*)	1·450(*b*)
B	0·815	0·800	0·815
C	0·450	0·450	0·448
D	0·152	0·185	0·168

(*a*) *Proc. Eng. of Western Penna.*, ix., [9], 35.
(*b*) *Ztschr. anorg. Chem.*, iv., [3] und [4], 505.

The agreement of the results on the first three samples is quite marked. The discrepancy on the fourth sample has not been explained. The matter is discussed in considerable detail in reference (*a*), but we think it safe to conclude that, so far as method goes, the determination of total carbon in pig- or cast-iron, wrought iron, and steel, is reasonably accurate.

The speed of the combustion method as at present worked in good laboratories is quite remarkable, compared with the possibilities twenty-five years ago. A sufficient supply of sample borings being at hand, one operator using two furnaces may readily make from fourteen to sixteen combustions in a day of eight hours; it being understood that the bulbs are weighed with oxygen gas in them instead of air, and that the last weight of each combustion, except the last one at night, is taken as the first weight of the succeeding one. It is, of course, assumed that when turning out the amount of work above described, the furnaces and apparatus are all in good order, and everything working well. Accidents, an occasional overhauling of the apparatus, blank combustions from time to time for testing purposes, and once in a while an obstinate steel that refuses to dissolve in time or gives trouble in filtration, will tend to diminish output. The results obtained with this rapid work show, when duplicates are made, occasional discrepancies, as high as three hundredths of a per cent in a steel containing 1 per cent of carbon, but we have seen very large numbers of duplicates, made as above described which did not disagree one one-hundredth.

Again, when work is not so plentiful as to admit of the procedure described above, the method still permits satisfactory speed. Starting with a fresh sample of borings and everything in good order, but cold, it is not difficult to get two closely-agreeing determinations on the same sample in two hours and a half. Of course, in investigation or referee work, more time would undoubtedly be used, especially if the interests involved are very great. But we have many times been astonished in our own laboratory at the close agreement between the results obtained in the rapid manner described above, and the duplicate analysis made on the same sample for confirmatory purposes, but using much more time and pains.

Turning now to the determination of combined carbon and graphite, we do not find the state of affairs so satisfactory. As is well known, these two constituents are usually found by first determining total carbon, then dissolving another portion of the sample in hydrochloric acid, filtering, and washing with caustic potash, alcohol, and ether, and then burning the residue; collecting and weighing the carbon dioxide formed, as in an ordinary combustion. The result is called graphite, and the combined carbon is the difference between the total carbon and the graphite. But, as Shimer (*Trans. Am. Inst. Min. Eng.*, xxv., 395) has so well shown, what we actually get by this procedure is not necessarily the graphite and the total combined carbon in the sample, but only the combined carbon which exists in the metal as a carbide soluble in hydrochloric acid. If the sample contains carbides not soluble in that acid, nor in the materials used in washing, the carbon of these carbides appears with, and is counted as, graphite. Shimer shows that titanium, and possibly vanadium carbide, are apparently not infrequently thus counted. The use of sulphuric instead of hydrochloric acid leads to the same error, while the employment of nitric acid as solvent, apparently gives the graphite much more definitely, but leaves us in doubt as to whether the combined carbon is really the combined carbon which we want, in order to have light on the quality of the metal we are dealing with. It is obvious that the difficulty here is in our lack of knowledge as to what carbides actually exist in pig- and cast-iron, and if there are several of them, which one or ones do we actually want to know the carbon content of. If we knew positively that the combined carbon wanted was that which exists in the metal as carbides of iron and manganese, and that these carbides were soluble in hydrochloric or sulphuric acid, while all other carbides present were not soluble in these acids, obviously we should use these acids when determining combined carbon. On the other hand, if we want to know only graphite, and care little about the combined carbon, apparently nitric acid is the solvent to use. It is clear that much more work is needed on this subject—a state of affairs which, as we progress, we shall find is characteristic of other constituents of the metals we are considering.

(To be continued).

Researches on the Composition of Wheats and on their Analysis.—Aimé Girard.—The exclusion from human consumption of 30/100 of the mass of wheat known as "low produce" and refuse milling, places at the disposal of agriculture a very rich residue for the food of cattle. These products are very rich in fatty matter, but their woody nature presents a certain resistance to the action of solvents. To facilitate this action, I advised, some years ago, to moisten these products with hydrochloric acid at 5 per cent, and to dry them afterwards, so as to transform the cellules and the vessels into pulverulent hydrocellulose, which is easily penetrated by benzene or ether.—*Comptes Rendus*, cxxiv., No. 18.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 29th, 1897.

Professor Dewar, F.R.S., President, in the Chair.

Messrs. Arthur Croft Hill, Edward G. Guest, and Horatio Ballantyne were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Gerald Noel Brown, 8, The Esplanade, Plymouth; George Lawson Johnston, Kingswood, Sydenham Hill, S.E.; William Taverner, 1, Stapenhill Road, Burton-on-Trent.

The President announced that the Council had ordered a re-count of the balloting papers handed in at the Anniversary Meeting. The re-count would be conducted by the two Scrutators appointed by the Society at the Anniversary Meeting, in the presence of the Secretaries.

Mr. Cassal enquired whether the actual numbers would be announced.

The President replied that he assumed that they would.

Of the following papers those marked * were read:—

*53. "*On the Explosion of Chlorine Peroxide with Carbonic Oxide.*" By H. B. Dixon, M.A., F.R.S., and E. J. Russell, B.Sc.

To test the question whether dried carbonic oxide is more readily attacked by "nascent" than by ordinary oxygen, the authors have fired a dried mixture of chlorine peroxide and carbonic oxide. They find that the carbonic oxide is not completely burnt in the flame although the oxygen is in excess; and the drier the mixture the less carbonic oxide appears to be burnt. The results do not favour the view that "nascent" oxygen attacks carbonic oxide more readily than ordinary oxygen.

Discussion.

Dr. Scott thought it desirable to try the effect of some compound, such as chloride monoxide, which contained only one atom of oxygen, before concluding that "nascent" oxygen was inoperative.

Professor Armstrong referred to the difficulty of ascertaining whether a gas was completely free from water.

The President thought that the ultra-violet spectrum of water vapour, which he and Professor Liveing and Dr. Huggins had simultaneously discovered, would be found to be a very delicate test of its presence in flames or explosive mixtures.

Mr. Crookes agreed with the President as to the delicacy of this test.

*54. "*On the Decomposition of Iron Pyrites.*" By W. A. Caldecott, B.A.

In "Watts' Dictionary" (1892 edition, vol. iii., p. 64) it is stated that ferrous sulphide "is formed by the reduction of Fe_2O_3 on ferric salts by decomposing organic matter in the presence of sulphates," also that "finely-divided yellow pyrites (FeS_2) oxidises in air forming chiefly $FeSO_4$." T. K. Rose ("The Metallurgy of Gold," 1896, page 343) states that "FeS_2 is oxidised by air and water, $FeSO_4$ and free H_2SO_4 being formed."

In the treatment of auriferous pyritic Witwatersrand conglomerate, a large percentage of the ore is reduced by wet crushing in the battery to an impalpable powder. This fine material constitutes "slimes," and is carried in suspension by water into extensive dams, where it settles. The slimes leaving the battery are free from ferrous sulphide, but this compound may be detected in them a few days after deposition in the dams. The settled slimes form a clayey mass, practically impermeable to air and water, and consequently subsequent oxidation of the ferrous sulphate proceeds extremely slowly.

When iron pyrites are crushed to an impalpable powder in an iron mortar ferrous sulphide is formed.

It thus appears that ferrous sulphide and not ferrous sulphate may be the first product of the decomposition of iron pyrites.

Owing to the almost total absence of acidity in slimes deposited as above, even when containing 0·89 per cent ferrous sulphide, it is probable that under these conditions FeS_2 undergoes dissociation, and the sulphur is separated as such; the author is engaged in further investigating this subject.

*55. "*Monochlordiparaconic Acid and some Condensations.*" By Henry C. Myers, Ph.D.

An attempt to prepare methylparaconic acid by the reduction of the trichlor-acid furnished the dichlor-acid, which on treatment with barium hydroxide suffered condensation, forming the acid $C_9H_9ClO_2$, which has been called monochlordiparaconic acid; its constitution is under investigation. This acid loses its chlorine on treatment with nascent hydrogen, producing a compound having in all probability the formula $C_9H_{12}O_2$, but it is so unstable that its investigation is very difficult. These condensations are being further investigated.

56. "*Corydaline.*" Part V. By James J. Dobbie, M.A., D.Sc., and Fred Marsden, M.Sc., Ph.D.

When corydaline is heated on the water-bath with very dilute nitric acid (about 1 : 20), a difficultly soluble nitrate, $C_{22}H_{29}NO_4 \cdot HNO_3$, is first formed.

On further heating, the solution becomes dark red in colour, and soon ceases to give any precipitate on testing with ammonia. If at this stage the solution be allowed to cool, groups of bright yellow prismatic crystals separate out on the sides of the vessel. The crystals consist of the nitrate of a base—dehydrocorydaline—differing from corydaline by four atoms of hydrogen (*cf. Trans.*, 1897, lxxii., i., 175). The free base is very soluble in water and alcohol, and is difficult to obtain in crystals. The nitrate, $C_{22}H_{25}NO_4 \cdot HNO_3$; the chloride, $C_{22}H_{25}NO_4 \cdot HCl$; the platinochloride, $(C_{22}H_{25}NO_4 \cdot HCl)_2PtCl_4$; and the chloroform compound, $C_{22}H_{25}NO_4 \cdot CHCl_3$, are described. The solutions of dehydrocorydaline and its salts have an intense yellow colour, and give a vivid green colour with blue litmus. Reducing agents re-convert dehydrocorydaline into optically inactive corydaline.

If concentration of the acid solution be continued beyond the point at which dehydrocorydaline is formed until platinum chloride no longer gives a precipitate, yellow coloured crystals of an acid melting at 218° separate out on cooling. This, acid, to which, for convenience of reference, the name *corydic* is temporarily given, is readily soluble in hot water and in alcohol, but insoluble in ether. Its aqueous solution has an intense yellow colour, and does not give precipitates with any of the metals in aqueous solution.

A silver salt, $C_{18}H_{15}NO_6Ag_2$, is obtained by precipitating an alcoholic solution of the potassium salt of the acid with an alcoholic solution of silver nitrate. Corydic acid contains two methoxy-groups and is dibasic. Its formula is $C_{14}H_9N(OCH_3)_2(COOH_2),\frac{1}{2}H_2O$. When heated with hydrogen iodide it yields, a highly insoluble phenolic acid, $C_{14}H_9N(OH)_2(CO \cdot OH)_2 \cdot 2H_2O$, which separates from a large quantity of hot water in brilliant yellow spangles. The lead salt of this derivative, dried at 130°, has the composition $C_{16}H_{11}NO_6 \cdot Pb$.

When corydic acid is boiled with a solution of potassium permanganate, it yields a mixture of at least four acids.

(1). An acid, $C_{12}H_6N(OCH_3)_2(CO_2H)_3$, which crystallises from hot water in small white acicular crystals melting at 228°. This acid, which is the chief product of the oxidation, contains two methoxy-groups. A silver salt, having the composition $C_{17}H_{12}NO_8Ag_3$, has been prepared. (2). A hemipinic acid, yielding an ethylimide which melts at 228°, and differs therefore from the hemipinic acid previously described as occurring amongst the products of oxidation of corydaline with potassium permanganate. It is thus established that corydaline contains two benzene nuclei, and the formation of corydic acid from the alkaloid is easily explained on the assumption that one of the rings is oxidised. (3). A nitrogenous acid melting at 208° which contains no methoxy-groups and gives a faint brownish yellow colour with ferrous sulphate solution, and evolves a strong odour of pyridine when heated with lime. This acid has the formula $C_9H_7NO_6 \cdot H_2O$, and is apparently a methylpyridine tricarboxylic acid. It is not identical with any of the known acids of this composition. It forms a silver salt, $C_9H_4NO_6Ag_3$, and gives precipitates with lead, barium, and copper. (4). A nitrogenous acid melting at 243°, which gives a yellowish red colour with ferrous sulphate and contains methoxyl.

Oxalic acid and the nitrogenous acid melting at 208° were obtained from the mother-liquors of corydic acid.

Ordinary Meeting, May 6th, 1897.

Professor Dewar, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. William Ackroyd, 9, Grandsmere Place, Halifax; William Malam Brothers, Beechwood House, Prestwich, near Manchester; William Cranfield, 5, Second Avenue, Halifax; A. F. Bilderbeck Gomez, 24A, Alfred Place West, South Kensington; Frederick Roscoe Grundy, B.Sc., 20, Derby Road, Douglas, Isle of Man; Edward Halliwell, Alexandra Crescent, Dewsbury; Harold Harman, Brewers Sugar Co., Greenock; William Robertson Pollock, Kirkland, Bonhill, Dumbarton.

The President stated that, in accordance with the instructions of the Council, the two Scrutators, in the presence of the Secretaries, had re-counted the votes recorded for the Presidency at the Anniversary Meeting. The Scrutators' report will be presented to the Council in due course, but he thought he might now venture to say that he learned from the Senior Secretary that the votes accepted by the Scrutators were 166 for the Council's nominee, and 152 against.

The following were duly elected Fellows of the Society:—Messrs. Herbert W. L. Barlow, M.A., M.B.; William Barlow; Alfred Hunter Boylan; James Brierley; Henry Norris Davidge; Louis Charles Deverell; Alexander Duckham; Alaric Vincent C. Fenby, B.Sc.; Charles Henry Field; Thomas Girtin, B.A.; R. Glode Guyer; Harold William Harrie; Sydney Hill; W. J. G. Lasseter, M.A.; Charles Macculloch; Willie Lee Mallinson; George Fowlie Merson; Edmund Howd Miller, M.A., Ph.D.; Tom Mitchell; Frederick Filmer de Morgan; Joseph Previte K. Orton, B.A., Ph.D.; Harry E. W. Phillips, B.A.; Robert Howson Pickard, B.Sc.; Thomas Tickle; William Herbert Waite, B.A.; Charles Thomas Foster Watts; John Welsh; Charles Alfred West; Paul Thomas White.

Of the following papers those marked * were read:—

*57. "*A Bunsen Burner for Acetylene.*" By A. E. Munby, M.A.

The cheap production of calcium carbide has placed a powerful illuminant within the reach of those who possess no gas supply, but so far little has been heard of the use of acetylene as a heating agent. Our laboratory is, as far as we know, the first to make use of the gas for this purpose. We employ a Bunsen burner of special dimensions, the tube being 5 m.m. in internal diameter. A slightly wider tube may be used, provided the mouth be curved inwards, so that the actual exit does not exceed the diameter mentioned; if larger, the flame tends to strike down. The gas jet is very small, being only capable of delivering about 1 cubic foot of acetylene per hour under 6 inches water pressure, such a rate of consumption giving an ordinary working flame. The air-holes and collar are arranged as in an ordinary Bunsen, the exact size of the former not being of much importance provided they be large enough to admit the air required. The burner is protected with a cap, when not in use, as its efficiency depends upon the jet maintaining its dimensions. A generator capable of giving gas under 7 inches water pressure with the full number of burners in use is required. Under this pressure a large, perfectly blue flame is obtained, which may be turned down to what may be termed a quarter Bunsen flame, equivalent to burning the gas under 3 to 4 inches water pressure. This is the smallest pressure with which the burner will give a non-luminous flame; when turned lower, the zone of partial combustion appears, since the draught is then insufficient.

The heating effect of the flame is of course very great, enabling one to dispense with the blowpipe for some operations, such as small fusions. From a few experiments on heating equal quantities of water under like conditions with coal-gas and acetylene, it would seem that in practice, for equal volumes burnt, the latter has nearly twice the heating power of the former.

The use of the gas should do much to stimulate research in country places and on private estates.

*58. "*The Reactions between Lead and the Oxides of Sulphur.*" By Henry C. Jenkins and Ernest A. Smith. (This paper appeared in our last issue, p. 241).

Discussion.

Professor Roberts-Austen said that he was much gratified by the fact that the accuracy of the time-honoured equations given by his distinguished predecessor, Dr. Percy, as representing the metallurgy of lead, had been abundantly justified by work done in the Metallurgical Laboratory of the Royal College of Science. He could testify to the extreme care which Messrs. Jenkins and Smith had given to the work, and the reversible reactions they had discovered were not only very interesting, but of much industrial importance. In justice to Mr. Hannay, it might be conceded that the singular nature of the reactions discovered by the authors of the paper justified Mr. Hannay in questioning the accuracy of the old equations, and it was satisfactory that the difficulty had now been solved.

The President, Mr. Groves, and Prof. Armstrong thought the authors' experiments showed that it was unnecessary to suppose that any new compound of lead and sulphur was concerned in the metallurgical process.

*59. "*X Ray Photographs of Solid Alloys.*" By C. T. Heycock, F.R.S., and F. H. Neville.

In a previous communication (*Trans.*, 1889, lv., 666) we discussed the behaviour of gold in sodium and the state of the gold in the solid alloy. We have lately examined alloys of gold and sodium by cutting thin sections from cylinders of the alloy of various concentrations, placing these on a photographic plate, and photographing them by means of the X rays.

On account of the much greater transparency of sodium to these rays as compared with gold, the individual crystals of the alloy are clearly shown. The plates were about 12 m.m. thick, and the alloy had been allowed to cool and solidify very slowly. Pure sodium shows no crystalline structure, but an alloy containing 3 per cent of gold shows a mass of transparent sodium crystals, with dark spaces between the crystals where the gold has concentrated during the process of solidification.

A 10 per cent alloy of gold shows the same phenomena, but the crystals of sodium are narrower, and the dark spaces occupy a larger area.

The appearance of the sodium crystals strongly recalls the fern-like pattern seen when ammonia chloride is crystallised on a microscopic plate, doubtless due to the fact that sodium, like so many other metals, crystallises in the regular system. An eutectic alloy of gold and sodium (23·1 per cent gold), shows, as one would expect, scarcely any structure, because the crystals of gold and sodium separate out simultaneously, and are too minute to be detected by such a method.

A solution obtained by saturating sodium with gold at a temperature considerably above the melting point of sodium shows a net-work of black, opaque needles, which are no doubt crystals of gold which have separated and grown to a considerable size as the liquid cooled.

No sodium crystals are here visible, as the groundwork consisted of the eutectic alloy. We have been able to demonstrate the internal structure of a solid alloy, and to show that the process of solidification is strictly comparable to that of a saline solution, the details being perfectly visible to the naked eye.

We have already examined some aluminium alloys by this method, and hope to present a complete account of the work to the Society. The method will probably be applicable in all cases where there is a considerable difference in transparency between the metals of an alloy.

Discussion.

Prof. Roberts-Austen said that the use of Röntgen rays for revealing the structure of certain alloys possessed advantages when it was desirable to view the alloys as transparent, as distinguished from the structure shown by a section in a single plane. The structure of alloys as revealed by microphotography had now attained great perfection, notably in the hands of M. Osmond in France, and it was a subject to which Professor Austen had recently given much attention; but the X rays might be very useful in the case of alloys containing one transparent metal. When Röntgen's great discovery was first published, Prof. Austen had examined the relative transparency of certain metals, and endeavoured to detect the difference between hard and soft steel, but the sections of steel employed were too thick, and the experiments were abandoned.

It had been shown by Osmond and by Charpy that eutectic alloys have a pearly structure, and Prof. Austen thought that the gold-sodium eutectic shown on the screen by Mr. Heycock also had the pearly structure. As a good example of the distribution produced by freezing, Prof. Austen stated that if a triple alloy of copper, antimony, and lead was cast as a rod and fractured transversely, a purple ring of the "regulus of Venus" (the copper antimony alloy) surrounded the grey alloyed lead which was driven to the centre, so that there was a grey rod inside a purple tube. He hoped that Messrs. Heycock and Neville, who were so greatly extending our knowledge of alloys, would continue their investigations.

The President remarked that this was an important and interesting communication, as illustrating the service the Röntgen rays might be to the chemist. Soon after the announcement of the original discovery, he made experiments on the transparency of the elements to the new rays, and took a number of photographs. In a verbal communication to the Royal Society, he had announced that opacity of elements to the rays increased in the same series with their atomic weight. He thought the rays might sometimes be of use in settling doubtful cases of atomic weight. For example, if liquid or solid argon were found to be less transparent than oxygen or nitrogen in a similar condition, it might be safely concluded that its atomic weight is higher than that of either of the other constituents of air.

Research Fund.

A meeting of the Research Fund Committee will be held in June. Applications for grants, accompanied by full particulars, should be sent to the Secretaries before June 8th.

List of Fellows.

A new list of Officers and Fellows of the Chemical Society being in course of preparation, it is requested that Fellows will send any alteration of address, without delay, to the Assistant Secretary, Burlington House, London, W.

NOTICES OF BOOKS.

Tea: a Text-book on Tea-planting and Manufacture. Comprising Chapters on the History and Development of the Industry, the Cultivation of the Tea-plant, the Preparation of the Leaf for the Market, the Botany and Chemistry of Tea, &c.; with some Account of the Laws affecting Labour in Tea-gardens in Assam and elsewhere. By David Crole (late of the Jokai Tea Company, &c.). Illustrated. London: Crosby Lockwood and Son, Stationers' Hall Court, Ludgate Hill. 1897. 8vo., pp. 242.

We have here an encyclopedic monograph on tea, almost from every conceivable point of view. The planter, the merchant, the general consumer may all very well be interested in a natural product which is here truthfully pronounced as the great "rival of alcohol" among the British race, and which unfortunately shares its deleterious action on public health. The "tea-dinner" is a powerful agent in sapping our national health and vitality, by the simple process of rendering animal foods of various kinds indigestible, and by the equally unsatisfactory trick of substituting "bread and butter" for more nourishing viands. But our author, whilst fully admitting the perils of tea-drinking in excess, as indulged in by Samuel Johnson, lays down three conditions under which the Indian herb may be consumed not merely with safety, but even with benefit. He tells us not to use water which has been boiling before. "Put cold water in the kettle, and directly it comes to a boil use it for making the tea, and also for previously heating the tea-pot and cups."

"Infuse for about four minutes, and five at the outside, and then drain the liquor into another vessel, so that no tea-leaves remain soaking in the liquor.

"It is best, from every point of view, to use only Indian or Ceylon tea."

These rules substantially agree with the practice of experienced tea-brokers, but unfortunately they disagree with many laundresses and other poor women, who allow a minute dose of tea to simmer on the hob until not only all the tea but all the tannin have been extracted. Mr. Crole refers to the very extensive use of non-narcotic beverages,—tea, maté, coffee, cocoa, &c.,—and suggests that they are in some unknown method utilised in the human economy. To solve this and similar questions would doubtless be a worthier expenditure of brain-power than preparing for examinations.

In Assam the greater part of the tea crop grows in the rich soil of the valleys. A bush to do its best requires about 16 square feet of well-cultivated soil around it. The tea-plant requires a very rich soil, a tropical rainfall such as, *e. g.*, 10 inches daily, and a very hot sun.

The author thinks that not only British colonies, but Russia, are preferring Assam tea to those imported overland from China. Without this increasing demand the tea-trade of India and Ceylon will be swamped by overproduction. The author suggests that it would be a wise policy if the tea-growers would seek to open out new markets. At present they are chiefly following out the suicidal policy of opening up fresh lands. One of the perils of the planter must be sought in the inroads of stray beasts, buffaloes, and — what is much worse — elephants, unless the prepared lands are fenced in with barbed wires.

Among the animal parasites which work havoc in a plantation is the "red spider," not unknown in our conservatories at home.

The mosquito blight is a scourge incorrectly named, but fatally destructive. The only remedy known is to burn down, root and branch, all the bushes affected. Mr. Crole recommends the most jealous inspection, lest the enemy should, like the coffee-bug of Ceylon, suddenly overwhelm all the plantations. The number of possible antidotes, and the season and manner of their application, require careful study. Copper sulphate has been tried for "mosquito blight," but not with sufficient perseverance to admit of a decisive judgment. We hope that some experimentalist will appear more successful than Dr. Koch has proved against the *Rinderpest.*

In "Appendix B" we find a list of blight, microbia, and their supposed remedies and their enemies,—proved or hoped for,—which will prove suggestive reading.

The aspirant after laurels, in this most useful or rather necessary warfare, must bear in mind that what will destroy an animal may be absolutely harmless to a parasitical plant, and *vice versa.*

The operations of withering and drying the tea-leaf have given scope to no little skill, and the results, those especially of the Gibbs machine, leave little if anything to be desired.

Mr. Crole remarks it as an inconsistency that, after the utmost care has been used in every detail of the tea-manufacture, it is stamped into the boxes with the boot-shod feet of the people engaged in the warehouses in London.

Mr. Crole's work must commend itself to the favourable notice of a vast and influential portion of the British public.

Respiratory Proteids, Researches in Biological Chemistry. By A. B. Griffiths, Ph.D., F.R.S. (Edin.), F.C.S., Lecturer on Chemistry at the Brixton School of Pharmacy, Member of the Chemical Societies of Paris and St. Petersburg, Author of "Physiology of the Invertebrata," "A Manual of Bacteriology," "Researches on Micro-organisms," &c. London: L. Reeve and Co. 1897. Pp. 126.

The purpose of the present work is to expound recent researches in biological chemistry, giving details of the respiratory proteids in the blood of animals. The author concludes that the blood of the earthworm is chemically comparable to that, *e.g.*, of the dog. The blood of insects (*e.g.*, the house-fly) contains hæmoglobin. The blood of the Lepidoptera is principally green. Lepidoptera are free from respiratory *pigments*, but have still a respiratory function. According to Regnault, Reiset, and Munk, insects, in proportion to their weight, take up as much oxygen as the highest vertebrates. Poulton has shown that larval blood coagulates much more rapidly than pupal blood.

The blood of three species of arachnids has been analysed, and found in every case to contain copper in the form of hæmocyanin. The blood of most gasteropods and cephalopods also contain hæmocyanin.

The spectra of certain respiratory pigments (*e.g.*, echizochrome, oxychlorocruentin, oxyhæmoglobin, hæmoglobin, myohæmatin, alkaline hæmatoporphyrin, and acid hæmatoporphyrin) are shown in a diagram; the serum shows two bands in the green, but turns to a violet-red if allowed to remain in contact with the clot. Chlorocruorin, a green colouring-matter found in the blood of *Saballa*, is a respiratory pigment.

Hæmocyanin, the chief oxygen carrier in the blood of the higher invertebrates, may be conveniently studied in the blood of the lobster, the crab, and the sepia, which contain it to the extent of about 0·30 per cent. Hæmogonin gives a characteristic rose-colour with Millon's reagent. Pinnaglobine contains manganese. The author points out that the respiratory products of animals (Mn=55, Fe=56, Cu=63) do not differ much from each other, and asks if these weights have any important meaning. "What bearing has Prout's hypothesis or Crookes's theory of the genesis of the elements on the subject? Why should the methods present in respiratory proteids have practically the same atomic weight, and be located about a quarter of the distance from the lowest weight (H=1) to the highest weight (U=240)? Has the subject any bearing on the doctrine of evolution, the theory of natural selection, and the action of the environment?"

These are questions which merit and will doubtless repay a careful study.

The Appendix contains much interesting matter concerning pelagine, pupine, cupine (containing lithium), carminic acid, lepidotic and lepidopteric acids.

To all students of biological chemistry this little book will prove deserving of close study.

The School of Mines, Laramie, Wyoming. Petroleum Series. Bulletin No. 2, January, 1897.

This Report comprises an account of the geology of the Popo Agie, Lander, and Shoshons Oil-fields, by W. C. Knight, Professor of Geology; and an analysis of the petroleum of the same districts, by E. E. Slosson, Professor of Chemistry.

Prof. Slosson remarks that the higher the specific gravity of an oil, the higher will be the flashing, burning, boiling, and freezing points, the darker also the colour, and the greater the viscosity. The specific gravities in this report have been taken at 15° C. by the Westphal balance or the flask. Viscidities have been taken by means of Engler's viscosometer. The Popo Agie oil is 0·90000, being lighter than samples taken in 1897 and 1887.

The flashing-point of the crude oil is 32° C., and the ignition-point 58° C. It is still fluid at −10° C. Its calorific power, as determined by the bomb-calorimeter, is 10·437 calories per grm. = 14·571000 foot-pounds of energy per lb. of oil. It is not fluorescent, and on distillation light oils and non-condensible gases are given off at 300°—32°, and paraffin appears in the heavier distillates.

In its crude state Popo Agie oil is inferior to the Salt-creek oil, on account of the presence of light oils, tar, and sulphur compounds.

All the products of the distillation of the Popo Agie petroleum can be capable of utilisation. The gases can be used for firing, and the coke, which is very hard and porous, is fit for metallurgical uses. The residues from filtration can be worked up into paraffin or vaseline.

Report of the Senior Analyst of the Department of Agriculture of the Cape of Good Hope, for the Year 1896. Cape Town: W. A. Richards and Sons. 1897.

The number of articles analytically examined and reported on during this year is lower than in the year immediately preceding, but is nevertheless very satisfactory when compared with the work of former years, being almost double that of the previous highest.

Among the foods analysed under the Adulteration Act, we note that that 21 per cent were found to be adulterated in 1896, as compared with 18 per cent and 30 per cent during 1895 and 1894 respectively. These figures show the great necessity existing for proper control over the quality of foods offered for sale; milk and coffee were the greatest sinners (or, perhaps, sinned against) in this respect.

As usual, a number of samples of water have been submitted for analysis to ascertain their suitability for drinking purposes, but no very definite results are here recorded. "In my last *three* annual reports," we read, "reference was made to the bad quality of practically all the water obtained from wells at Rondebosch and Claremont. Each year brought its evidence in the direction of pollution, and 1896 has not been exceptional in this respect. Again have samples of well water from Rondebosch been submitted for analysis, and again have these waters been found to be polluted and unfit for use." This points to a serious lack of control; if no steps can be taken in four years to remedy such a state of things, is it to be wondered at, that the death-rate from typhoid and fevers is so high in South Africa?

A most important matter in a large agricultural country like Cape Colony is the analysis of soils, and the recommendation of the most suitable fertilisers to be added. Eighty-nine of such analyses have been made over a widely extended area.

CORRESPONDENCE.

PERMEABILITY TO X RAYS.

To the Editor of the Chemical News.

Sir,—In an article on the "Permeability of Various Elements to the Röntgen Rays" published in the Chem. News of December 18th, 1896 (vol. lxxiv., p. 291), I mentioned an experiment with sodium fluoride, chloride, bromide, and iodide, with a view to seeing how the permeability of the halogens varied with atomic weight. Unfortunately the coil used gave such a small spark that the sodium fluoride alone showed any permeability. Since then I have obtained a larger coil and have been able to repeat the experiment. Instead of sodium iodide, however, I took the equivalent quantity of iodine. It was quite evident that fluorine is much more permeable than chlorine, which latter is more permeable than bromine or iodine, these two being nearly alike. Amorphous phosphorus and sulphur tested at the same time were somewhat more permeable than sodium chloride containing the same weight of chlorine, hut considerably more permeable than sodium fluoride. On the same plate I had the radiograph of a crystal of beryl, 12 m.m. thick, and of a crystal of zircon of half the thickness. The latter was practically opaque, the former very perceptibly permeable. (Beryllium has a low atomic weight and zirconium a high atomic weight; garnet and zircon are, I think, the only gems containing elements of high atomic weight, and they are the only impermeable ones). I have now tested the impermeability of *all* the elements whose atomic weight is not above 40, and of a very considerable number of those with high atomic weight.

All the elements with high atomic weight below that of phosphorus are a great deal more permeable than those of atomic weight higher than potassium, those elements with atomic weight between 30 and 40 filling in the transition space somewhat imperfectly.

The atomic weight of boron differs from that of aluminium by just the same amount that fluorine does from chlorine, but the permeabilities do not differ nearly so much in the former case as in the latter. There is always a great difference between the permeability of an element with atomic weight below 30 and a similar element whose atomic weight is above 30.—I am, &c.,

John Waddell.

Royal Military College,
Kingston, Canada.

ESTIMATION OF CARBON IN FERRO-CHROME.

To the Editor of the Chemical News.

Sir,—In your last issue appears the record of a very valuable series of experiments carried out by Messrs. Brearley and Leffler on the "Estimation of Carbon in Ferro-chrome." The authors, however, assert that my method is only capable of yielding about 4½ of the 9 per cent of carbon present in such alloys. Such a statement should only have been made on the surest grounds. As a matter of fact the method when properly carried out yields on an average 8 to 9 per cent of carbon as the contents of rich ferro-chromes, and that without the violent reactions described by the authors.

They also say "no naked tube obtainable would stand the ordinary furnace heat." It is true that such tubes are not easy to obtain, but they are nevertheless obtainable.

It would be interesting to know the type of furnace used by the authors, also the diameter of the main gaspipe. With a 2 inch gas main, a Hoffman furnace in which the openings of the clay burners have been enlarged, and with the gas at night pressure, a blowpipe is not necessary for the combustion of 0·5 grm. of ferrochrome flour with 10 grms. of chromate of lead. With a poor furnace, or a limited gas supply, the results are as described by Messrs. Brearley and Leffler. With reference to the authors' statements about moist and dry oxygen, it is evident that they do not quite grasp the meaning of these terms. It is also clear from their remarks that they have never used dry oxygen in which bright steel drillings are unoxidised at a full red heat. My instructions had reference to almost chemically dry oxygen issuing from a tube closely packed with minute granules of potash-pumice, previously well dried. To restore the necessary humidity to the gas it was passed over "some loose fragments of slightly moistened asbestos."

It is obviously impossible that gas taking up moisture from shreds of damp asbestos placed at the cool inlet end of the tube could deposit water at the hotter exit end. Moreover, I never obtain a deposit of "oxide of lead" in the position just named, for the simple reason that between the ferro-chrome and the exit there are three plugs of asbestos and a 6-inch column of closely packed small fragments of copper oxide.—I am, &c.,

J. O. Arnold.

The Technical School, Sheffield,
May 24, 1897,

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Bulletin de la Société Chimique de Paris.
Series 3, vols. xvii. and xviii., No. 8.

Study of the Hydration of Meta-phosphoric Acid.—MM. Berthelot and André.—The authors show that sodic meta-phosphates prepared—(1) By heating monosodic phosphate to 280°; (2) by melting this salt at a red heat—behave very differently in dilute solutions. The acid titration of the first salt, done immediately after its solution, and again after the lapse of a variable number of days, indicates the presence of a considerable quantity of a mixture of ortho- and pyro-phosphoric acids, while an acetic magnesia mixture produces, when warmed, an abundant precipitate of ammonia-magnesic pyrophosphate, representing 80 per cent of the total phosphorus present. The acid titration of the second salt, on the contrary, indicates that, under the same conditions, the formation of ortho- and pyrophosphoric acids is much slower; the precipitate only representing 50 per cent of the total phosphorus. The free acids prepared by means of these salts confirm these results.

Remarks on the subject of Colour Reactions of Quinine.—E. Blaise.—The Vogel reaction is independent of ferrocyanide of potassium; it suffices to treat the quinine salt with bromine-water and dilute ammonia to obtain the red colour; this becomes green if strong ammonia be used.

Law of Thermic Constants.—D. Tommasi.—A large nunber of measurements of the heat of combination have been made since 1882 confirming the views then put forth by M. Tommasi. Many objections were at first raised, but these have been finally swept on one side and satisfied.

Cause of Oxidation of Imitation Gold Foil.—Leo Vignon.—Not suitable for abstraction.

Research on the Coal-tar Colours in White Wines, and the Difference between these Colouring Materials and those of Caramel.—A. D'Aguiar and W. da Silva.—It has been suggested that the methods used to detect coal-tar colours in matured wines is at fault, and causes confusion of caramel with aniline, yellow and orange. The authors give the results of three series of experiments made by them with eleven aniline colours, one caramel, and one natural wine. They conclude that caramel, treated in the ordinary manner by amylic alcohol made alkaline with ammonia, gives results always very doubtful and sometimes negative. The yellow aniline colours, on the contrary, give very clear results. Experiments with amylic alcohol in barytic solution, and acetic ether in barytic and ammoniacal solution, gave no better results with regard to caramel. Further experiments were made with subacetate of lead, acetate of mercury and potash, and acetate of mercury and magnesia, and the authors finally conclude that the methods commonly in use may be in every way relied on.

Estimation of Small Quantities of Glycerin.—M. Nicloux.—The estimation of glycerin, based on the reaction of bichromate of potash and sulphuric acid, has been studied by many chemists. The author traverses the statement of MM. Bordas and Raczkowski that the reaction can be formulated by the following equation:—

$$8SO_4H_2 + 3K_2Cr_2O_7 + (CH_2OH)_2CH.OH = HCOOH + \\ + 2CO_2 + 11H_2O + 2Cr_2(SO_4)_3 + K_2SO_4 + K_2Cr_2O_7 + \\ + 2K_2SO_4.$$

The mistake, he says, cannot be accounted for by a printer's error, as on one side of the equation we have 3 molecules of bichromate, and on the other only 1 molecule of bichromate and sulphate of potassium.

Notice to Authors. — The Secretary begs that the authors of any papers (French or foreign) sent in to the Society will also send an abstract. This is rendered necessary by the large number of communications received, and the fact that the salient points may be unintentionally overlooked by reason of the abstractor not being so well versed in the particular subject as the author must be. It has been decided that such abstracts, when signed by the author, will be printed at the earliest opportunity, if not more than one page in length, and if sent in not later than a fortnight after the publication of the original.

MISCELLANEOUS.

Atomic Models (Patent No. 1999, 1897).—A patent has recently been granted to Mr. Frederick George Edwards, of London, by which the Government afford protection to his idea that all atoms can be represented by varying numbers of tetrahedrons. The germ of the idea appears to be that as there about seventy elements known to chemists, and that tetrahedrons can be grouped together in as many as seventy ways, the latter can illustrate the former. This is the idea; the practice, the inventor shows, is not so simple. For instance, he says:—"Regular tetrahedrons do not fit exactly, but each tetrahedron is so nearly regular that it may be supposed each of the elements were (*sic*) created from regular tetrahedrons in a plastic condition." This strikes us as a beautiful example of inventing facts to fit a theory. We are glad to find that Mr. Edwards has not patented atoms *per se*, but merely the form he thinks they take, together with a few names of elements, hitherto undiscovered, but predicted by him. These are:—Icosagon, atomic weight 10; *x*-odine, atomic weight 215; and zadmium, atomic weight 245. It will be interesting to watch the action for infringement of patent which will result if any chemist engaged in research should have the temerity, or the misfortune to discover either of these predicted elements. A lithographed diagram at the end gives the *shape* of thirty-two elements, with atomic weights made to fit; we are sorry to have to record the fact that many of these atomic weights are wrong, but then so probably are the shapes.

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.

Pile Oil.—Can any correspondent inform us who are the manufacturers or proprietors of a drug or preparation known as "Pile Oil."—A. O.

MEETINGS FOR THE WEEK.

Tuesday, June 1st.—Royal Institution, 3. "The Heart and its Work," by Dr. Ernest H. Starling.

Thursday, 2nd.—Chemical, 8. "Thermo-Chemistry of Carbohydrate Hydrolysis," "Thermal Phenomena attending the Change in Rotatory Power of Freshly Prepared Solutions of certain Carbohydrates, with some Remarks on the Cause of Multirotation," by Horace T. Brown, F.R.S., and Spencer Pickering, F.R.S. "Optical Inversion of Camphor," "Derivatives of Camphoric Acid—Part II. Optically Inactive Derivatives," "Racemism and Pseudoracemism," by F. S. Kipping, Ph.D., D.Sc., and W. T. Pope. "On Some New Gold Salts of the Solanaceous Alkaloids," by H. A. D. Jowett, D.Sc.

— Royal Institution, 3. "William Godwin and Mary Wollstonecraft," by Churton Collins, M.A.

Friday, 4th.—Royal Institution, 9. "Signalling through Space Without Wires," by W. H. Preece, F.R.S.

Saturday, 5th.—Royal Institution, 3. "Music in England during the Reign of Queen Victoria," by J. A. Fuller Maitland, M.A.

IMPORTANT NOTICE.

Change of Address.

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Vol. LXXV., No. 1958.

ON THE INTERVENTION OF MANGANESE IN THE OXIDATIONS INDUCED BY LACCASE.

By GABRIEL BERTRAND.

As I have already had occasion to remark, the soluble oxidising ferment of the lac-tree laccase yields, on incineration, an ash relatively rich in manganese oxide.

On combining the use of the colorimeter with Hoppe-Seyler's reaction, which consists in converting the manganese into permanganic acid by lead binoxide and nitric acid, I have found that 1 grm. of laccase extracted from Armamase lac contains—

Water of hydration	0·072
Ash	0·046
Manganese	0·0017

that is to say, a proportion of manganese close upon 2·5 per cent of the weight of the ash.

I have since submitted an aqueous solution of this laccase to a fractionated precipitation by alcohol, and I have thus obtained two novel ferments, one of which is more active and the other less active than the original laccase. But on comparing these samples with each other, I observed that their oxidising power varied in the same direction as their proportion of manganese.

Thus the volume of oxygen fixed in ninety minutes by 50 c.c. of solution of hydroquinone at 2 per cent, in presence of 0·260 grm. of the product supposed to be dry, has been:—

Sample No. 1	19·1 c.c.
,, No. 2	15·5 ,,
,, No. 3	10·6 ,,

whilst the determinations of manganese gave respectively—

No. 1	0·159 per cent
No. 2	0·126 ,,
No. 3	0·098 ,,

Is this a simple coincidence, or is the activity of the soluble ferment due to the presence of the manganese? It seemed important to establish this point.

To this end I first sought to eliminate all the manganese of the laccase at my disposal. But the problem being doubtless too delicate, I have not yet been able to solve it in a satisfactory manner. In some cases the elimination of the metal was too incomplete, and in others the reagent modified at the same time the organic matter.

Fortunately I had another method. It is known that laccase, or at least substances closely allied to it, are found in the generality of green plants. I have therefore extracted laccase from a series of different species, varying a little the method of operation, and probably by reason of a special composition of the cellular juice, I succeeded in obtaining from lucerne a product very poor in manganese, and having little activity under these conditions, but which resumes its activity on the addition of a minimum quantity of a salt of manganese. The product is prepared as follows:—Several kilos. of ordinary lucerne (*Medicago sativa*), gathered at the beginning of the flowering season, were at first bruised and submitted to the press. The juice, saturated with chloroform, was left to coagulate in the dark. After twenty-four hours the juice was filtered, 2½ vols. of alcohol were added to the precipitate, drained, and taken up in a little water. It gave on filtration a limpid liquid of a pale yellow, from which an excess of alcohol (about 5 vols.) separated flocks nearly white, easy to collect, and which rapidly dried *in vacuo*.

This specimen of laccase, extracted from lucerne, contained then—

Water of hydration (determined at 110°)	12·4 %
Organic matters	42·4
Ash	45·2

And a very small proportion of manganese, less than 1-50,000th.

On dissolving it, in the proportion of 0·100 grm. in 50 c.c. of solution of hydroquinone, we observe, even after twenty-four hours of continuous agitation in contact with air, merely a red colour. If, on the contrary, we add to the same solution 1 m.grm. of manganese (*e. g.*, in the state of sulphate), in about two hours there appear in the first crystals of quinhydrone evident signs of oxidation.

The experiment may also be conducted quantitatively. We then operate according to the method already described, and measure the oxygen absorbed. We thus find for the proportions above given, and a uniform agitation of six hours, at the ordinary temperature (about 15°):—

1. With manganese alone (check experiment) 0·3 c.c.
2. With laccase alone (from lucerne), 0·2 c.c.
3. For laccase with manganese, 6·3 c.c.

Manganese cannot be replaced in a useful manner by any other metal, not even iron. I have tried with the proportion of 1 m.grm. of metal, taken as sulphites:—Iron, aluminium, cerium, zinc, copper, calcium, magnesium, and potassium. In no case did the volume of oxygen absorbed exceed a few tenths of a c.c.

These facts show the physiological importance of manganese, and define its *rôle* in vegetables.—*Comptes Rendus*, cxxiv., p. 1032.

A TROPICAL FOOD.

By JOHN B. COPPOCK, F.C.S., Harris Institute, Preston.

In many parts of the island of Cuba the fruit of the banana tree or its allies is used as the "staff of life" by the natives, and upon it their strength is preserved unimpaired. A sample of a flour made from *Musa paradisiaca*, one of the banana tribe, yielded upon analysis—

Water	10·62
Albumenoids	3·55
Fat..	1·15
Carbohydrates	81·67
Fibre	1·15
Phosphoric acid	0·26
Salts other than phosphates ..	1·60
	100·00

We may therefore conclude it to be a starchy food. The nutritive value from a nitrogen point of view is small, but now it is beginning to be recognised that the nitrogenous tissues of the body have less mobility than hitherto assumed, we may consider whether nitrogen ought to occupy the pre-eminent position to which it gets assigned, but rather that less value should be attached to it and more to the carbohydrates, which are great sources of energy.

Now one of the most striking features of this natural product is the solubility of the carbohydrate portion; with only warm water the whole of it forms quickly a thin mucilage which is apparently very digestible.

The extreme solubility of this flour is further emphasized by the fact that it has long been used in the island of Cuba as a food or gruel for infants just leaving off breast feeding, despite its being essentially a starchy substance.

The phosphoric acid in it is fairly large; hence its value is enhanced when we consider the important part played by phosphorus in the economy.

A microscopic investigation of the structure of the starch grains led to these conclusions. The granules are elongated, fairly elliptical in shape; the layers of the grain are concentric, but only faintly visible; the granules vary much in size, but the large ones show a well-defined hilum.

The flour has the appearance of finely ground oatmeal, but possesses a distinct odour of an agreeable nature.

A few words on the botanical characters. The banana and the tree giving this product belong to the natural order *Musaceæ*. This order is very prolific in the production of fruit; it produces 45 times more fruit per acre than the productive potato and 131 times more than wheat. Of course this action makes it very exhausting to the soil: the soil does not seem to be replenished by artificial manures, but the tree is removed to fresh soil every few years.

M. sapientum is the ordinary banana, the variety giving this flour being *M. paradisiaca*. They are closely related, the two being distinguished by the sweetness, larger size, and succulent nature of the banana.

The young shoots of some species are also eaten after being boiled for food.

THE DISSEMINATION OF MICRO-ORGANISMS, AND THE BEST METHODS OF DESTROYING GERM EMANATIONS FROM SEWER GAS.*

By CHAS. R. C. TICHBORNE, F.C.S., F.I.C., Dep. Pub. Health, R.C.S.I., &c.

There are two characters of germ contagion, which may perhaps be best illustrated in the diseases of scarlatina and enteric fever.

In the scarlatina we know that the disease is largely conveyed by the desquamation.

In enteric fever the germs which are carried by sewer gas are supposed, with considerable force of evidence, to be a fertile source of spreading the disease.

In scarlatina we assume that the "Raft Theory," as Tyndall called it, plays an important part, whilst in the latter we must assume that the contagion is often carried with the vapours which emanate from the drains.

In my present communication I do not propose to deal at any length with the subject of the transmission of germs by the raft theory. It is fairly understood by most physicists and bacteriologists—but I may as well concisely describe it as most scientists understand it. We assume that the ordinary atmosphere, let us say at the sea-level, is largely contaminated with a visible and ponderable matter, which we term atmospheric dust. This atmospheric dust is found largely present in our homes, and also in the streets of populous towns. It consists of ponderable atoms, which, at an altitude of a few feet, almost entirely consists of organic matter. This fact was conclusively demonstrated by Tyndall's beautiful experiments, in producing what he called "optical vacuums," by the combustion of the organic matter. The coarser particles of this atmospheric dust act as kinds of floating rafts, and carry on their surface the finer structures of life. In the case of such a disease as scarlatina, we can easily see how this raft theory plays an important part in the dissemination of the desquamation.

Even the smallest germs that our microscopes have yet revealed have a certain weight. This fact is shown by the absence of germs at high altitudes, such as Mont Blanc, or in the very still atmospheres, such as is found in the vaults of St. Michau's church. I demonstrated this as far back as 1870, in an "afternoon lecture," delivered at the Royal Dublin Society. I showed that flasks placed all night in the vaults of St. Michau's church were, when sealed next morning, optically empty, or free from atmospheric dust, and were therefore free from germs. We get in these vaults exactly the same result that we should find on the top of Mont Blanc.

I believe this sterility of the vaults of St. Michau's church has been the subject of one if not more papers read before this Academy. I am sure it had escaped the authors' observation that the ground had been already "prospected."

It is worthy of note that the greater part of practical bacteriology is now worked out by an observation, which I think originated with Tyndall,—that cotton-wool is a perfect filter, as regards this atmospheric dust, and that it not only acted upon the coarser particles, but separated the finer micro-organisms.

I may be excused for still further referring to my own researches in this direction, mention of which will be found in the later editions of Parkes' "Hygiene," by De Chaumont. I was able to demonstrate that even the dust at the top of Nelson's pillar contained over 29 per cent of organic matter, and that it was capable of setting up lactic fermentation in a neutral solution of sugar of milk. (Here is a solution of sugar of milk, which, although sterilised, when left in an ordinary room containing atmospheric dust has fermented, and become solid from the formation of calcium lactate).

The composition at every yard that we rise from the ground becomes freer from the ponderous earthy constituents, but richer in germs. Of course we at last come to an altitude where even the micro-organism becomes scarce, and to such regions as the high altitudes of Switzerland, where the germ is unknown. Even on the Mer de Glace the germs may be said to be absent.

So much for the raft theory, which will account for the dissemination of any germs, provided they have arrived at the dry condition or can be attached to a dry particle. What can be more easy to conceive than the spreading of scarlatina by a process such as this? It is almost self-evident.

But there is another mode by which preventible disease is disseminated, which has never to my mind presented such a lucid explanation as regards its propagation. I refer to the theory which supposes that a certain germ—let us say like that accompanying enteric fever, cholera, or such disease, or the poison of yellow fever—are capable of acting as a poison when evolved in sewer gas.

We have an organism which, when carried in water or brought mechanically to a receptive surface, is capable of producing disease, and yet we also find that it is capable of rising in such a vapour as sewer gas. I use the term "vapour," not in the vulgar sense, which assumes a non-permanent gas capable of condensation, but in the sense that means anything flying or escaping off. In this sense atmospheric dust is volatile.

Two special diseases are supposed to arise from the air of sewers or fæcal emanations, typhoid fever and diarrhœa; yet if these diseases are caused by bacilli, how are they volatilised, for, however minute, these bacilli are still organic structures? Although a germ is so small that our finest balance will not weigh it, and, although it may only be 0·005 of a m.m. in length, we might as reasonably conceive that the coarser microscopic life—such as Rotatoria or Entomostraca, which we can almost see with our eye—would be volatilised as a vapour, as to conceive that pathogenic microbes would be so transmitted.

Prof. Frankland has shown that liquid sewage matter is not likely to be scattered into the air, except by gas generated in it. He experimented with lithia, a chemical substance, not volatile, but which could be easily detected, and might be said to represent micro-organisms. He

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* A Paper read before the State Medicine Section of the Joint Medical Association.

found that no ordinary agitation of the sewer water would produce indications of lithia in the air, but that directly gas began to be generated in the sewage by decomposition the bursting of the gas-bubbles carried lithia into the air (*Proc. Roy. Soc.*, 1877).

Now I think here is the clue to the dissemination of microbes, but not exactly in the direction which he indicated. Such a condition of sewage, *i.e.*, in active fermentation, is hardly conceivable in a general sense in the better constructed drains found connected with houses of a good class,—the houses, in fact, where typhoid seems to luxuriate. We must suppose, however, in a system of town sewage, certain spots in the mains where, from the Frankland cause, the microbes are scattered into the air during fermentation,—or, let us say, violent concussions breaking the sewage into spray,—and then comes the question, How are they disseminated through the whole area of the air space of the system of drains? I can easily conceive that they are there carried by a condensed vapour exactly represented by ordinary dew. At certain hours of the night, just as we see the rising vapour settling as dew in a valley, I believe that the temperature of the water-laden vapour of the sewer is lowered by being met with the layer of cold night air through the open traps, which determine a dew-point in the sewers themselves. I find from actual experiment that the temperature of the sewer water as it flows from the large sewers, or the temperature of the gas in the mains, is generally 2 or 3 degrees above the temperature of the night air. The gas mains bear a somewhat similar position underground to the sewers themselves, and give a very good idea of this variation of temperature. A variation of as much as 10° to 15° may be observed.

Even a sudden rise in the barometer will just determine the deposition of the liquid portions of the gas in the mains, and in the same manner will also determine, even more energetically, a dew line in the sewers. Each particle of dew becomes a raft which will carry microbes upon its surface, perhaps for miles, as long as this "dew" condition lasts, and, as the sun's warmth dissipates the morning dew, the water raft disappears, leaving the microbes suspended in mid air; or, suppose the sewer dew is carried into a warm shaft connected with a dwelling-house, is not the assumption apparent that again we have the water-rafts converted into permanent gas, whilst the now dry germs float about seeking whom they may devour?

I will just conclude by a few remarks upon sewage disinfection from this point of view.

The disinfectants employed in sewage purification can hardly be viewed as actual germicides. The modes in which they are necessarily used create such an amount of dilution that they can only be viewed as retarders of the development of microbes. It is no doubt chiefly from this reason that they are not more extensively used in sewage purification. The return in results, as regards the prevention of diseases, is not commensurate with the great expense of oxidisers such as permanganates and hypochlorites. They are not in favour, because without they are used in overwhelming quantities they are worse than useless. They destroy myriads of microbes, but they allow myriads to escape, and to these they only seem to add fuel to the fire. It is true that at the pumping stations in London manganate of soda is used, or was used; but in that case it is merely employed as a deodoriser at the end of the process, and whilst the supernatant fluid is poured into the river.

From the reason of cheapness, crude carbolic acid (which may be considered to owe its virtue to phenol, cresylic acid, and a little naphthalene) is extensively used. Although not a very decided germicide, phenol still holds an important place as one of the most valuable retarders of germ development. Naphthalene is still more powerful, and may be looked upon as a germicide proper; although very cheap, it has one objection, namely, its insolubility. I have here a fluid which I have used with some success for years, in controlling or instantly stopping germ development, for which there are many occasions where the use of mercuric chloride is inadmissible. It consists of—

Crystallised phenol	1 part,
Camphor	3 parts,
Naphthalene	½ part,

Coloured with rosaniline carbolate.

It will be observed that, though these are all solids, they form a liquid on rubbing together. One drop of this liquid will instantly arrest any tube of microbe culture in gelatin at any point, and may be used with advantage to place on record comparative experiments with microbe cultures.

In such experiments I have found it advantageous to use a little stiffer nutrient gelatin than that given in Crookshank. I increase the formula there given from 100 grms. of gelatin to 120 grms. (*vide* "Manual of Bacteriology," 3rd edit., p. 83).

Now it is a similar preparation to the above which I should propose for sewage purification, with one modification which I consider invaluable. Crude carbolic acid (phenol) is comparatively cheap, and naphthalene may be viewed as a waste product in the process of coal-tar distillation. For the camphor I would substitute terebene, which may be looked upon almost as a liquid camphor. Where the sewers of a large city are being provided for, and where money is a question of importance, the light oils of tar may be substituted.

Now I will describe the scientific theory by which I believe this can be made a trap for typhoid or germs of a like nature in sewer gas.

The principle involved consists in adding some liquid body which shall bring the specific gravity of the antiseptic below that of the sewer matter. When such a body is used the antiseptic forms at once a fine pellicle on the surface of the sewage, and all fluids that are volatilised or mechanically eliminated by the escape of gas must pass through the germicide layer.

If carbolic acid or the crude phenol products are used by themselves, we find in practice that they immediately sink to the bottom of the flowing sewage which passes along over the top in a continuous stream of untouched pollution. The crude product obtained from the distillation of coal-tar is specially suited to this purpose. When coal-tar is distilled, in the first instance, it is divided into two divisions; one is called "light coal-tar oil," the other "heavy coal-tar oil." The first are all the products which come over as long as they will float on water, and they are specially rich in the benzene, naphthalene, and terebene series, all of which are powerful germicides. By substituting these oils for terebene, we get an antiseptic fluid which immediately spreads on the surface of the sewage, locking in the deleterious vapours, and at the same time passing downwards the heavier antiseptics, such as the phenol, by the simple act of solution.

This can be illustrated by the following simple experiment:—If we pass, by a pipette, a layer of carbolic acid into a shallow dish of water, and after standing some time draw off some of the supernatant water, we shall find, on testing it with a little bromine water, that it contains no carbolic acid. If in a second experiment we use such a mixture as I have specified, which has a gravity of 0·850 to 0·950, we shall find, on introducing it into the water with the pipette, that it immediately rises to the surface, and if we at once remove some of the water from the interior, it gives, on testing with bromine water, a copious precipitate, showing that the carbolic acid has permeated at once through the water, which represents the sewage. We should find, on further examination, that the powerful antiseptic naphthalene had been carried with it.

I have endeavoured, in the above experiments, to show why, in many cases, the use of carbolic acid has been a practical failure as a sewage purifier, and to indicate that, as regards dealing with such contagions as are diffused through sewer gas, a principle should be adopted in the use of antiseptics. This principle has not, so far as I know, been openly enunciated, namely, that we must disinfect from the surface of the flowing sewage, and not from the bottom.

CONTRIBUTION TO THE STUDY OF HYPONITROUS ACID.*

By A. HAUTZSCH and A. L. KAUFMANN.

(Concluded from p. 256).

Conductivity of Hyponitrous Acid.

Perfectly pure hyponitrite of silver is added in excess to a 1/32 normal solution of hydrochloric acid at 0°. The 1/32 normal solution of hyponitrous acid thus obtained is filtered at 0°, and this filtrate is used for the determination of the conductivity.

I. Molecular amount in 64 litres. Temperature 0°.

μ^1 = 2·98 μ^5 = 3·65 μ^9 = 4·14
μ^2 = 3·06 μ^6 = 3·78 μ^{10} = 4·24
μ^3 = 3·40 μ^7 = 3·87 μ^{11} = 4·29
μ^4 = 3·46 μ^8 = 3·92 μ^{12} = 4·32

II. Solution prepared exactly the same as No. I., but kept at 0° for fifteen hours.

μ^1 = 1·96 μ^5 = 2·07 μ^9 = 2·18
μ^2 = 1·98 μ^6 = 2·09 μ^{10} = 2·19
μ^3 = 2·00 μ^7 = 2·11 μ^{11} = 2·22
μ^4 = 2·02 μ^8 = 2·14 μ^{12} = 2·25

The result obtained was similar to that of the first experiment. The initial value was smaller, but it gradually increased.

III. The solution used for the first experiment was examined again after standing for fifteen hours at 0°.

μ^1 = 21·65 μ^5 = 23·56
μ^2 = 21·92 μ^6 = 23·68
μ^3 = 21·94 μ^7 = 22·80
μ^4 = 21·83 μ^8 = 23·68

These experiments show that the conductivity of hyponitrous acid increases with the duration of the current. Under the action of an alternating current, hyponitrous acid ought to give rise to products which would be better conductors than hyponitrous acid itself. As a matter of fact solutions thus treated give, with sulphuric acid, iodide of potassium, and starch, an intense blue colour. Thus we see that the decomposition previously described is effected by the action of an alternate current at 0°.

Experiment III. shows clearly that nitrous acid once formed accelerates the decomposition of hyponitrous acid in a similar manner. As probable equivalent of the conductivity of hyponitrous acid, we must take into account what was observed in the first place. Its value should therefore be, assuming v to be equal to 64, $\mu = \infty 3$.

The determination of the conductivity of very weak solutions, and the calculation of the constants of dissociation, have naturally been impossible to effect with a body which is such a bad conductor and so unstable as hyponitrous acid. But contrary to the general opinion, hyponitrous acid is a very weak acid. It is, in fact, very similar in that respect to carbonic acid, whose conductivity is, according to Knox, K=0·00000008.

Conductivity of Hyponitrite of Soda.

Having proved by previous experiments that the acid hyponitrite of soda, $NaHH_2O_2$, was a very unstable compound, we endeavoured to determine the conductivity of the neutral salt. This latter salt could not be prepared by the direct action of hyponitrite of silver in excess on a solution of chloride of sodium, on account of these bodies acting very slowly and incompletely on one another. We obtained it by mixing equal quantities of hyponitrous acid and caustic soda. The hyponitrous acid was prepared in the ordinary way, by the action of hyponitrite of silver on a normal solution of hydrochloric acid; the caustic soda was prepared according to Hautzsch and Gerilowski's method. The two solutions, mixed at 0°, were diluted so as to contain a 1/32nd normal quantity of hyponitrite of soda.

I. v = 64.

μ_1 = 111·66 μ_4 = 109·56 μ_6 = 109·26
μ_2 = 110·76 μ_5 = 110·26 μ_7 = 109·16
μ_3 = 109·56

II. v = 126.

μ_1 = 139·06 μ_3 = 135·4 μ_5 = 134·12
μ_2 = 137·06 μ_4 = 134·42 μ_6 = 132·92

III. v = 256.

At first μ = 148·04, after 13 minutes μ = 141·14, after 15 hours μ = 126·34, after 7 minutes μ = 143·04, and after 16 minutes μ = 139·64.

The three series of experiments show that the values of the molecular conductivity diminish from one experiment to another. This can be accounted for in two different ways. We can imagine that the fixation of the carbonic acid in the air, by the strongly alkaline hyponitrite of silver, would have the effect of decreasing the conductivity of the latter. The facts observed in the determination of the conducting power of carbonate of soda show that this supposition is probable. But we may also suppose that, under the influence of the electric current, hyponitrite of soda, strongly hydrolysed, gives rise to products of decomposition of very bad conductivity.

In spite of these difficulties it is easy to see that the conductivity diminishes considerably on dilution. The most probable value is that first observed. With v = 64, and t = 0°, $\mu = \infty 112$. In any case, however, this high number shows a noticeable splitting up of the disodic salt, easily shown by phenolphthalein.

Comparison of Nitramide with Hyponitrous Acid.

The chemical properties being known, the comparison has been completed by the determination of the molecular weight and the conducting capacity of the nitramide.

The *determination of the molecular weight* of the nitramide gave the same value as that we found for hyponitrous acid.

Molecular weight: found, 61; theory $H_2N_2O_2$, 62.

Conductivity of Nitramide.

I. v = 32; temperature = 0°.

Five series of experiments were made, each comprising four determinations. The following figures show the average of each series:—

1. μ = 1·97.
2. μ = 1·95.
3. μ = 1·93.
4. μ = 1·93.
5. μ = 1·96.

II. $v.$ = 64; temperature = 0°.

Means of two series of experiments:—

1. μ = 1·69.
2. μ = 1·69.

These results show that, contrary to the opinion expressed by Thiele (*Zeitsch. f. Physik.*, xvii., p. 185), nitramide is a very weak acid, the same as hyponitrous acid.

The low conductivity makes the determination of the constant of dissociation impossible. But at any rate the values for nitramide ($\mu = \infty 2$) are lower than in the case

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* *Moniteur Scientifique*, vol. xi., p. 336, May, 1897.

of hyponitrous acid ($\mu = \infty 3$). The acidity of the former is therefore slightly more pronounced than that of the latter; but unlike hyponitrous acid, the conductivity of nitramide is not modified under the influence of an alternate current. Nitramide in the free state is thus considerably more stable than hyponitrous acid.

The interchangeability of these two substances, one into the other, by inter-molecular transposition, appeared to be very probable, in view of their isomerism, and the analogy of their proportions which exists; but the numerous experiments undertaken with a view to cause this transformation have up to now given only negative results.

SOME PRESENT POSSIBILITIES IN THE ANALYSIS OF IRON AND STEEL.[*]

By C. B. DUDLEY.

(Continued from p. 258).

Much might be said in regard to the colour test for determining carbon in steel. It is difficult to over-estimate the value and importance of this method, especially in the daily operation of steel works, and there seems little doubt but that if proper precautions are employed, the method in skilful hands will give results that are fairly reliable to within three- or four-hundredths of a per cent. It would hardly be possible in this paper to discuss all the precautions which are deemed essential by those best informed. A chemist of wide experience with the method has enumerated twenty-four points that must be observed, if reliable results are to be expected. Let it suffice for us to say that even approximate accuracy cannot be expected.

1. If the steel whose carbon is to be determined and the standard steel do not have their carbon in the same condition. For example, if the standard steel has been annealed, and the sample to be tested has been tempered, the results will be worthless.

2. If the attempt is made to determine the carbon in any steel by using a standard widely different from it, in carbon content. Using a 0·20 per cent carbon standard, with a steel containing 0·50 or 0·60 per cent, is apt to lead to very fallacious results.

The best results seem to be obtained by having the carbon in all steels both standards and tests in the condition given by annealing, by having a number of standards which differ little from each other in carbon content, and by not attempting to use the method on steels containing very little or very large amounts of carbon. It may not be amiss to add here that the practice so prevalent in many of the steel works, of using this method for all carbon determinations, including those where contracts are involved, is reprehensible, and should be discontinued. The chemist at the works does the best he can with the method he is using, and the amount of work required of him, as well as the facilities furnished, do not admit of the use of a better method. On the other hand, when a dispute arises, and it is ultimately shown that the works are in error, the chemist is blamed and analytical chemistry brought into disrepute, not because either is really at fault, but because more is expected of the colour test method than it is really able to give. To the steel makers we say, "Do not expect your chemists to render you the bricks of good chemical analyses, without you give him the requisite straw of time and appliances to do good chemical work."

Few of the constituents of iron and steel have more important influences on their valuable qualities than phosphorus, and upon few has more chemical work been done. The present condition of the methods for determining this constituent seems fairly satisfactory, provided we are willing to take time enough to do the work. In confirmation of this statement, the work (*Proc. Am. Soc. Civil Eng.*, xxi., 59) done by the Sub-committee on Methods of the International Committee on Standards for the Analysis of Iron and Steel may be cited. This sub-committee consisted of five members, each of whom analysed five samples of steel, and each used his own method, without any attempt at consultation or agreement with each other before the work was done. The methods employed may be briefly indicated as follows, those interested being referred to the Report of the Committee published as per the reference given for the details. Mr. Blair used what is known as the acetate method. Mr. Shimer used the molybdate magnesia method. Your speaker used a combination of the acetate and molybdate magnesia methods. Dr. Drown used a combination of certain features of the modern rapid methods with the molybdate magnesia method. And Mr. Barba on one sample used the acetate method as described by Blair, and on the other four samples employed certain features of the molybdate method to separate the phosphorus from the iron, and then used the reductor to get the amount of phosphorus, instead of weighing as magnesium pyrophosphate. It will be evident to any one carefully reading the Report referred to that the methods employed differed widely in principle, in strength of solution, and in manipulation, and yet these methods gave the following percentages of phosphorus in the five samples.

	1.	2.	3.	4.	5.
Mr. W. P. Barba ..	0·041	0·015	0·095	0·091	0·041
Mr. A. A. Blair ..	0·040	0·016	0·098	0·091	0·041
Dr. T. M. Drown ..	0·042	0·016	0·104	0·090	0·042
Dr. C. B. Dudley ..	0·040	0·016	0·099	0·097	0·039
Mr. P. W. Shimer ..	0·041	0·017	0·098	0·096	0·039

In explanation of the results, we quote from the Report of the Sub-committtee:—

"Sample No. 1 is an ordinary open-hearth steel. Sample No. 2 is a crucible steel. Sample No. 3 is an open-hearth steel to which metallic arsenic was added while in the molten condition in a crucible. Sample No. 4 is an ordinary Bessemer rail steel. Sample No. 5 is the No. 5 sample of the Committee on International Standards, and is an open-hearth steel.

"It will be observed that the agreement in the results on phosphorus obtained by the different chemists is very good. The exceptions are the No. 3 steel, which contains arsenic in considerable amount, and where the discrepancy is 0·009 per cent, and in the No. 4 steel, where the discrepancy is 0·007 per cent. Considerable work was done on the No. 4 sample, in an effort to reconcile discrepancies, and it was found that the turnings from this sample were irregular, and that two different bottles of the sample gave different results. The average of six determinations from one bottle was 0·1057, and the average of five determinations from another bottle was 0·0964 per cent. Furthermore, siftings from quite an amount of the turnings gave 0·140 per cent."

But these methods are long and laborious. It would be impossible with the most rapid of them to get a result in much less than a day, while two days would certainly be required for some of the others. Accordingly, since the demand for rapid phosphorus determinations during the last ten or fifteen years has been very great, an enormous amount of work has been done in trying to meet this demand. Modification after modification has been introduced, and paper after paper has been published on the subject. It is perhaps not too much to say that few chemical journals that publish any original work at all have escaped three or four articles per year, on the determination of phosphorus in iron and steel, or on some phase of a rapid method for such determination. The result of all this work has apparently been constantly in-

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[*] Presidential Address delivered at the Troy Meeting of the American Chemical Society, December 29, 1896. From the *Journal of the American Chemical Society*, xix., No. 2.

creased rapidity, with constantly greater approximations to accuracy. The present state of the matter is perhaps best shown by Thackray (*Trans. Am. Inst. Min. Eng.*, xxv., 370), in his paper "A Comparison of Recent Phosphorus Determination in Steel." This writer sent to some twenty-three different chemists borings from two different samples of steel, with a request to have the phosphorus determined in each sample, and a description of the method used sent with the results. Each chemist was told that samples had been sent to others, but no attempt was made to have any special method used. The chemists embraced a professor in a technical school, the chemist of a large consumer, a number of commercial chemists, and a number of chemists employed by steel and iron works. On one sample thirty-six different results were sent in, and on the other thirty-eight. Twenty-seven different methods were employed, some of the chemists sending in results by two, and even three methods, and some sending duplicate determinations. The results obtained were obtained as follows, the figures being percentages of phosphorus in the steels:—

Sample.	1.	2.
Average of all determinations	0·0496	0·0835
Highest result..	0·055	0·091
Lowest result	0·045	0·076
Maximum difference	0·010	0·015

The methods employed may be divided on the basis of time required into three classes:—

1st. Those which may be called rapid, and which give a result in two hours or less.

2nd. Those which may be called slow, and which require considerably more than two hours, but still give a result the same day.

3rd. Those which may be called very slow, and which do not give a result until the second day or later.

Thirteen results on each sample were given by "rapid" methods, eleven on the No. 1 sample, and twelve on the No. 2 sample by "slow" methods, and twelve on the No. 1 and thirteen on the No 2 by "very slow" methods. Arranging the results in accordance with this classification of the methods (and we have some very interesting data), the figures being as before, the percentages of phosphorus in the two steels are:—

	Rapid methods.		Slow methods.		Very slow.	
	1.	2.	1.	2.	1.	2.
Average ..	0·0499	0·0840	0·0490	0·0826	0·0496	0·0837
Highest ..	0·054	0·091	0·052	0·086	0·055	0·089
Lowest ..	0·045	0·078	0·046	0·076	0·046	0·078
Max. diff..	0·009	0·013	0·006	0·010	0·009	0·011

To our minds these figures are very impressive. It is worthy of note—

1st. That the average results given by the "rapid" methods only differ on either steel from the averages given by the "slow" or "very slow" methods, by a little over 0·001 of a per cent.

2nd. That the maximum difference between the highest and lowest results given by the "rapid" methods on either steel is but a trifle greater than is shown by the "slow" or "very slow" methods.

In other words, if we interpret these results correctly they show that the rapid methods for determining phosphorus in steel now known and in use in many laboratories give results that are well nigh as accurate and reliable as those yielded by the longer and more laborious methods, and it must not be forgotten that although we have placed two hours as the time characterising a rapid method, a number of the results given above were obtained by the use of methods which give a single determination in forty-five minutes, and enable one operator to make twenty phosphorus determinations in a day. We are frank to say we do not believe such a showing would have been possible five years ago.

But these results still leave something to be desired. The discrepancy between the highest and the lowest result is still too great. It is, perhaps, a little hazardous to place limits, but we do not think the chemists of the country should be satisfied until they are in possession of a method or methods which are so carefully worked out and so well described that in the hands of different chemists of good fair ability and experience, results will be obtained by all, when working on the same steel, that will not differ from each other more than 0·003 per cent. The Sub-committee on Methods of the International Committee on Standards for the Analysis of Iron and Steel, before referred to, have had in hand now for some two years studies on a rapid and accurate method for the determination of phosphorus in steel. It has been the hope of the Sub-committee that the ideal above given would be attainable by this method. In reality, the work of the Sub-committee has embraced an examination of almost every chemical point involved, taking very little if anything for granted, and checking and proving every step. The work is not yet quite ready for publication, one or two points remaining which are not entirely settled, and it has been deemed advisable to withhold the method until these are completely cleared up.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 20th, 1897.

Professor Dewar, F.R.S., President, in the Chair.

Messrs. H. E. Gardner, William Barlow, and Paul Thomas White were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Walter Harry Barlow, 152, Osbaldiston Road, Stoke Newington, N.; Ernest Stuart Cameron, 51, Pembroke Road, Dublin; Medwin Caspar Clutterbuck, B.Sc., Ph.D., 61, Beaconsfield Villas, Brighton; Frank William Harbord, Egham; B. J. Harrington, Ph.D., McGill College, Montreal; A. G. Kidston Hunter, Princes Street, Dunedin, N.Z.; John Edwin Mackenzie, B.Sc., Ph.D., 7, Ramsay Garden, Edinburgh; Lionel Walter Kennedy Scargill, B.A., 14, Brunswick Place, W. Brighton; James Porter Shenton, 34, Lansdowne Road, W. Didsbury, Manchester.

Of the following papers those marked * were read:—

*60. "*The Theory of Osmotic Pressure and the Hypothesis of Electrolytic Dissociation.*" By Holland Crompton.

The author applies the results obtained by Guye, Ramsay, and Shields, and others in their investigations on the molecular complexity of liquids to the theory of osmotic pressure. It is found that van 't Hoff's view, that the osmotic pressure of the dissolved substance is in dilute solution equal to the pressure which the substance would exercise in the same volume if in the gaseous state, is applicable when both the dissolved substance and the solvent form normal or monomolecular liquids. It may also apply if both liquids are associated. But if the dissolved substance is associated and the solvent is monomolecular, the osmotic pressure is then smaller than the theoretical, and becomes inversely proportional to the factor of association x_1 of the dissolved substance. If the solvent is associated and the dissolved compound is monomolecular, the osmotic pressure is greater than the theoretical, and is directly proportional to the factor of association x of the solvent. If the solvent has also an abnormal vapour density, the factor of association of the vapour being a, the osmotic pressure is directly proportional to x/a.

By application of the above conclusions, it is shown that the latent heat of fusion r, melting-point on the absolute scale T, and density at the melting-point, d, of a liquid are connected by the expression $rd/T = \text{const.}$ in the case of monomolecular liquids, or $rdx/Ta = \text{const.}$ in the case of associated liquids. The mean value of the constant is 0·099, or roughly 0·1. This formula is exactly similar to the Trouton formula, which connects the latent heat of vaporisation, gaseous density, and boiling-point on the absolute scale of liquids.

The molecular reduction of the freezing-point for monomolecular substances in monomolecular solvents is given by van 't Hoff's formula, $E = 0·01976\,T^2/r$, or by the derived formula $E = 0·2\,Td$. If, however, the dissolved substance or the solvent are associated, this formula no longer applies, but $E = 0·01976\,T^2x/rax_1$, or $E = 0·2\,Td/x_1$. Exceptions to van 't Hoff's formula for the molecular reduction of the freezing-point appear, therefore, whenever association of either the dissolved substance or the solvent takes place, and it is shown that those exceptions observed in the case of electrolytes in aqueous solution are in perfect keeping with the view that electrolytes are monomolecular compounds in solution in an associated solvent, *e.g.*, water. The hypothesis of electrolytic dissociation is not only unnecessary in explanation of these exceptions, but is inconsistent with what is now known of the molecular character of liquids.

A connection is supposed to exist between the specific inductive capacity of a liquid and its power of promoting electrolytic dissociation. The author shows that it is only associated liquids that have high specific inductive capacities, and that the specific inductive capacity is approximately proportional to the cube of the factor of association of a liquid. It is therefore not on the degree of electrolytic dissociation of the dissolved substance, but on the degree of association of the solvent, that the conductivity depends, and the view is taken that electrolytes are salts in the monomolecular fluid state in solution in associated solvents.

*61. "*Molecular Rotations of Optically Active Salts.*" By Holland Crompton.

A fact which is usually quoted as strong evidence in favour of the hypothesis of electrolytic dissociation, is that salts which contain a common optically active ion—either positive or negative—exhibit, in sufficiently dilute aqueous solution, the same equivalent rotatory power. If, however, electrolytes are salts in the monomolecular fluid condition (preceding paper), the observed regularities indicate that monomolecular salts which contain a common optically active radicle have the same equivalent rotation. Those peculiarities which have been observed in the case of the equivalent rotations of optically active electrolytes in aqueous solution, are shown by the author to be also exhibited by the amylic salts of certain organic acids, when these are examined in the free state and not in solution in any solvent. As electrolytic dissociation is in this case entirely out of the question, the hypothesis becomes an unnecessary one in other instances, and the behaviour of optically active electrolytes is merely in keeping with that of other optically active monomolecular salts.

*62. "*Heats of Neutralisation of Acids and Bases in Dilute Aqueous Solution.*" By Holland Crompton.

The constancy of the heat of neutralisation of an acid by a base is usually explained in accordance with the electrolytic dissociation hypothesis by the assumption that the acid, base, and the resulting salt are all in a dissociated state, and that the only change occurring in the system is the formation of water from its ions. In this paper, the author calls attention to the fact that from Thomsen's "Thermochemische Untersuchungen." Band IV., it may be inferred that the replacement in any monomolecular organic compound RH of the H atom by one and the same radicle M, is attended with a constant heat change, which is independent of the character of R, and that for monomolecular compounds the heat of the reaction $RH - H + M$ is constant if M is constant and independent of variations in R. From this it also follows that the heat of the reaction $ROH - OH + M$ is constant. In the neutralisation of an acid RH by a base MOH, we have the changes $M - OH$, $R - H$, $M + R$, $H + OH$. If M is kept constant then two terms in the reaction will be constant, $M - OH$ and $H + OH$. The only variation is then in $R - H$ and $M + R$. But as shown above, for monomolecular compounds $RH - H + M$ is attended with a heat change that is independent of R, and hence if acids and bases in dilute aqueous solution are monomolecular compounds, the heat of neutralisation of any acid by one and the same base is a constant quantity. It may be shown in similar manner that the heat of neutralisation of any base by one and the same acid is constant, and hence the heats of neutralisation of acids by bases are always the same. The hypothesis of electrolytic dissociation is unnecessary in explanation of the observed phenomena, if it be granted that the dissolved electrolytes are monomolecular compounds.

In the above, since OH is simply another negative radicle R, the heat of the reactions $M - OH$ and $H + OH$ might be expected to exactly balance that of the reactions $H - R$ and $M + R$. This is probably the case when the reactions do not occur in dilute aqueous solution. But in solution, while the acid, base, and salt are in a condition comparable with that of their vapours, the water which is formed in the reaction must be transformed from that state to the liquid state of the solvent by which it is surrounded. This implies that the heat of neutralisation of an equivalent of an acid by an equivalent of a base in aqueous solution contains as main factor the heat of condensation of a molecule of water. This latter quality has a value of about 10,800 cal., and the mean value of the heat of neutralisation is 13,500 cal. The difference between the two values is to be mainly attributed to the state of partial association of the base.

Discussion.

Mr. Pickering said whether Mr. Crompton had established his views or not, he had succeeded in throwing much new light on the subject under examination, and had given us further evidence that the theory of dissociation was not the only one through which we might look for an explanation of the phenomena of dissolution.

By way of criticism, the speaker suggested that the means of recognising a liquid to be of the associated or non-associated class at the freezing temperatures was somewhat imperfect, and might, in many cases, lead to erroneous conclusions. He doubted, also, whether the numbers obtained showed that the same solvent indicated consistently the same degree of association when pitted against various monomolecular solutes, as should be the the case, and whether the same associated solute, when pitted against various monomolecular solvents, gave similarly consistent results. A stronger objection, however, might be raised in the behaviour of diatomic and triatomic electrolytes in water. According to Mr. Crompton's views, these should both give values of 55·2 for the depression of the freezing-point when in extreme dilution; the triatomic electrolytes do so, but diatomic electrolytes give values which show little or no tendency to surpass 37, which is only double instead of three times the "normal" value.

As regards the heat of neutralisation, the speaker considered Mr. Crompton's application of a general principle which has been established in organic transformations to similar transformations in inorganic solutions to be both legitimate and ingenious. The simplicity of the principle for organic substances, no doubt, depends on the fact that these substances are nearly saturated compounds, and in dilute solutions of inorganic compounds we are probably also dealing with saturated compounds. Some years ago, the speaker brought before the Society an explanation of the constancy of the heat of neutralisation which was based on chemical grounds, without recourse to the theory of dissociation. Residual affinity was the explanation which was offered, and Mr. Crompton's explanation could be improved by taking residual affinity into consideration. Mr. Crompton accounts for the heat evolved on neutralisation by the condensation of the molecule of water formed; this condensation should certainly be recognised (a fact which the speaker had overlooked in his own communication on the subject), but the heat evolved by it falls short of that of neutralisation by some 3000 cal., and it seems probable that this excess may be accounted for by the salt formed becoming, in the presence of water, more fully saturated than either the acid or the alkali. Each of these latter contains a radicle, H and OH, which is identical with one of the radicles in water itself, and such compounds would, therefore, probably not have their residual affinity entirely saturated by the water, whereas this is not so with the salt, and there is nothing in its case to prevent complete saturation.

Mr. W. C. D. **Whetham** said that although it was impossible to criticise such an interesting paper without having considered its details, he would like to ask Mr. Crompton how he would explain the phenomena of electrical conductivity. On the theory that the ions were free from each other, the observed fact that the conductivity of a dilute solution varied as the concentration was at once explained. The alternative supposition, that the ions worked their way through the solution by means of a continual series of interchanges between the opposite parts of molecules at the instants of collision, would lead to a different result, for the frequency with which such collisions would occur, and therefore the ionic velocities must vary as the square of the concentration, and since the conductivity depended on the product of the number of ions and their average velocity, it would be proportional to the cube of the concentration.

Then, again, the fact that the velocity of an ion in dilute solution was independent of the other ion present, not only as calculated from the conductivity, but also as directly observed, seemed to favour the idea of dissociation, and was of greater weight than other additive relations, since it involved the properties of the ions when in motion.

The successful calculation of potential differences at the contact of two solutions on the assumption that the faster-travelling ion moved independently of the other, and so diffused more quickly, must also be remembered. Such phenomena as these must be explained before the dissociation theory could be abandoned. No doubt the theory presented many difficulties, and a successful attempt to explain the facts in some other way would be of extreme interest; but at present the evidence in favour of the dissociation theory seemed very strong.

Dr. **Shields**, after referring to the difficulty of discussing the paper until all the details were before them, stated that he was not satisfied that Mr. Crompton had made out his case that abnormally large osmotic pressures were due to the association of the solvent. According to the well-known equation, the osmotic pressure, π, of a solution containing n molecules of dissolved substance in N molecules of solvent is represented thus:—

$$\pi = \frac{n}{N} \cdot \frac{RT\ 1000\rho}{M} \ ;$$

where M denotes the molecular weight of the solvent, ρ the specific gravity of the solution, T the absolute temperature, and R is a constant, viz., 0·0819 litre-atmospheres, when we express the osmotic pressure in atmospheres, and the volume of the solution containing 1 g-molecule in litres. In the above equation, the product N M is the weight in grms. of the solution containing n g-mols. of the dissolved substances.

If we make up a dilute solution to contain, by intention, n g-mols. of dissolved substance in N g-mols. of a solvent supposed, in the first instance, to be normal or monomolecular, then we get a certain definite value for the osmotic pressure. If, however, the solvent is associated, and x is a measure of its molecular complexity, then instead of having weighed out N g-mols. of solvent, we have in reality only N/x, and since the weight of the solution remains the same, the osmotic pressure must be—

$$\pi = \frac{n}{N/x} \cdot \frac{RT\ 1000\rho}{xM} \ ;$$

or, in other words, remain uninfluenced by the degree of association of the solvent.

As regards aqueous salt solutions, Dr. Shields thought Mr. Crompton would encounter serious difficulties in attempting to explain why dilute solutions of binary compounds, such as potassium chloride had a maximum osmotic pressure of twice the theoretical value, whilst compounds like calcium chloride gave three times the pressure one would expect.

Dr. Shields also called attention to the fact that associated liquids, such as water, become less associated as the temperature is raised, and asked whether when the particular temperature were reached at which water becomes "normal," salt solutions also become "normal," *i.e.*, show the theoretical osmotic pressure corresponding to that temperature and otherwise behave like indifferent substances or non-electrolytes.

Mr. **Crompton**, in reply, explained that in assigning to a particular liquid a momomolecular or an associated character the general results of the work of Guye, Ramsay and Shields, and others had as far as possible been adhered to. That the molecular reduction of the freezing point of water by electrolytes was in certain cases, even in the most dilute solutions, below the value required for monomolecular compounds, indicated that the salt was originally associated and that the complex molecules only broke down slowly with rising dilution. Similar instances could be observed in the case of solutions of associated compounds in other solvents, *e.g.*, benzene. Alcohol, which in concentrated solution in benzene gave a molecular weight far higher than the normal, would be found to give correct values in very dilute solution. On the other hand, acetic acid gave even in very dilute solution in benzene a molecular weight of about 110 in place of 60, the splitting up of the associated molecules taking place apparently with greater difficulty in the case of this compound than in that of alcohol. The adequacy of the dissociation hypothesis to explain the electrical properties of salt solutions had not been called in question, but it had been shown that the hypothesis gave no true account of certain other properties of salt solutions which it had hitherto professed to explain. The additive character of the molecular conductivities of dilute salt solutions was merely in keeping with the additive character of nearly all the properties of monomolecular compounds in the fluid condition, as, for example, the molecular volumes, the molecular refractions, the molecular viscosities. If a dissociation hypothesis were adopted to explain additive properties in one case, this would have to be extended to all, and such a thing as a monomolecular fluid compound would be non-existent.

*63. "*A Comparative Crystallographical Study of the Normal Selenates of Potassium, Rubidium, and Cæsium.*"

By A. E. **Tutton**.

The main conclusions of this investigation, which is analogous to the one formerly presented concerning the corresponding sulphates (*Trans*, 1894, lxv., 628), are as follows.

1. The order of solubility of the three salts follows that of the atomic weights of the three respective metals contained.

2. The values of the morphological angles of the crystals of rubidium selenate are without exception intermediate between those of the analogous angles of the potassium and cæsium salts. The angles are therefore a function of the atomic weight of the metal present.

3. The morphological axial ratios of rubidium selenate are likewise intermediate.

4. The usual habits of the crystals of the three salts exhibit a progressive development of the primary forms, following the progressive change in atomic weight.

5. The directions of cleavage are identical.

6. The relative density and molecular volume increase when a lighter is replaced by a heavier alkali metal. The increase in density is greater when potassium is replaced by rubidium than when the latter is replaced by cæsium, and the increase in molecular volume is, on the contrary, greater when rubidium is replaced by cæsium. The replacement of sulphur in the sulphates by selenium is accompanied by an increase of molecular volume varying from 6·5 to 6·7 inversely as the weight of the initial molecule.

7. The replacement of potassium by rubidium, and of the latter by cæsium, is accompanied in each case by an increase in the separation of the centres of contiguous units of the homogeneous crystal structure, along the directions of each of the morphological axes, the influence of the nature of the alkali metal becoming relatively greater as the atomic weight rises. An extension of volume in all directions also accompanies the replacement of sulphur by selenium.

8. An increase of refractive index is observed to accompany an increase in the atomic weight of the alkali metal, and the increase becomes relatively greater as the atomic weight rises. The replacement of sulphur by selenium is also accompanied by an increase of refractive index, and such increase diminishes in amount as the weight of the initial molecule increases.

9. If the closed optical ellipsoidal figures, the optical indicatrices, of the three salts were constructed about the same origin, the indicatrix of the cæsium salt would contain within it that of the rubidium salt, and this again would contain that of the potassium salt. The indicatrix of the rubidium salt would lie nearer to that corresponding to the potassium salt.

10. The replacement of one alkali metal by another of higher atomic weight is accompanied by a diminution of the already feeble double refraction. In the convergence of the axial values of the optical indicatrix towards unity the c value proceeds much more rapidly than the others.

11. The latter fact causes a reversion of the sign of double refraction from positive to negative on attaining the cæsium salt.

12. The optic axial angles are precisely such as would naturally follow from the progressive development of the optical indicatrix; a change of direction of the acute bisectrix and of the optic axial plane occurs when the cæsium salt is reached, as the direct result of the continuity of the progression according to atomic weight.

13. The optical properties of the selenates exhibit marked specific differences from those of the sulphates, owing to the progressively different effect of replacing sulphur by selenium in the three sulphates, but the whole of the relationships of these optical properties exhibited by the three salts of each group are of a precisely parallel nature, being functions in each case of the atomic weight of the alkali metal which they contain.

14. Progressive changes occur in the optical properties on raising the temperature, following, even to the least detail, the order of the atomic weights. An interesting direct consequence is that a 60° prism of cæsium selenate whose vibration-directions are parallel to b and c affords at 90° C. only one image of the spectrometer slit, the two images usually observed coinciding at this temperature, the crystal being then apparently uniaxial.

15. A further consequence of the foregoing is that the crystals of cæsium selenate exhibit unique interference phenomena in convergent polarised light when their temperature is raised, including crossed axial plane dispersion, and two reversals of the sign of double refraction. Section-plates perpendicular to all three axes in turn require to be employed in order to follow the optic axial changes even as far as 280° C.

16. The whole of the molecular optical constants of rubidium selenate are intermediate between those of potassium and cæsium selenates. The replacement of sulphur by selenium is accompanied by an increase of molecular refraction of 3·4—3·8 Lorenz or 6·2—6·7 Gladstone units, according to the direction chosen for comparison. The relations of the three salts of each group as regards molecular refraction are identical, but the actual differences are slightly greater in the selenate group than in the sulphate group.

17. The molecular refraction of each of the three selenates for the state of solution in water is approximately the same as the mean of the three values for the crystal. When potassium selenate is dissolved in water, its refraction equivalent rises by 2·8 per cent; in the case of rubidium sulphate, a less rise of 1·0 per cent is observed, while for cæsium selenate there is no longer a rise but a decrease, to the extent of 0·5 per cent. These slight differences, due to change of state, thus exhibit a progression varying directly as the specific refractive energy and inversely as the atomic weight of the alkali metal contained in the salt. After subjecting Kanonnikoff's value for dissolved potassium sulphate of revision, precisely similar differences for the two states are shown to exist in the sulphate group.

18. The author finally concludes as regards the selenates that—

The whole of the morphological and physical properties of the crystals of the rhombic normal selenates of potassium, rubidium, and cæsium are functions of the atomic weight of the alkali metal present.

19. It is shown that the joint results of the investigations of the sulphates and selenates agree with the assumption that—

The characters of the crystals of isomorphous series are functions of the atomic weight of the interchangeable elements, belonging to the same family group, which give rise to the series.

Discussion.

Dr. Gladstone remarked that everyone recognised in a general way that in groups of analogous elements there is a gradual progression in the properties, the middle member of the group being intermediate, not only in atomic weight, but also in other respects. The value of Mr. Tutton's elaborate papers, is, that he has proved this up to the hilt quantitatively in the case of two similar, well defined groups of salts, and that with regard to a large number of properties. The change in the specific refraction of the selenates of the alkalis in their crystalline and their dissolved condition is especialy instructive, as it involves the change from *plus* in potassium and rubidium to *minus* in cæsium. The correction of Kanonnikoff's number for the potassium sulphate which Mr. Tutton has made brings the atomic refraction back to a figure practically identical with that published in Dr. Gladstone's paper of 1870, viz., 33·11.

*64. "*The Platinum-Silver Alloys; their Solubility in Nitric Acid.*" By John Spiller.

Referring to the published statements in the text-books, and particularly to those in Percy's "Metallurgy" and Bloxam's "Chemistry," according to which 5 or even 9 per cent of platinum followed the silver into solution when their alloys were treated with nitric acid, the author investigated the properties of ten graduated alloys constituted as follows:—Series I, containing 12, 9 and 5 per cent of platinum; series II, containing 2, 1·5, 1 and 0·75 per cent of platinum; series III, containing 0·5, 0·4 and 0·25 per cent of platinum. These alloys were prepared by fusion of the requisite proportions of silver and platinum under a gas-air blow-pipe flame in shallow porcelain cups, and then attacked by nitric acid of three different strengths, when it was found that the ordinary concentrated acid of 1·42 sp. gr., warmed, proved the best solvent, but that even under the most favourable conditions no more than 0·75 to 1·25, mean 1 per cent of platinum, could be dissolved along with the silver.

When diluted nitric acid of 1·2 sp. gr. was employed, the maximum amount of platinum taken up was only about 0·25 per cent; whilst the highly concentrated acid of 1·50 sp. gr. proved altogether inappropriate, giving a bulky, insoluble product consisting of platinum black, intermixed with nearly the whole of the silver nitrate formed.

It would appear, then, that Berthier's account, quoted by Percy, and the statement in Bloxam's "Chemistry" are incorrect.

Discussion.

Mr. **Vernon Harcourt** suggested that the composition of the alloys of platinum and silver might vary with the temperature at which they were formed, and that Mr. Spiller should determine the solubility of alloys formed at higher temperatures than those he had employed.

Mr. **Friswell** thought that impurities in the nitric acid might account for some of the discrepant statements on record.

65. "*Dalton's Law in Solutions. The Molecular Depression of Mixtures of Nonelectrolytes.*" By **Meyer Wilderman**, Ph.D.

Since van 't Hoff has shown that the generalisations arrived at by Boyle and Guy-Lussac in the cases of gases are equally applicable to dissolved substances in dilute solutions, the conclusion must be drawn that the third gaseous law, the law of Dalton, holds for dilute solutions also, this being a necessary consequence of the nature of osmotic pressure. Following up the thermodynamic considerations of Planck, the equations for mixtures of two or more electrolytes and the experimental proof of them are given.

66. "*The Action of Bromdiphenylmethane on Ethyl Sodacetoacetate.*" By **G. G. Henderson**, D.Sc., M.A., and **M. A. Parker**, B.Sc.

While bromtriphenylmethane and ethyl sodacetoacetate interact to give a disubstituted derivative—

$$(CPh_3)_2{:}CAc{\cdot}CO_2Et,$$

and ethyl acetoacetate, bromdiphenylmethane, on the other hand, appears to yield only a monosubstituted ester, *ethyl α-acetyl-β-diphenylpropionate*,—

$$CHPh_2{\cdot}CHAc{\cdot}CO_2Et.$$

This substance was prepared by heating bromdiphenylmethane (1 mol.) and ethyl sodacetoacetate (1 mol.) in presence of pure dry benzene or xylene till the reaction was completed, filtering from sodium bromide, concentrating the benzene solution, and purifying the crystals, which then separated, by recrystallisation from alcohol. It crystallises in shining, colourless needles, m. p. 85°, is sparingly soluble in alcohol but readily in benzene, and decomposes almost entirely when distilled.

On hydrolysis of this ester with cold dilute aqueous potash, a small quantity of *α-acetyl-β-diphenylpropionic acid*, $CHPh_2{,}CHAc{\cdot}COOH$, was obtained in the form of extremely unstable crystals, which melt about 90° and decompose at a slightly higher temperature. The salts of this acid are also very unstable. *β-diphenyethylmethylketone*, $CHPh_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, was prepared by hydrolysing the ester with hot dilute alcoholic potash. It crystallises in colourless prisms which melt at 87·5° and distils with almost no decomposition at 315°. It is fairly readily soluble in alcohol, and very readily in benzene. The *oxime*, $CHPh_2{\cdot}CH_2{\cdot}C(CH_3){:}N{\cdot}OH$, forms small, colourless crystals, m. p. 86—87°. It is sparingly soluble in alcohol but readily soluble in benzene. The *semicarbazone*, $CHPh_2{\cdot}CH_2{\cdot}C(CH_3){:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, crystallises from alcohol in small, white clusters of minute crystals, which melt at 181°. It is sparingly soluble in alcohol and in benzene.

PHYSICAL SOCIETY.

Ordinary Meeting, May 28th, 1897.

Mr. **Shelford Bidwell**, President, in the Chair.

Mr. **Elder** read a paper communicated by Dr. **Albert A. Gray**, M.D., on "*The Perception of the Difference of Phase by the Two Ears.*"

The investigation relates to certain acoustical results obtained some years ago by Dr. S. P. Thompson; they may be summarised as follows:—(*a*). When two simple tones in opposite phases are conveyed separately, through tubes or otherwise, to the two ears, the sensation of sound appears localised at the back of the head. (*b*). If the respective tones from two forks mistuned to give "beats" are conducted separately to the two ears, they still produce the sensation of "beats"; and, to the observer, this sensation also seems localised at the back of the head. The "beats" are distinct, but there are no true silences,—at any rate so long as attention is fixed on the note. (*c*). Although "beats" are heard under these circumstances, no beat-tones are discernible by the binaural method. The author proceeds to explain the phenomena on the assumption that there is a physiological connection between the nerves of both ears. His evidence is derived from the following experiments:—(*d*). A vibrating fork is held opposite one ear; the opposite ear is then closed by a finger; the sound of the fork now appears louder to the open ear. (*e*). If the fork is held opposite one ear, and the chain of ossicles of the second ear is then pressed gently inwards by a fine probe, the sound of the fork is heard with increased loudness by the first ear. (*f*). If the chain of ossicles in the second ear is dragged outwards by rarefaction of the air in the meatus, the above changes in loudness are no longer perceptible. The theory put forward by the author in explanation of these results is, that they are due to reflex contractions of the tensor tympani or stapius (or more probably both) of the first ear. A further observation, of Pollak, is also brought to bear upon the question, *i.e.*, (*g*). Stimulation of one cochlea by sound causes contraction of the tensor tympani of both ears, and the contraction is permanent while the sound continues. This is known to be true for the lower animals, and is probably true for man.

With regard to (*a*), the author observes that the muscular sense is there being appealed to in a manner quite new to it. The tympani are by nature trained each to relax or expand with the other, and they are thrown out of reckoning if the phases differ. Or again, the stimuli from the two ears may collide at one of the lower nerve centres, and thus be annulled before any intimation has been received by the brain. The path taken by such stimuli is from the nucleus of one nerve, just after its entrance into the medulla, across to the corresponding nucleus of the opposite side. In these nuclei the stimuli from both ears mix. Some of the nerve-fibres have no nuclear intercommunication at the base of the brain; consequently, stimuli passing by these paths are not subject to interference; this agrees with (*b*), where the silences are not complete. (*h*). It is to be observed that beat-tones are sometimes perceived by the ear under circumstance where they cannot set a resonator into vibration. This indicates that beat-tones may be produced either in the ear or nerve-centres of the listener, and not exteriorally. (*i*). It has been shown by Dr. Thompson that when two simple tones, such as in ordinary hearing produce a differential tone, are led singly to the ears, no differential tone is heard. From this the author concludes that differential tones are not produced in the mind of the listener, nor in any of the cerebral centres. From (*h*) and (*i*) together, the point of production is restricted down to the ear itself; something of the sort was suggested by Helmholtz. Again, from (*g*), it appears that when two notes are sounded so as to give a differential tone, the tensor tympani must be in a state of continual contraction, for the intervals of silence are too short to permit of any relaxation. Meanwhile, there are certain periods during which the tympani membranes are not acted upon by any force external to the ear. The author is of opinion that if the movements of the ossicles upon one another were absolutely frictionless, the membranes would come to rest in a position where the force of the contracting muscle was balanced simply by the tension of the membrane and the ligaments of the ossicles; but since the articulations of the ossicles have some friction, the equilibrium is otherwise, and he conjectures that the state of affairs is such that any force acting upon the hammer, tending to draw it inwards, produces a slight jerk, and this repeated gives the necessary impulses for the sensation of differential tones. The mechanics of this theory is not fully worked out.

Mr. J. Rose-Innes read a paper on "*The Isothermals of Isopentane.*"

The author takes advantage of the recent experimental work of Ramsay and Young, upon the thermal properties of isopentane, to test a formula giving the relation of pressure to temperature for gases generally, over a considerable range of volume. From the linear equation, $p = bT - a$, for the pressure at constant volume, where a and b are functions of the volume, no formula could be found to give close agreement with observed results. More definite results are obtained by examining a quantity depending upon a and b together; such a quantity is the temperature τ, at which, for each volume, the substance behaves as a perfect gas. It is shown by tables that τ is nearly a constant for volumes from 350 to about 8. Below vol. 8 it diminishes very rapidly with volume. A further investigation refers to the—

$$\left[(a v_2)^{-1} ; v^{-\frac{1}{3}} \right]$$

curves of Young, for isopentane, and a corresponding formula. At vol. 3·4 on this curve there is a decided peak, suggesting discontinuity. Ether gives a similar curve, and the question arises whether such curves would not be better represented by two or more equations.

Prof. Young said the diagrams representing the observed and calculated isothermals were probably the best ever obtained. Divergence among the values of τ was explained in part by the smallness of the angle between the theoretical isochor for a perfect gas, and the real isochor. The point of coincidence was difficult to define. Moreover, the values of τ were obtained from "unsmoothed" values of v. The evidence against the linear law consisted in a certain similarity in the shape of the different curves. It was not easy to see where experimental errors could come in. The peak was a very striking feature of the curves, and the agreement between the results with ether and those of isopentane was very remarkable. These two substances had their boiling-points close together, their critical temperatures close together, and their molecular weights nearly alike. The two substances not only agreed in each giving a peaked curve, but the peak corresponded to almost identical volumes. Prof. Young hoped at some future time to examine normal pentane, and to determine whether τ was a constant for this substance also.

The President proposed votes of thanks to the authors of the papers, and the meeting was adjourned until June 11th.

Results obtained by the Transformation of Ammonium Carbonates into Urea.—Leon Bourgeois.—The author finds that 6·0 per cent of the carbonate employed is represented by the average amount of urea obtained, the figures varying from 3·2 to 9·5 per cent when using commercial sesquicarbonate: bicarbonate of ammonia gave 2·5 to 2·9 per cent of urea; and carbamate of ammonium, $CONH_2,ONH_4$, gave 2·6 to 3·7 per cent of urea.—*Bulletin de la Société Chimique de Paris*, xii.-xiii., No. 9.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Journal de Pharmacie et Chemie.
Series 6, vol v., No. 10.

Contribution to the Study of Pilocarpine and Pilocarpidine.—A. Petit and M. Polonovski.—To show the difference existing between pilocarpine and pilocarpidine a table has been compiled giving the properties and principal characteristics of these two bases and their derivatives. From an intimate knowledge of these properties the authors are enabled to state that the impurity often found in commercial salts of pilocarpine is nothing else but pilocarpidine. These are, as is well known, the alkaloids of *jaborandi*, and the authors have proved that pilocarpidine exists in the plant itself. This assertion is based on the following facts:—1. In the absence of strong acids and alkalis, the action of boiling water alone will not explain the formation of the large quantities of pilocarpidine which is sometimes obtained, in view of its feeble action on pilocarpine. 2. Even when carefully guarding against heat during its preparation we always find in the end more or less considerable quantities of pilocarpidine. 3. The return of pilocarpidine varies considerably in quantity, viz., from 5 per cent up to 75 per cent, according to the species of *jaborandi* used. And, 4. That the stalks generally produce a much greater quantity than the leaves of the same plant.

Revue Générale des Sciences Pures et Appliqués.
No. 9.

Production and Utilisation of Acetylene.—F. Dommer.—Lighting by means of acetylene gas has recently experienced a temporary check, attributable to the absence of carbide of calcium on the market, and to the fact that there have been a few accidents which were caused by inexperience and faulty apparatus. Acetylene gas when properly dealt with is no more dangerous than coal-gas, provided it is not subjected to greater pressure than two atmospheres. Still the manufacture of carbide of calcium may now be regarded as a definite industry, and in this paper the author goes fully into the merits and disadvantages of the different furnaces used for its manufacture, all based, it is needless to say, on M. Moissan's electric furnace; but besides the chemical aspect of the question, M. Dommer thoroughly considers and analyses the question of cost, of fitting and erecting a factory, and running it successfully when completed.

The New Tuberculine of Koch.—Dr. R. Romme.—Seven or eight weeks ago the medical world was startled by the news that Dr. Robert Koch had discovered a true cure for tuberculosis. A few days afterwards a memoir was published in the *Deutsche medicinische Wochenschrift*, in which Koch described his *new* tuberculine. It differs entirely from the *old* of 1890, which was admittedly a failure. The latter was a glycerin extract of tuberculous cultures, and when injected subcutaneously caused local inflammation, accompanied by a general reaction, high fever, palpitation, sickness, &c. The new tuberculine, which is obtained by the mechanical trituration of the *Bacillus tuberculosis*, dried by successive "centrifugations" of the matter added to water, causes none of these symptoms—no morbid phenomena appear. Both are toxic, but while the *old* accelerated the disease, and, to use the true word, killed the patient, the *new* kills the disease when not too far advanced, and thus cures the patient. Animals and human beings are immunised by progressive increasing injections until they are quite insensible to tuberculosis. This paper is principally devoted to explaining in detail the directing idea which guided Dr. Koch in his work and the technical procedure which ensured his success.

Bulletin de la Société Chimique de Paris.
Vol. xvii.-xviii., No. 9.

M. Béchamp made a first communication on soluble ferments.

M. Matignon announced the preparation of carbide of sodium and monosodic acetylene, both pure, by the direct action of acetylene on sodium. The reactions of these bodies will be communicated later on.

M. Léger has studied the action of hypobromite of sodium in excess on certain phenols, and gives a short account of his results. He proposes to extend his researches to a certain number of bodies, enclosing one or more molecules of phenolic OH, and to weigh the products formed.

On a Reaction of Carbonic Oxide.—A. Mermet.—Air containing 1/500th to 1/5000th of carbonic oxide will decolourise a weak solution of permanganate of potash acidulated with nitric acid. The action is accelerated by the addition of nitrate of silver, the time varying from 1 hour to 24 hours. The strengths of the solutions used to demonstrate this new reaction are—2 or 3 grms. of nitrate of silver in 1 litre of water; the permanganate of potash is prepared by boiling a litre of distilled water containing a few drops of nitric acid (free from HCl), then adding a strong solution of permanganate drop by drop until the rose colour is persistent; this is to destroy what organic matter may be present. On cooling dissolve 1 grm. of crystallised permanganate of potassium and add 50 c.c. of pure nitric acid, and keep in the dark. To perform the experiment 20 c.c. of the silver solution is mixed with 1 c.c. of the permanganate and 1 c.c. of pure nitric acid, and made up to 50 c.c. with distilled water free from organic matter. On passing air which has been cleansed by first being passed through a tube containing cotton-wool, another containing phosphoric anhydride, another containing baryta water, &c., through this liquid, the decolouration is complete.

Action of Chromate of Strontium on Mercuric Chloride.—H. Imbert and G. Belugou.—The authors find that chromate of strontium and mercuric chloride in a hydrochloric acid solution form a double salt—

$$CrO_4Sr,2HgCl_2,HCl,$$

which is undecomposable by water. They are also able to predict the existence of a certain number of double salts containing an excess of hydrochloric acid. In a further note on the same subject M. Belugou obtains analytical results which lead him to believe that a basic mercuric chromate is also formed which is mixed with the principal substance as an impurity.

Preparation of $\alpha\alpha\beta$-Triphenylethane.—J. Rawitzer.

Benzylidenes-diphenyl-hydrazine, and their Derivatives; and the Transformation of these Bodies into Dibenzylidene-diphenyltetrazol. — H. Causse. —Neither of these last two papers are suitable for abstraction.

Essence of Cedar Wood. — L. Rousset. — Absolutely pure essence of cedar wood, free from any adulteration, was obtained from the pencil-works at St. Paul-en-Jarez, and fractionated *in vacuo*. Four-fifths of the essence constitutes a hydrocarbide, boiling at 125° to 130°, at 9 m.m. pressure. This hydrocarbide is *cedzene*, $C_{15}H_{24}$. It is a sesquiterpene, and acts on polarised light $\alpha_D = -47° 54'$.

Research on Essence of Geranium. — Eugene Charabot. — The author finds that the lævo-rotatory ether, stated to be one of the constituents of essence of pelargonium, is not contained in essence of palmrosa.

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.

Thorium.—Could any reader give outline of cheap and practical method for the extraction of thorium from monazite sand?—F. B.

MEETINGS FOR THE WEEK.

TUESDAY, 8th.—Royal Institution, 3. "The Heart and its Work," by Dr. Ernest H. Starling.

THURSDAY, 10th.—Royal Institution, 3. "Wordsworth and Coleridge," by Churton Collins, M.A.

FRIDAY, 11th.—Royal Institution, 9. "On Diamonds," by William Crookes, F.R.S.

— Physical, 5. "The Effect of Sea-water on Induction Telegraphy," by C. S. Whitehead. "A New Definition of Focal Length, and an Instrument for its Determination," by T. H. Blakesley. "Decomposition of Silver Salts under Pressure," by Dr. J. E. Myers and Dr. F. Braun. "New Way of Determining Hysteresis in Straight Strips," by Dr. Fleming, F.R.S.

SATURDAY, 12th.—Royal Institution, 3. "Music in England during the Reign of Queen Victoria," by J. A. Fuller Maitland, M.A.

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THE LIQUEFACTION OF FLUORINE.[*]

By H. MOISSAN and J. DEWAR.

The physical properties of a large number of mineral and organic compounds of fluorine indicated theoretically that the liquefaction of fluorine could only be accomplished at a very low temperature. Whilst the chlorides of boron and silicon are liquid at ordinary temperatures, the fluorides are gaseous and very far from their points of liquefaction. This is also true with the organic compounds; chloride of ethyl boils at +12° C., and the fluoride of ethyl at −32°.[†] Chloride of propyl boils at +45°, and the fluoride of propyl at −2°.[‡]

Similar observations have been made by Paterno and Oliveri,[§] and by Vallach and Heusler.[||]

Gladstones' experiments on atomic refraction[¶] can well be compared with these facts.

In fact fluorine by certain of its properties resembles oxygen, though at the same time it is distinctly at the head of the chlorine group.

The conclusion to be drawn from these observations appears to be that fluorine can only be liquefied with great difficulty. One of us showed that at a temperature of −95°, at the ordinary pressure, there is no change at all.[**]

In the new experiments which we now publish, fluorine was prepared by the electrolysis of fluoride of potassium in solution in anhydrous hydrofluoric acid. The fluorine gas was freed from vapours of hydrofluoric acid by being passed through a serpentine of platinum, cooled by a mixture of solid carbonic acid and alcohol. Two platinum tubes filled with perfectly dry fluoride of sodium completed the purification.

The apparatus used for liquefying this gas consisted of a small cylinder of thin glass, to the upper part of which was fused a platinum tube. This latter contained in its axis another smaller tube, likewise of platinum. The gas to be liquefied enters by the annular space, passes through the glass envelope, and escapes through the small inner tube. This apparatus was fused to the tube by which the fluorine was supplied.

In these experiments we used liquid oxygen as the refrigerant. It was prepared according to the method already described by one of us—and this research, we may remark, required several litres.[††]

The apparatus being cooled down to the temperature of quietly-boiling liquid oxygen (−183°), the current of fluorine gas passed through the glass envelope without becoming liquid. But at this low temperature, it has lost its chemical activity, and no longer attacks the glass.

If we now make a vacuum over the oxygen, we see, as soon as rapid ebullition takes place, a liquid collecting in the glass envelope, while gas no longer escapes from the apparatus. At this moment we stop with the finger the tube by which the gas had been escaping, so as to prevent air from entering, and the glass bulb soon becomes full of a clear yellow liquid, possessed of great mobility. The colour of this liquid is the same as that of fluorine gas when examined in a stratum one metre thick. According to this experiment, fluorine becomes liquid at −185°.

As soon as this little apparatus is removed from the liquid oxygen the temperature rises, and the yellow liquid begins to boil with an abundant disengagement of gas, having all the energetic reactions of fluorine.

We took advantage of these experiments to study some of the reactions of fluorine on bodies kept at extremely low temperatures.

Silicon, borax, carbon, sulphur, phosphorus, and reduced iron, cooled in liquid oxygen and then placed in an atmosphere of fluorine, did not become incandescent. At this low temperature fluorine did not displace iodine from iodides. However, its chemical energy is still sufficiently great to decompose benzene and essence of turpentine with incandescence, as soon as their temperatures rose to −180°. It would thus seem that the powerful affinity of fluorine for hydrogen is the last to disappear.

There is still another experiment we ought to mention. When we pass a current of fluorine gas through liquid oxygen, a flocculent precipitate of a white colour, which quickly settles to the bottom, is rapidly formed. If we shake up this mixture and throw it on a filter, we separate the precipitate, which possesses the curious property of deflagrating with violence as soon as the temperature rises.

We intend to follow up the study of this body, as well as that of the liquefaction and solidification of fluorine, which demand further experiments.—*Comptes Rendus*, vol. cxxiv., No. 22, p. 1202.

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[*] M. Moissan brought all his apparatus for the production of fluorine to the Royal Institution on the occasion of his lecture there on Friday, the 28th of May. The next day the writer had the good fortune to witness in the laboratories of the Institution by M. Moissan and Professor Dewar some of the experiments which resulted in the liquefaction of fluorine. These experiments mainly owed their success to the unrivalled appliances for the production of intense cold possessed by the Institution, and the skill and experience of Professor Dewar and his assistants in preparing a special apparatus suitable for the examination of, and experimenting with, fluid fluorine, and in the manipulation of large quantities of liquid air.—W. C.

[†] H. Moissan, "Propriétés et Préparation du Fluorure d'ethyle," *Ann. de Chim. et de Phys.*, Series 6, vol. xix., p. 266.

[‡] Meslans, *Comptes Rendus*, vol. cviii., p. 352.

[§] Paterno and Oliveri, "Sur les trois Acides Fluobenzoiques Isomères, et sur les Acides Fluotoluidique et Fluoanisique," *Gazetta Chimica Italiana*, vol. xii., p. 85, and vol. xiii., p. 583.

[||] Vallach and Heusler, *Annales de Liebig*, vol. ccxliii., p. 219.

[¶] J. H. Gladstone and G. Gladstone, "Refraction and Dispersion of Fluobenzene and Allied Compounds," *Phil. Mag.*, Series 5, vol. xxxi., p. 1.

[**] H. Moissan, "Nouvelles Recherches sur le Fluor," *Ann. de Chim. et de Phys.*, Series 6, vol. xxiv., 224.

[††] J. Dewar, "New Researches on Liquid Air," Royal Institution of Great Britain, 1896, and *Proc. Roy. Inst.*, 1893.

ON THE

DISTILLATION OF VERY DILUTE MIXTURES OF ETHYLIC ALCOHOL AND WATER. APPLICATION TO THE ESTIMATION OF ALCOHOLIC SOLUTIONS CONTAINING ONLY 1/3000TH TO 1/10,000TH PART.

By M. NICLOUX and L. BAUDUER.

Last June one of us brought forward a method of estimating alcohol in solutions containing only 1/500th to 1/3000th part (M. Nicloux, "Dosage de l'Alcool Ethylique dans les Solutions où cet Alcool est Dilué dans des proportions comprises entre 1/500 et 1/3000," *Comptes Rendus de la Soc. de Biol.*, 10th Series, vol. iii., p. 841, July 31, 1896). We will recall this method in a few lines.

"If to a very dilute solution of alcohol (from 1/500th to 1/3000th part) a weak solution (2 per cent) of bichromate of potash be first added, then a little sulphuric acid, the alcohol becomes oxidised and the bichromate becomes a chromic salt, in proportion to the quantity of alcohol present.

"If the bichromate is not in excess the solution is bluish green, the colour of weak sulphate of sesquioxide of chromium. If, on the contrary, it be ever so little in excess, it is yellowish green. The difference between the two tints is very easily noticed.

"By using 5 c.c. of the alcoholic solution under examination and a solution of 20 grms. per litre of pure crystallised bichromate of potash, of which 1 c.c. is equal to 1/1000th c.c. of absolute alcohol in the solution used—or, what comes to the same thing, 0·1 per cent in volume, the number, *n*, of cubic centimetres or fractions of cubic centimetres used to obtain the yellowish green colouration, which indicates the slight excess of bichromate, will at once give the amount of alcohol present; this will be *n*/1000, or 0·*n* per cent.

"The recognition of the yellowish green tint is made much easier by having tubes with definite quantities of alcohol, such as 1/500th, 1/666th, 1/1000th, 1/1500th, 1/2000th, 1/3000th, for comparison. 50 c.c. is a convenient quantity to work with."

It is well known that in distilling mixtures of alcohol and water, the alcohol being present in such quantity as to be easily measured, the whole of the alcohol is supposed to come over in the first third of the distillate. We thought it would be interesting to see if very dilute solutions behaved in the same manner.

The following is the method we used:—

600 c.c. of the dilute solution (1/500th to 1/3000th) is placed in a 1-litre flask and distilled, 1/20th of the distillate, or 30 c.c., is collected; the operation is repeated with another 600 c.c., and 2/20ths of the distillate is collected. This is repeated a third time, and 3/20ths is collected, and so on. *A priori*, it would appear to be simpler to collect consecutive 1/20ths and to estimate the alcohol in each; but alcohol comes over so rapidly that the estimation of fractions over 2/20ths becomes difficult, and the errors of observation are increased.

The method we adopted is longer, but, on the other hand, is much more exact. Our experiments were carried out on mixtures of 1/500th, 1/1000th, and 1/3000th. The following table shows the results we obtained:—

Fractions of distillate collected.	Amount per cent of alcohol in the distillate.		
	1/500th.	1/1000th.	1/3000th.
1/20th	50	52	55
2/20ths	75	78	79
3/20ths	88	90	91
4/20ths	90	92	94
5/20ths	91	93	97
6/20ths	92	94	100
7/20ths	93	98	100
10/20ths	100	100	100

An examination of these figures shows that:—

1. The distillation of alcohol is relatively quick. The first 1/20th of distillate containing 50 per cent of the total quantity present.
2. The quantity per cent of total alcohol for a given fraction is greater as the mixture is more dilute.
3. In mixtures of 1/500th and 1/1000th the third part (fractions of 6/20ths and 7/20ths) does not contain all the alcohol present.
4. But with the mixture of 1/3000th we are not wrong in assuming that the alcohol is entirely contained in the first quarter of the distillate.

The direct consequence of these results was the attempt to estimate alcohol in solutions containing not more than 1/3000th to 1/10,000th. Two experiments made with solutions of 1/5000th and 1/10,000th gave, in the first quarter, distillates containing 1/1250th and 1/2500th, which, estimated by the method described above, gave us the total alcohol present.

It may be remarked that the size of the flask, in proportion to the amount of liquid distilled, did not appear under the conditions described to have any particular influence.—*Bull. de la Société Chimique de Paris*, xii.-xiii., No. 7.

Disinfection with Formic Aldehyd.—Referring to our note on this subject (Chem. News, lxxv., p. 251), we are informed that the Medico-Hygienic Inventions Co., Lim., are the sole agents for the apparatus known as Trillat's autoclave, used by Dr. Winter Blyth in his experiments on disinfection with formic aldehyd.

RELATIONS BETWEEN THE MELTING-POINTS AND THE LATENT HEATS OF FUSION OF THE METALS.*

By JOSEPH W. RICHARDS, Ph.D.

In a lecture before the Franklin Institute in January, 1893, on "The Specific Heats of the Metals," I announced the fact that in the case of most of the metals whose latent heats of fusion were known, this quantity bears a simple relation to the heat required to raise the metal from absolute zero −273° (C.) to its melting-point. In most cases the former is one-third the latter. I even ventured to predict that the latent heat of fusion of gold was about 14 calories, and it has since been determined by Roberts-Austen as 16·3. Further, several latent heats have since been determined which conform to the above relation, and I have thought it opportune to collect these data and point out the limits of the relation, with some other observations which later thought on the subject has developed.

In the following table there is given, first, the heat required to raise 1 kilogrm. of the metal from the absolute zero to its melting-point (using the most probable values for the specific heats and exterpolating to −273°, for a discussion of which data reference is made to the paper already quoted); second, a simple fraction of this quantity; and, lastly, the actually determined latent heats of fusion, the experimental errors of which are probably 5 to 10 per cent:—

Element.	Heat absorbed from −273° C. to the melting-point.		Latent heat of fusion. (Experimental).
Sodium	107·8	$\frac{1}{3}$ = 35·9	32·7
Aluminium. ..	215·0	$\frac{1}{2}$ = 107·5	100·0
Potassium.. ..	54·9	$\frac{1}{3}$ = 18·3	15·7
Copper	145·3	$\frac{1}{3}$ = 48·4	43·0
Zinc	71·2	$\frac{1}{3}$ = 23·4	22·6
Gallium	21·9	$\frac{1}{1}$ = 21·9	19·2
Palladium.. ..	125·0	$\frac{1}{3}$ = 41·7	36·3
Silver..	74·7	$\frac{1}{3}$ = 24·9	24·7
Cadmium	30·7	$\frac{1}{3}$ = 10·2	13·1
Tin	27·6	$\frac{1}{2}$ = 13·8	14·5
Platinum	83·4	$\frac{1}{3}$ = 27·8	27·2
Gold	45·3	$\frac{1}{3}$ = 15·1	16·3
Mercury	7·5	$\frac{1}{3}$ = 2·5	2·8
Lead	17·7	$\frac{1}{3}$ = 5·9	5·4
Bismuth	14·4	$\frac{1}{1}$ = 14·4	12·4

Of the fifteen cases, the relation in eleven cases is one-third (in almost every case within the limits of the experimental errors); in two cases the fraction is apparently one-half, and in two cases unity. That for ten cases the ratio should be so uniform, with latent heats ranging from less than 3 to nearly 50, is an indication of some intimate connection between these physical constants of the elements.

Regarding the exceptional cases it occurred to me that aluminium, tin, and bismuth are known to act anomalously in many relations, as if their molecular structures were different from that of the other metals. (We have no data from which to discuss gallium in these relations). For instance, in lowering the freezing-point of other metals, aluminium is known to act as if its molecular formula were double that of other metals in the molten state. In Pictet's observation of the connection between the melting-point, coefficient of expansion, and atomic volume of an element, bismuth and tin are among the chief exceptions.

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[*] A Paper read before the Chemical Section of the Franklin Institute. From the *Journal of the Franklin Institute*, May, 1897.

[Pictet's rule is that the melting-points of the elements (T in absolute degrees) are, in many cases, inversely proportional to their coefficient of expansion by heat (a = linear expansion 0° to 100° C.) and to the relative distance of their atoms apart ($\sqrt[3]{V}$, where V is the atomic weight divided by the specific gravity, or atomic volume) for which Pictet's relation is expressed by—

$$T \, . \, a \, . \sqrt[3]{V} = 4{\cdot}5$$

or—

$$T = \frac{4{\cdot}5}{a \, . \sqrt[3]{V}} \, .$$

In fact, the products of these three quantities are not exactly equal, but vary between 4 and 5, the reason being, doubtless, that the average specific gravity and rate of expansion from $-273°$ to the melting-point varies somewhat from the gravity at 20° and rate of expansion at 0° to 100° as used in his calculations].

As already mentioned, bismuth and tin were Pictet's chief exceptions, and since they were anomalous in regard to their latent heat relations, I was led to compare these several relations among themselves, and to the following chain of reasoning:—Since the atomic heats of the elements (specific heat into atomic weight) at 20° to 100° are, by Dulong and Petit's law, approximately equal to 6·4, then, assuming that the average specific heat from $-273°$ to the melting-point does not vary much from the figure for 20° to 100°, the heat in atomic weight of a metal at its melting-point is approximately 6·4 T; and, assuming the relation between the latent heat of fusion and the total heat in the metal at its melting-point as $\frac{1}{3}$, the latent heat of fusion of an atomic weight of a metal becomes approximately 2·1 T.

But we can at once connect this expression with Pictet's rule, and write:—

$$L = 2{\cdot}1 \, T = \frac{4{\cdot}5 \times 2{\cdot}1}{a \, . \sqrt[3]{V}} = \frac{9{\cdot}5}{a \, . \sqrt[3]{V}},$$

where L is the latent heat of fusion of an atomic weight of the metal.

To test the validity of this expression (which, for reasons already explained, cannot claim exact accuracy), we will take Pictet's values for $a \, . \sqrt[3]{V}$ (which are based on the best available data) and make the calculation for the metals whose latent heat of fusion and coefficient of expansion are both known.

	$L = \frac{9{\cdot}5}{a \, . \sqrt[3]{V}}$.	$\frac{L}{\text{At. wt.}}$ = for 1 kilo.	Latent heat experimentally obtained.
Aluminium ..	1900	70·4	100·0
Copper	3006	46·2	43·0
Zinc	1561	24·6	22·6
Palladium . ..	3832	36·1	36·3
Silver	2541	23·5	24·7
Cadmium	1253	11·1	13·1
Tin	1712	13·7	14·5
Platinum	5106	26·3	27·2
Gold	3035	15·5	16·3
Mercury	654	3·3	2·8
Lead	1284	6·2	5·4
Bismuth	2777	13·4	12·4

Excepting aluminium, the coincidences are so close in the case of all the others that the calculated values in every case fall within the permissible limits of experimental errors, and it must be remembered that the above table contains *all* the metals for which the data are at present available. The non-metal sulphur expands so irregularly that no calculation can be made for it.

The closeness of the above coincidences may lead us to apply the formula to those other elements whose coefficients of expansion are known, but whose latent heat has not yet been determined, and thus to predict approximately the probably value of their latent heat of fusion.

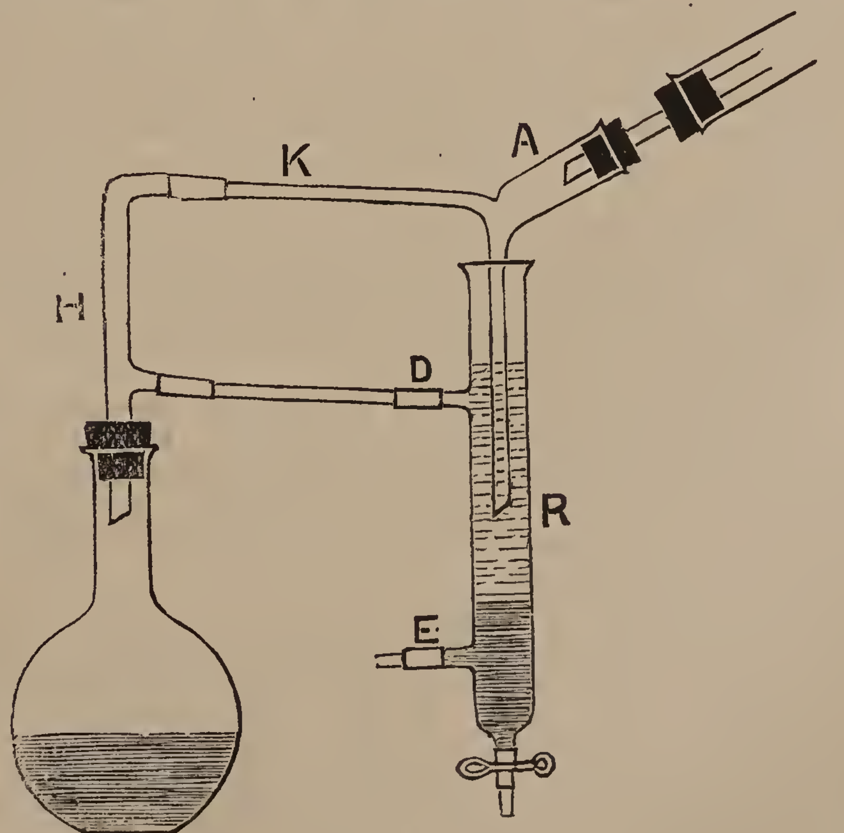
	Calories.
Magnesium	58·
Pure iron	69·
Cobalt	68·
Nickel	68·
Selenium	13·
Ruthenium	46·
Rhodium	52·
Indium	8·
Antimony	16·
Tellurium	17·
Osmium	35·
Iridium	28·
Thallium	5·8

In the case of those other elements whose coefficients of expansion and specific heat are both unknown, the latent heats of fusion may be predicted, approximately, simply from the melting-point, by using the relation L=2·1 T. The above comparisons, however, have shown that the dependence of the atomic latent heat of fusion on the absolute temperature of the melting-point, or on the total heat in the metal at its melting-point, is less exact than the dependence on the coefficient of expansion and atomic volume, and we should give the latter relationship preference in predicting unknown latent heats.

APPARATUS FOR STEAM DISTILLATION.

By WM. CORMACK.

In using the apparatus for steam distillation described by Matthews in the *Journal of the Chemical Society*, vol. lxxi., p. 318, it occurred to me that by a slight modification in the structure and arrangement of the parts a gain both in point of simplicity and freedom of construction might be secured. The modified apparatus, a sketch of which is annexed, consists of a head-piece, H, an adapter, A, and a receiver, R. The head-piece, which resembles that of a Drechsel extraction apparatus, is fitted into the neck of the flask by means of a cork or of rubber tubing. The vapours from the flask pass along the tube K to the condenser through the adapter, A, which is an ordinary bent adapter with a short tube sealed on at the bend. After



condensation, the liquid runs down the vertical tube of the adapter into the receiver, R. As shown in the figure, the apparatus is set up so as to collect a liquid which is heavier than water. In this case the liquid sinks to the bottom of the receiver, and the water floats on the top. As soon as the level of the water has attained a certain height it flows back through the upper side-tube, D, into the flask. It is esential that D should be at a lower level than the lower side-tube of H. The receiver is drawn out at the bottom and furnished with a rubber tube, clip, and jet, so that it may act at the same time as a separator. The lower side-tube, E, of the receiver is closed by a cap of rubber and glass rod.

If the liquid to be collected is lighter than water, the upper tube, D, is closed by the cap, and connection made by glass and rubber tubing between the lower tube, E, and the head-piece. The water then sinks to the bottom, and flows back into the flask through the lower tube and its connections.

The chief points in which this modification differs from the original apparatus of Matthews, is that there is no fast connection between the condenser and the receiver, but merely a water-joint, and that the same apparatus may be used for collecting liquids which are heavier or lighter than water. I have found the apparatus very satisfactory, so far as I have tested it, especially when small quantities of substances are being dealt with. The liquids in the receiver become warm after a time, which may or may not be advantageous, according to the nature of the substance. If cooling is required, this is best done by jacketting the receiver.

University College, Dundee.

EXPLANATION OF SOME EXPERIMENTS OF G. LE BON'S.

By H. BECQUEREL.

THE *Comptes Rendus* of one of our last sessions contains a paper (April 20th, 1897), by M. Perigot, in which the author, in giving account of certain experiments by G. Le Bon, after some very judicious remarks, invokes the transparency of ebonite for white light. The fact of the transparence of the ebonite plates used in these experiments for the active radiations is undeniable, but I purpose showing that the phenomena observed are not due to what we call *white light*,—that is to say, to the radiations employed most generally in photography,—but to the red radiations from the least refrangible extremity of the spectrum, and the ultra-red radiations for which ebonite is very transparent.

An experiment which M. G. Le Bon has described, in reply to M. Perigot, leaves me no doubt in this respect, and since Monday last I have indicated the following explanation to our colleagues MM. d'Arsonval, Lippmann, and Poincaré. I have verified its correctness the next day by several experiments.

This is, in the first place, what constitutes the experiments of M. Le Bon to which I have just alluded. We take a surface covered with phosphorescent zinc sulphide, and expose it to the light; then we cover it with a plate of ebonite, upon which we arrange as screens various objects,—*e. g.*, coin,—and expose the whole to the sun for some seconds. On examining afterwards, in the dark, the surface of the zinc sulphide (originally phosphorescent), we find that it is almost extinguished, except under the piece of metal where the phosphorescence is still very visible. M. Le Bon thought himself entitled to conclude from this experiment that the metal sent out rays which excite phosporescence. The explanation is quite different. These red and ultra-red rays sent by the sun traverse the ebonite, and, as it has been known long ago, extinguish the phosphorescence over the whole luminous surface, except at the points protected by the metallic screen; at these points the phosphorescence obtained by the previous illumination fades very slowly. I have not proposed to determine what are the radiations transmitted through the ebonite. I will recall that it results, from the very ancient experiments of my father and from those which I have had occasion to publish, that the red and ultra-red rays determine a rapid extinction and the phosphorescence of bodies previously illuminated, an extinction generally preceded by a temporary excitement which is not visible with phosphorescent zinc sulphide or hexagonal blende. If we project a spectrum upon the surface of a phosphorescent sulphide, the ultra-red region appears in black upon a luminous ground, in consequence of the extinction set up by the corresponding radiations; and I have shown that this extinction presents maxima and minima, variable not only with the nature of the luminous source, but with the nature of the phosphorescent substance.

For hexagonal blende the spectrum of extinction extends from the red of the visible region to the wave-length 1 μ 5, presenting a minimum about 1 μ 1 and 1 μ 2, and a strong maximum between 1 μ 3 and 1 μ 4.

If we project upon a screen of hexagonal blende, previously illuminated, a spectrum obtained with the solar radiations having traversed a plate of ebonite 0·6 m.m. in thickness, we note the immediate appearance of the infra-red extinction-band of 1·3 μ to 1·8 μ; then, after a few instants, we see appear, rather less intense, the extinction between the wave-lengths 1·3 μ 2 and the extreme visible red near A.

On concentrating the solar light with a lens we perceive red rays near the extreme visible red of the solar spectrum.

Ebonite is therefore transparent for the radiations which extinguish phosphorescence of zinc sulphide, and the explanation of Le Bon's experiment is evidently that which I have given above.

If in this experiment we form the screen of a substance which arrests the ultra-red rays, as the red rays transmitted are much enfeebled, the silhouette of the screen appears luminous on an extinguished ground. If the screen is formed of a diathermous substance like rock-salt, the totality of the phosphorescent surface is extinct. A red glass, or any substance transmitting the ultra-red rays and arresting the luminous rays,—blue, violet, and ultra-violet,—which excite the phosphorescence of blende, will give the same results if substituted for ebonite.

This transparence, perfectly demonstrated, enables us to explain in all their details the photographic experiments of M. Le Bon through ebonite.

It is known that my father showed, as early as 1840, that a photographic plate insensible to the yellow and the red rays, becomes sensitive to these rays and even to the ultra-red rays if it is exposed for a short time to light, *i.e.*, slightly veiled. The red and ultra-red rays continue the action commenced by the white, blue, or ultra-violet light.

This phenomenon, discovered with Daguerre plates, is manifested with most sensitive photographic surfaces, and in particular with plates of silver gelatino-bromide.

In the experiments of M. Le Bon a photographic plate, previously veiled (the condition essential to the success of the experiments), is exposed under a plate of ebonite to the action of the solar rays. Metallic screens placed on the ebonite mark their silhouette when we come to develop the plate. Under these conditions the photographic plate undergoes through the ebonite the continuing action of the red and ultra-red rays. The metallic screens protect the plate against this action; if the exposure has been relatively short, the ground appears on development darker than the silhouette of the screens; if the exposure has been prolonged, it results that, in consequence of a phenomenon of reversal well known, the background appears less affected than in the region protected by the screen.

The active rays in these experiments of continuation are the extreme red rays near A. As these radiations are much weakened by the ebonite, the exposure must be relatively very long, and the phenomena are not as distinct as with the highly sensitive gelatino-bromide.

The same phenomena are obtained on substituting red glass for ebonite.

I will add that a plate of ebonite of 0·6 m.m. in thickness, if examined with Melloni's apparatus, transmits 0·04 per cent of the dark heat emitted by a plate of copper at 400°, and arrests almost entirely the radiation from a source of heat at 100°.

In sum, the phenomena which M. G. Le Bon endeavours to ascribe to an assumed *black light* of an unknown nature are simply effects produced by the red or ultra-red rays, the principal properties of which have been well known for more than fifty years.—*Comptes Rendus*, vol. cxxiv., p. 984.

RESEARCHES ON THE BIOLOGICAL ACTION OF THE X-RAYS.

By J. SABRAZES and P. RIVIERE.

The apparatus used in our experiments consisted of a bi-anodic focus tube (M. Segny's design), excited by powerful Ruhmkorff coil, yielding a current of 6 ampères and 16 volts, sparks of 35 c.m. in length. With the aid of this tube we obtained radiographs at the distance of 3·50 metres and behind a screen of boards. This arrangement evidently permitted the easy exploration of the limbs and of the thorax.

The objects studied were arranged at about 15 c.m. from the fluorescent source; they were enclosed in black paper to protect them from luminous radiations, and were placed in metallic communication with the earth.

1. *Experiments on Microbacillus prodigiosus.*

We proposed to study the action of the X-rays on a microbe peculiarly sensitive to changes brought on in the physico-chemic conditions of its development, and apt to translate this sensitiveness by modifications permanent and easy of observation.

The *Microbacillus prodigiosus* answers to these requirements, especially if we address ourselves, as we have done, to a race eminently chromogenous.

If we cultivate this microbe at a dysgeneric temperature of 37°, — if we modify the reaction of the medium by alkalising it strongly,—if we diminish the access of atmospheric oxygen,—if we expose the culture to the solar radiations, to the action of an injurious substance, *e.g.*, of an antiseptic,—the pigmentary properties are attenuated and effaced progressively, and in time, although the colonies continue to grow, they remain more or less colourless. We know also that it is sufficient to acidify the culture-bouillon, or to raise the temperature of the stove to 50°, to modify profoundly the aspect of the microbian cells which become filamentary or even spiriform. It will therefore be easy to appreciate the modifications impressed on this microbe by bringing into play a novel biological condition; it will be sufficient to examine the oscillations of the chromogenic power and the morphologic variations of the cellules as compared with type cultures in a long series of successive generations.

We have proceeded as follows:—The cultures, of a fine carmine-red, were collected on gelose, and arranged in the form of a small pointed heap, in the middle of a sterilised watch-glass wrapped in black paper. The X-rays act directly through the paper upon the seed, the cavity of the watch-glass being placed opposite the phial.

We operate exactly in the same manner with a check-culture, except that the watch-glass covered with black paper was screened from the X-rays.

Daily for twenty days we caused the X-rays to act upon he microbe for an hour each day.

In spite of the power of our phial, the number of passages, and the duration of exposure to the X-rays, we have not observed any appreciable modification of the *Microbacillus prodigiosus*, either in its chromogenic properties or in its morphological characters or its vegetability. This microbe has shown itself indifferent to Röntgen's rays.

2. *Experiments on Leucocytes.*

Two frogs, as nearly as possible of the same bulk, were fixed upon cork in the ordinary manner.

After cauterisation with the thermo-cautery, so as to avoid any loss of blood, we introduced—at a point of the leguments chosen at the level of the mean part of the abdomen—at the aperture thus made, a pointed tube, previously washed with a culture of microbes yielding products of positive chæmiotaxis.

We exposed one of the frogs to the X-rays after having taken the precautions mentioned above. The other, which served as a check-type, was withdrawn from the influence of the radiation by a metallic enclosure. We prolonged the experiment for several hours, and at the end of the time collected the liquid which had transuded into the tubes. We counted the *leucocytes* existing in the lymph thus collected, and examined with the microscope the figured elements held in suspension.

From the numerous experiments thus made the conclusion follows that the X-rays do not interfere with the efflux of the white globules; their number is sensibly the same in both cases. Phagocytosis is equally effected. In some experiments even the quantity of lymph emanating from frogs submitted to the X-rays was slightly greater than that in the check-tubes.

3. *Action of the X-rays upon the Heart.*

Some observers have detected in man cardiac disturbances following on application of the X-rays.

The tracings of the heart of a frog placed below a powerful source of X-rays showed us that the rhythm of this organ was not modified in its periods even after an exposure of more than one hour. —*Comptes Rendus*, vol. cxxiv., p. 979.

DETERMINATION OF PHOSPHORUS IN CHEMICO-LEGAL INVESTIGATIONS.

By M. SPICA.

The author proceeds as follows: — The substance in question is divided into three parts, of which one is reserved for check-experiments; a second serves for the qualitative detection of phosphorus by Mitscherlich's process; and the third for the quantitative determination of phosphorus. For the last purpose he employs the free phosphorus, or that present in the direct volatile state, according to the procedure of R. Fresenius and Newbauer, which he has somewhat modified. The flask containing the material is closed with a stopper having three perforations for the usual entrance and exit of gas, and for a tube-funnel closed with a glass cock. To the flask is connected a tubulated receiver, which is again connected with three Peligot tubes containing neutral solutions of silver nitrate. After the transmission for six to eight hours of carbonic acid washed in solution of silver nitrate, it is tested anew by fresh tubes filled with silver solution, to determine if phosphoriferous substances pass over on a further passage of carbonic acid.

If this is not the case we proceed to determine those compounds of phosphorus which are not reduced by nascent hydrogen, for which purpose the author uses the procedure of Dusart as modified by Blondlot. After the contents of the flask have been allowed to cool in the current of carbonic acid, the purest zinc is rapidly introduced into the flask, which is then closed, and sulphuric acid is run in through the funnel tube until there sets in a slight development of hydrogen, which is kept in very slow action for five to six days. After this lapse of time we satisfy ourselves as above of the completion of the reaction.

For the ultimate gravimetric determination of the phosphorus, the author oxidises the liquid found in the receivers with nitric acid, and determines the phosphorus in the solution as ammonium phospho-molybdate.—*Zeit. Anal. Chemie*, xxxvi., p. 347.

COLORIMETRIC DETERMINATION OF SMALL QUANTITIES OF NITROUS ACID.

By Prof. Dr. E. RIEGLER.

In connection with my communication on the detection of nitrous acid with naphthionic acid, I point out that by means of this reaction small quantitis of nitrous acid can be easily determined colorimetrically. We dissolve 0·406 grm. pure dry silver nitrite in hot water, add sodium chloride in slight excess, and dilute after cooling to 1 litre. After the deposit has subsided we take 100 c.c. of the clear solution, and dilute again to 1 litre with distilled water. Of this last solution we put 100 c.c., corresponding to 0·001 grm. N_2O_3, into a flask, add a small penknife-point (about 0·05 grm.) full of crystalline naphthionic acid and 5 or 6 drops of concentrated hydrochloric acid; shake up well, and add 30 drops of concentrated ammonia (liquid). After thorough shaking we have a rose-coloured liquid, the tint of which serves as a standard for the above concentration. In order to find the proportion of nitrous acid in a water, we place 100 c.c. of the water in a flask, add a small penknife-point full of naphthionic acid, shake well up, and then add 30 drops of concentrated liquor ammoniæ. We then compare, by means of the colorimeter, the intensity of this solution with that of the standard, and calculate according to known rules the quantity of the nitrous acid.

In this manner 0·00001 grm. N_2O_3 can be determined in 100 c.c. of water.

In case the water in question contains more than 0·001 grm. N_2O_3 in 100 c.c., it must be suitably diluted with distilled water before determination.—*Zeit. Anal. Chemie*, xxxvi., p. 306.

FOURTH ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS.
RESULTS PUBLISHED IN 1896.*

By F. W. CLARKE.

During 1896 the activity in the determination of atomic weights was only moderate. Comparatively few papers on the subject appeared, but some of these were of excellent quality. The question is often asked, Why are new determinations important? Are not those we have good enough for all practical purposes. To this question I have an interesting answer, such as has not hitherto been published.

There are two rival values for the atomic weight of chromium. One, 52·5 approximately, based on the old work of Berlin, is still used by European analysts. The other, 52·1, depends upon later and more accurate researches, and is used in the United States. Mr. William Glenn, of the Baltimore Chrome Works, informs me that that establishment imports chrome iron ore by the shipload, the value being determined by a volumetric assay in which the atomic weight of chromium is involved. It is assayed in Glasgow with the older value for chromium,

	H = 1.	O = 16.
Aluminum..	26·91	27·11
Antimony	119·52	120·43
Argon..	?	?
Arsenic	74·44	75·01
Barium	136·39	137·43
Bismuth	206·54	208·11
Boron..	10·86	10·95
Bromine	79·34	79·95
Cadmium	111·10	111·95
Cæsium	131·89	132·89
Calcium	39·76	40·07
Carbon	11·92	12·01
Cerium	139·10	140·20
Chlorine	35·18	35·45
Chromium..	51·74	52·14
Cobalt	58·49	58·93
Columbium	93·02	93·73
Copper	63·12	63·60
Erbium	165·06	166·32
Fluorine	18·91	19·06
Gadolinium	155·57	156·76
Gallium	69·38	69·91
Germanium	71·93	72·48
Glucinum	9·01	9·08
Gold	195·74	197·23
Helium	?	?
Hydrogen	1·000	1·008
Indium	112·99	113·85
Iodine	125·89	126·85
Iridium	191·66	193·12
Iron	55·60	56·02
Lanthanum	137·59	138·64
Lead	205·36	206·92
Lithium	6·97	7·03
Magnesium	24·10	24·28
Manganese	54·57	54·99
Mercury	198·49	200·00
Molybdenum	95·26	95·99
Neodymium	139·70	140·80
Nickel	58·24	58 69
Nitrogen	13·93	14·04
Osmium	189·55	190·99
Oxygen	15·88	16·00
Palladium	105·56	106·36
Phosphorus	30 79	31·02
Platinum	193·41	194·89
Potassium..	38·82	39·11
Praseodymium.. ..	142·50	143·60
Rhodium	102·23	103·01
Rubidium	84·78	85·43
Ruthenium	100·91	101·68
Samarium	149·13	150·26
Scandium	43·78	44·12
Selenium	78·42	79·02
Silicon	28·18	28·40
Silver..	107·11	107·92
Sodium	22·88	23·05
Strontium	86·95	87·61
Sulphur	31·83	32·07
Tantalum	181·45	182·84
Tellurium	126·52	127·49
Terbium	158·80	160·00
Thallium	202·61	204·15
Thorium	230·87	232·63
Thulium	169·40	170·70
Tin	118·15	119·05
Titanium	47·79	48·15
Tungsten	183·43	184·83
Uranium	237·77	239·59
Vanadium	50·99	51·38
Ytterbium	171·88	173·19
Yttrium	88·35	89·02
Zinc	64·91	65·41
Zirconium..	89·72	90·40

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* *Journal of the American Chemical Society*, xix., No. 5.

and in Baltimore with the modern datum. A cargo amounts to about 3500 tons; and the difference in price due to the difference between 52·1 and 52·5 for chromium amounts to about 367.50 dols. per shipload. This difference is large enough to show the importance of accurately determined constants from a commercial point of view, and suggests that other similar cases might be found by a careful scrutiny of our analytical processes.

My own "Recalculation of the Atomic Weights," a new edition of the work published originally in 1882, is now complete and in the printer's hands. It will probably be published early in 1897, and the appended table of values represents the results obtained by combining all the best data.

The following new determinations of atomic weights represent the work published during the year:—

Oxygen.—In the report for 1895, J. Thomsen's gravimetric measurements of the H : O ratio were cited. Early in 1896 the same chemist (*Zeit. Anorg. Chem.*, xii., 4), by a novel method, determined the ratio of densities. First, he found the volume of hydrogen in litres, liberated by the solution of one grm. of aluminum, to be as follows:—

1·24297
1·24303
1·24286
1·24271
1·24283
1·24260
1·24314
1·24294

Mean .. 1·24289 ± 0·00004

In his earlier research Thomson found the weight of hydrogen corresponding to 1 grm. of aluminum to be 0·11190 ± 0·000015 grm. Hence 1 litre of hydrogen at 0°, 760 m.m., and 10·6 metres above sea-level, is 0·090032 ± 0·00012 grm.; or at sea-level in latitude 45°, 0·089947. For the volume of one grm. of oxygen at 0°, 760 m.m., and at Copenhagen, Thomsen found, in litres:—

0·69902
0·69923
0·69912
0·69917
0·69903
0·69900
0·69901
0·69921
0·69901
0·69922

Mean .. 0·69910 ± 0·00002

At sea-level, latitude 45°, 0·69976 ± 0·00002.

Hence one litre weighs 1·42906 ± 0·00004 grm. Dividing this by the value found for hydrogen we have for the ratio desired—

15·8878 ± 0·0022.

Correcting this by the known data for the volumetric composition of water we get—

O = 15·8690 ± 0·0022,

a value identical with that found gravimetrically, and very close to the measurement by Morley.

Silver.—The atomic weight of silver has been determined electrolytically by Hardin (*Journ. Am. Chem. Soc.*, xviii., 990; CHEM. NEWS, lxxv., 28 *et seq.*). The nitrate, acetate, and benzoate, mixed in aqueous solution with solutions of pure potassium cyanide, were electrolysed in platinum dishes. The data are as follows, with vacuum weights, and reduced with N = 14·04, C = 12·01, H = 1·008, and O = 16.

Nitrate Series.

Weight $AgNO_3$.	Weight Ag.	Atomic wt. Ag.
0·31202	0·19812	107·914
0·47832	0·30370	107·900
0·56742	0·36030	107·923
0·57728	0·36655	107·914
0·69409	0·44075	107·935
0·86367	0·54843	107·932
0·86811	0·55130	107·960
0·93716	0·59508	107·924
1·06170	0·67412	107·907
1·19849	0·76104	107·932
	Mean ..	107·924

Acetate Series.

Weight salt.	Weight Ag.	Atomic wt. Ag.
0·32470	0·20987	107·904
0·40566	0·26223	107·949
0·52736	0·34086	107·913
0·60300	0·38976	107·921
0·67235	0·43455	107·896
0·72452	0·46830	107·916
0·78232	0·50563	107·898
0·79804	0·51590	107·963
0·92101	0·59532	107·925
1·02495	0·66250	107·923
	Mean ..	107·922

Benzoate Series.

Weight salt.	Weight Ag.	Atomic wt. Ag.
0·40858	0·19255	107·947
0·46674	0·21999	107·976
0·48419	0·22815	107·918
0·62432	0·29418	107·918
0·66496	0·31340	107·964
0·75853	0·35745	107·935
0·76918	0·36247	107·936
0·81254	0·38286	107·914
0·95673	0·45079	107·908
1·00840	0·47526	107·962
	Mean ..	107·938

The mean of all three series is—

Ag = 107·928.

This value agrees well with the values found by Stas and by Marignac, and so creates a presumption in favour of the electrolytic method, which Hardin has also applied to determining the atomic weights of mercury and cadmium.

(To be continued).

SOME PRESENT POSSIBILITIES IN THE ANALYSIS OF IRON AND STEEL.*

By C. B. DUDLEY.

(Concluded from p. 270).

SOME years ago, with the publication (*Trans. Am. Inst. Mining Eng.*, ix., 397) of what is commonly known as Ford's method, the determination of manganese took a decided step forward, at least in this country, so far as speed is concerned. Previous to that time the long and laborious acetate method, which involved the separation of the iron from the manganese as basic acetate and subsequent precipitation of the manganese by means of bromine or as pyrophosphate, had held full sway.

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* Presidential Address delivered at the Troy Meeting of the American Chemical Society, December 29, 1896. From the *Journal of the American Chemical Society*, xix., No. 2.

Ford's contribution consisted, as is well known, in separating the manganese from hot nitric acid solution of the iron or steel, by means of potassium chlorate, and Williams (*Trans. Am. Inst. Mining Eng.*, x., 100) added the modification, now in common use, of determining the separated oxide of manganese, by its action on a standard solution of ferrous sulphate or oxalic acid. This method, as now worked in many laboratories, gives a single result in forty minutes and two in an hour, and enables one operator to turn out twenty to twenty-five determinations in a day. The accuracy of this method has been questioned. We are not aware of any recent symposium on manganese, where different chemists using different methods have worked on the same steels. In our hands this method gives results closely agreeing with check work done by the more laborious and generally accepted accurate methods, provided the sample contains not more than three-fourths of a per cent. On samples containing over 1 per cent of manganese the results are apt to be low, owing probably to the fact that the manganese does not separate from the nitric acid solution as manganese dioxide, but as some other oxide whose composition is not positively known. In the calculation it is customary to regard the separated oxide as manganese dioxide, and this leads to perceptible error on large amounts. Producers and consumers rarely contend much over manganese in steel, and methods for its determination have perhaps not received, on that account, all the attention they deserve. There is evident need of more work on this subject.

The methods for the determination of silicon can hardly be regarded as in a perfectly satisfactory condition. If evaporation to dryness to render silica insoluble is employed, the time required is considerable. If dehydration by means of sulphuric acid and heat, as suggested by Drown (*Trans. Am. Inst. Mining Eng.*, vii., 346) is employed, there are difficulties which interfere somewhat with accuracy. There seems little doubt but that in skilled hands, with sufficient care taken in the manipulation, a couple of determinations may be made on the same sample, using Drown's method, that will agree closely with each other and with results given by the longer and more laborious methods. On the other hand, where one operator is making a number of determinations at the same time there is much danger of error, due either to failure to dehydrate sufficiently or to over-heating, resulting in the formation of insoluble iron salts. Our experience indicates that the margin between these two extremes is not very wide, and that it is fully as frequent to have duplicates on the same sample disagree as to agree. Our observations point to the view that the difficulty of insufficient dehydration is due to the separation of iron salts as the sulphuric acid concentrates. These salts enclose gelatinous silica, and prevent the dehydrating acid from getting at it. Unless great pains are taken, therefore, to secure this contact by sufficient stirring, the results will be low. If by some modification the iron salts could be kept in solution until the silica is rendered quite insoluble, it would apparently be a decided step forward with this method. It may not be amiss here to call attention to the fact first noticed in the laboratory of the Pennsylvania Railroad Company,* that after the dehydration and subsequent dilution are finished, if an interval of a few hours is allowed to elapse before filtration, the silica will re-dissolve and the results be low. Apparently, as we are able to work the method, the silica is not completely dehydrated, but only sufficiently so that if filtered at once fairly accurate results will be obtained.

It is difficult to say anything positive about the speed and output of Drown's method. It is probably safe to say that a couple of determinations could be made in an hour and a half, but, on account of the difficulty mentioned above, the method does not lend itself well to working on a large number of samples at once, and consequently a large daily output is somewhat interfered with.

It must also be said of the methods for the determination of sulphur in iron and steel, that those most in use are hardly as satisfactory as could be desired. The studies of Phillips (*Journal of the American Chemical Society*, xvii., 891) conclusively show that when using the evolution method the whole of the sulphur content is not given off in such a form as to be retained by the usual means employed to catch the gas. It seems not too much to say that it is hazardous to use the evolution method on pig or cast iron, even when fusion of the residue is employed. The formation of unoxidisable gases containing sulphur, in the application of the evolution method to steel, has not, so far as our knowledge goes, yet been demonstrated, and accordingly the evolution method is still used largely on steels. But on pig and cast irons the oxidation method seems the only one applicable, and some recent studies of Blair, described in a paper at this meeting (see *Journ. Amer. Chem. Soc.*, xix., 114), indicate that on certain pig irons all the sulphur is not given, even by this method, unless the graphitic residue is fused with sodium carbonate and nitre. Both methods are somewhat slow, and there is need of further study. If some means could be found by which barium sulphate could be readily and accurately converted into sulphide, so that a volumetric method could be applied to this sulphide, it would be a decided step forward. The necessity in accurate work for purifying barium sulphate, as first obtained from almost any solution, by fusion and re-precipitation, adds quite considerably to the time required. With steels and two sets of evolution apparatus, using bromine for oxidation, two determinations may be made in two hours. With four sets of evolution apparatus, one operator can make twelve determinations in a day. In these cases purification by fusion is not attempted. By the oxidation method on pig or cast iron, two determinations require about five hours, while one operator with a supply of borings ahead and sufficient appliances, can get from ten to twelve results in a day. With this output purification by fusion is not attempted. If this is done, the time for a pair of determinations must be extended an hour and a half, and the daily output would be cut down at least a third.

From what has preceded in this hasty and necessarily imperfect survey of a portion only of the analytical methods in use in the iron and steel industry, it is clearly evident that there still remains an enormous amount of work to be done in conection with methods. We have touched upon only five of the fifteen or twenty constituents occurring in and affecting the quality of iron and steel, and find the methods for determining even those more or less imperfect, and needing more work. What will be our condition as chemists if, as seems probable, nickel, chromium, aluminum, tungsten, and the gases, oxygen, hydrogen, and nitrogen, either free or combined, within the next few years, come into prominence as constituents of iron and steel, and are made elements in important commercial contracts? Still further, thus far our methods are concerned almost entirely with the total content of the various constituents we are determining. We know very little about the compounds of the various constituents occurring in iron and steel, with the metal or with each other. Is the phosphorus present as phosphide or phosphate, or both? How besides as sulphide does the sulphur occur? Do the various carbides which are revealed by the microscope, and which are believed to be so closely dependent on the heat treatment which steel receives, and which are so intimately related to the value of the metal, differ from each other in carbon content, or only in crystalline form? Who will be the first to isolate any of these carbides? Who will first give us a practicable, accurate, and sufficiently rapid method for determining oxides in steel? Who will first completely investigate the relation between the chemistry and the chilling properties

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* Address to the members of the Chemical Section of the Engineers' Society, at Pittsburgh, September 27th, 1892, by C. B. Dudley, on "Discrepancy in Chemical Work by Different Workers."

of cast iron? And who will first give us a study on the form in which nitrogen occurs in this metal, and a sufficiently rapid and accurate method for its determination? Truly the harvest of chemical work before us in connection with iron and steel is bounteous. Will the labourers be forthcoming to gather the harvest?

NOTICES OF BOOKS.

Water and Public Health. The Relative Purity of Waters from Different Sources. By James H. Fuertes, Member of the American Society of Civil Engineers. First Edition. First thousand. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1897. Pp. x—75. 12mo., Ill.

In this little volume the author has grouped the principal cities of the world into classes according to the quality of their public water supplies, and has made a comparative study of their mortality statistics. This statistical method of treatment makes the importance of pure water stand out in bold relief.

The author admits the uncertainty resulting from incorrect reports of health boards and physicians, as well as from unreliable figures of population; but he assumes that "in all large cities these causes of error are perhaps equal," and the inaccuracies will counterbalance so as not to seriously influence the general deductions that may be drawn.

The four chapters of the book are entitled:—I. Etiology and Prophylaxis of Typhoid Fever. II. When does Pure Water pay? III. Sanitary Value of Impounded and other Supplies. IV. Conclusion. Following this are four Appendices, containing much statistical information.

The work is illustrated by no less than seventy diagrams, showing in a graphic way the relations of pure water and foul water to public health in a large number of cities in Europe and America.

The author's conclusions are those of a common-sense view of the subject, based upon the facts presented.

It is surprising to learn that the important commercial city of Baltimore, having a population of 435,000, "has as yet no sewerage," and "the house-drainage is disposed of largely into cesspools and outhouses."

The author discusses the outbreaks of cholera and typhoid fever in Hamburg, Germany, and it is truly appalling to read the terrible figures of mortality in that unhappy city during the epidemic years.

The author believes that "properly designed and operated filters may be relied upon to purify any waters at present used for a public water-supply in the United States."

In Chapter II. the author treats of the question "When does pure water pay?" and discusses in a cold-blooded way the economic value of an individual to the community, and the amount of money which the community is authorised to expend to accomplish a reduction in the death-rate. He finds that the "community can afford to invest about three thousand dollars for every death forefended."

The Index to the volume is unusually full.

H.C.B.

Ninth Annual Report of the Agricultural Experiment Stations of the Louisiana State University for 1896. Baton Rouge. 1897.

At the Audubon Park Station sugar-cane has been both the chief crop, and the chief study in the laboratories. In the field, experiments covering the entire subject of proper fertilisation of the cane have been continued. Physiological investigations of the sugar-cane, both in the field and under the microscope, have been energetically pushed during the year, and valuable results obtained.

The young *citrus* grove continues to grow and increase, and hardy growths of oranges, such as the Satsuma and Kumquat, grafted on the *trifoliata* stock, have resisted the most intense cold ever known in the neighbourhood.

The fibre plants, such as jute, hemp, and ramie, have also been successful, but unfortunately no trials of decorticating by machinery were made.

At No. 2 Station, Baton Rouge, as at the others, special attention was given to the growth of Egyptian cotton; the crops have been gathered in, and now await the arrival of a cotton gin from England. We should have thought it cheaper to send the cotton to England, as other people do.

Station No. 3, at Calhoun, has been unfortunate; the drought was so severe and prolonged that everything has been eaten up by the stock, and all the experiments vitiated.

Bulletin of the Agricultural Experiment Station. Second Series, No. 46. *Leguminous Root Tubercles*, by Prof. W. R. Dodson. Baton Rouge. 1897.

It has long been known that leguminous plants are restorative in their character, when used for improvement of soils in a system of rotation of crops. Some years since it was discovered that the chief virtue of these plants was in fixing the nitrogen from the air, which was due to the tubercles which occur upon their roots. With the object of throwing more light on this subject, a number of experiments were made by Prof. Dodson.

When thin slices of these tubercles are examined with a high-power microscope, they are found to be filled with myriads of organisms resembling bacteria. It has been shown that when plants are cultivated in pots, under conditions where contact with these organisms is prevented, the accumulation of nitrogen in the plant is only equal to what is lost by the soil; but in the opposite case, when these organisms are present, the increase of nitrogen can only be accounted for by the assumption that the free nitrogen of the air has been used.

To find the influence of deep and shallow planting on the tubercle formation of the roots, experiments were made on cow peas, pea-nuts, garden beans, &c. Seeds were planted at a depth of 1, 2, 3, 4, 5, and 6 inches. After eight weeks the soil was thoroughly softened and carefully washed from the roots. Planting at 2 or 3 inches seemed to give the maximum roots that spread near the surface, and the greatest number of tubercles. The observations made in these plantings were supplemented by an examination of all the leguminous plants found in the vicinity, and it was shown that the nature of the soil had much to do with the depth at which the tubercles are well developed; they are deeper in sandy than in clayey soil, and deeper where deep cultivation has been practised than where shallow cultivation prevailed.

In the second set of experiments it was sought to obtain an approximate idea of the depth to which the nitrifying organisms penetrate, and find conditions favourable to their development. Pots containing sterilised soil were planted with several kinds of seeds,—clover, lima bean, lupins, &c.,—and watered with nutritive solution; but all grew very badly, and it was eventually found, by modifying the experiments somewhat, that though the organisms are found at a depth of 1 foot, they are not very abundant, and in no case was the infection so general by watering as from a surface inoculation.

Other experiments show that each plant, or at most, each genus of plants, will support but one kind of parasitic organism capable of developing the tubercles on its roots. For instance, in order that tubercles may be developed on alfalfa, a particular organism must be in the soil, and any quantity of cow peas, or other leguminous plants, will not furnish that organism, The cow pea likewise has its own peculiar parasite, and so on with the others. Yet dozens may be grown side by side in the same soil, and each will develop its own tubercles.

Chemistry of Artificial Colouring-matters. ("Chimie des Matières Colorantes Artificielles"). By A. Seyewetz and P. Sisley. (Part 5). Pp. 821. Paris: Masson and Co. 1897.

The fifth and final instalment of this work has just appeared, and we must confess to a sense of great disappointment. The whole book has up to the present been produced in an excellent manner, beyond the style of the ordinary French book, both as regards printing and quality of paper used; but with this last number before us we cannot help thinking of Mark Twain's description of one of his own humorous sketches, which, he explains, is only a study in black and white, not a finished picture. The present work is decidedly a study; but when we come to twelve large pages of *errata*, comprising no fewer than 128 corrections, many of them apparently important ones, we feel more as if we were reading proof sheets than a published book.

We hope in a future edition the work will be sent out more fitted for the reviewer.

Papers and Notes on the Genesis and Matrix of the Diamond. By the late Henry Carvill Lewis, M.A., F.G.S. Edited from his unpublished MSS., by Professor T. G. Bonney, D.Sc., LL.D., F.R.S. London, New York, and Bombay: Longmans, Green, and Co.

It is indeed a mournful story told by the Editor in his Preface,—first the sudden death of the author, Prof. H. C. Lewis, in July, 1888, followed soon after by that of Prof. G. H. Williams, to whom the MSS. had been handed for publication. It is a matter of great satisfaction that it should have fallen to Prof. Bonney, who had the privilege, as he himself informs us, of hearing the papers read by the author at the meetings of the British Association, in 1886 and 1887, to prevent the valuable and interesting contributions to our knowledge of diamond-bearing rocks being lost to Science. The present time is very opportune for their publication, when the genesis and history of the diamond, brought into prominence by the researches of Prof Moissan and others, is occupying considerable attention in the scientific world.

The book is small, well printed, and the illustrations—particularly those of a fragment of diamond-bearing rock from Kimberley and the micro-photographs of sections—are very good. The care shown by the late Prof. Lewis in the collection of his notes is very apparent, and it is not often that we are fortunate enough to find so much solid matter in so small compass.

The book is divided into three sections. The first—"On a Diamond-bearing Peridotite and on the History of the Diamond"—contains illustrations of sections of the diamond-bearing "pipes" at the de Beer's mine, and, in support of the suggestion that the gabbro or euphotide in which the diamonds are found is the "mother rock," the well-known fact is quoted that each of the several pipes furnish diamonds distinct in character, easily distinguishable from the others; the accompanying minerals and the formation and character of the pipes are fully discussed.

Section II., "The Matrix of the Diamond." This section occupies the greater part of the book; the various minerals occurring in the "blue clay" are very fully described; in fact, the material involves a mineralogical study of no mean order. Prof. Lewis deals with it very thoroughly, giving a complete list of the constituent minerals, and then describing each in order. The very pleasant manner in which the notes are given adds much to the interest of the subject. The occurrence is noted of a variety of garnet, called "demantoid" in microscopic crystals, so closely resembling diamonds in appearance as to be sometimes mistaken for them. A very full account is given of the mica which is generally looked upon as an indication of the presence of diamonds.

As a result of his study of the diamantiferous clay, Prof. Lewis concludes that "There appears to be no named rock-type having at once the composition and structure of the Kimberley rock. For this reason, as also on account of its importance as the matrix of the diamond, it is now proposed to name the rock Kimberlite." At the conclusion of this section the resemblance between kimberlite and that class of meteorites known under the name of chondrites is pointed out.

Section III., "Kimberlite from the United States," only occupies a few pages, and consists of notes on various specimens of diamond-bearing rock that had been collected by Prof. Lewis, but which he evidently had not had the opportunity to thoroughly examine.

The book concludes with a short note by Prof. Bonney, giving data of the work done at the De Beer's mine up to date 1896.

CORRESPONDENCE.

ESTIMATION OF CARBON IN FERRO-CHROME.

To the Editor of the Chemical News.

Sir,—We are obliged to Prof. Arnold for his complimentary notice of our paper, and I beg to make the following observations on the objections he raises.

It will be noticed that the statement respecting Prof. Arnold's method is not an unqualified one. The kind of combustion furnace used (Bunsen's) and the approximate heat of the tube was given; after this, I was justified in stating the results. It is my opinion that the furnace used can be made as hot as those generally employed. In one particular, however, it did not comply with the conditions stated in Prof. Arnold's letter. The combustions were all made between 10 a.m. and 5 p.m. The inconvenience of waiting for night pressure during the summer months needs no comment. The gas-supply is through a 1½ (outside diam.) pipe, and gives as much gas as can be efficiently burned. It should be noticed in your correspondent's favour that it was necessary to coat the tubes with asbestos.

It was lamented in the article that so vague a description of the necessary tubes should be deemed sufficient; I am sorry to note that even now the Professor goes no further than to say "such tubes are not easy to obtain, but they are, nevertheless, obtainable." I have tried to get such tubes, and admit failure. It is a small thing to ask, will Prof. Arnold oblige myself and others by saying what the tubes are called and where they may be had?

As is surmised, I have never heated bright steel drillings in dry oxygen, but I am pretty certain of the difference between moist and dry oxygen. For instance, that even carbon cannot be combusted in chemically dry oxygen ("Combustion in Dried Gases," H. B. Baker, *Journ. Chem. Soc.*, 1885; Chem. News, li., 150); but Prof. Arnold's oxygen is not chemically dry, and since traces of moisture make the most marked difference it is impossible to argue about the need for employing moistened asbestos with "almost chemically dry oxygen." Moreover, why the necessity of drying the gas so completely if it must needs be re-moistened. Our own arrangement, which is very efficient, is KHO solution and successive towers of KHO sticks and well-dried granular $CaCl_2$.

Water taken up in a current of gas cannot, of course, be deposited in a hotter place; but the diagram in "Steel Works Analysis" does not indicate, nor does the accompanying text insist, that the exit end should be the hotter. In fact, if the dimensions of the diagram be adhered to, the inlet tube is actually the hotter—for the packing stops about equidistant from both ends—and in the general instructions for combustion it is expressly stipulated that the first plug (inlet end) shall be three burners within the furnace (p. 34), while the last plug is partly without the furnace (p. 36). It is right to state, though it by no means affects the instructions just noted, that the ends of our tubes were protected from direct flame radiation by a sheet of asbestos millboard, and kept cool by means of a strip of filter paper resting with its loose ends in water.

The lead protoxide deposit was most noticeable in those cases which were combusted three and four hours.

The reason in favour of their non appearance is very "simple" indeed. Surely Prof. Arnold does not rely on the three asbestos plugs: they are all purposely perforated!—I am, &c.,

R. L. Leffler.

P.S.—It may be well to state plainly what is incidentally noted in the paper, that I alone am responsible for the remark on Prof. Arnold's method and what follows.—R. L.

The Laboratory,
Messrs. Thos. Firth and Sons, Lim.,
Sheffield, May 31, 1897.

ESTIMATION OF CARBON IN FERRO-CHROME.

To the Editor of the Chemical News.

Sir,—in March, 1896, having a number of ferro-chromes to test for carbon, I met with similar difficulties to those mentioned by Brearley and Leffler (Chemical News, vol. lxxv., p. 241), which led me to make experiments to find an efficient method.

These experiments took me in much the same direction as Brearley and Leffler, but ended, as I venture to think, in a method which, while giving good results, is not so complicated as theirs; the ordinary combustion furnace is used with a porcelain tube, the heat required being only a bright red. No difficulty being experienced from spurting.

I also found that with copper oxide alone only about half the carbon is obtained, but that by mixing copper oxide with litharge the whole of the carbon was oxidised in about twenty minutes.

The litharge was freshly-prepared by fusing red-lead—possibly, as suggested by Brearley, peroxide of lead might be better, if free from substances which might be given off and absorbed by the potash.

The Method.—The ferro-chrome is ground fine in an agate mortar. 0·5 grm. is then mixed with 4·5 grms. CuO and 1·5 grms. litharge, and the mixture placed in a porcelain boat. The boat is then placed in the furnace and the combustion proceeded with in the ordinary manner. In about twenty minutes the whole of the carbon is burnt off. The following results have been obtained by this method:—

11 per cent ferro-chrome ..	5·41 per cent carbon.
20 ,, ,, ..	5·67 ,, ,,
30 ,, ,, ..	7·13 ,, ,,
50 ,, ,, ..	7·94 ,, ,,

The object of using copper oxide with the litharge is to prevent the latter attacking the porcelain, which it does very rapidly when used by itself; it also prevents any spurting.—I am, &c.,

E. H. Saniter.

Messrs. Whittaker and Co. will publish immediately a work on Organic Chemical Manipulation, on which Dr. J. T. Hewitt, of the East London Technical College, has been engaged. The first part of the text-book will give an account of the methods adopted in organic analysis, and the determinations of molecular weight; the second part being devoted to a typical set of organic preparations, systematically arranged and intended to give an idea of the methods adopted in organic work.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 18, May 3, 1897.

Researches on the Composition of Wheats, and on their Analysis.—Aimé Girard.—Already inserted.

New Property of Kathodic Rays which reveals their Complex Constitution.—H. Deslandres.—This paper requires the three accompanying illustrations.

Partial Polarisation of the Radiations Emitted by some Sources of Light under the Influence of the Magnetic Field.—P. Egoroff and N. Georgiewsky.—The rays of hydrogen and of helium in Geissler tubes have hitherto not given any definite results, The metals employed (Cu, Tl, Zn, Ca, In, Mg, La, Ba, Fe) demonstrate polarisation.

Rôle of Peroxides in the Phenomena of Slow Oxidation.—A. Bach.—The author's experiments show that the theory of Hoppe-Seyler is devoid of foundation. They also show that the oxidation product of hydrogen contains an oxidiser more energetic than H_2O_2, but showing with permanganate the same quantity of active oxygen. This oxidising agent is probably the the tetroxide H_2O_4, which is decomposed into H_2O+O_2+O, and would act upon permanganate like H_2O_2. What has been said concerning the formation and the oxidising action of the peroxides applies equally to the processes of oxidation which take place in the animal organism. The oxidising ferments which exist in the blood are probably nothing but these easily oxidisable substances eminently apt to form peroxides.

Study of the Action of Potassium Permanganate upon Cupric Bromide.—H. Baubigny and P. Rivals.—We have shown in a former paper that all the bromine of an alkaline bromide is set free if, after adding copper sulphate and permanganate to the solution we evaporate to dryness at an ordinary temperature, whilst the chlorides are not decomposed under the same conditions. They have ascribed this difference to the fact that the oxidising action of the permanganate is produced only upon the bromide. The permanganate therefore behaves with cupric bromide in a neutral liquid as it does with organic matter. In order that the total elimination of the bromine may be possible a large excess of copper must be present in a soluble state. In practice it is preferable to introduce a weight of permanganate notably in excess.

Constitution of Metallic Alloys.—Georges Charpy.—The author views alloys as either eutectic, those fusible at the minimum temperature, or definite, The existence of the latter class has been strongly contested, but the existence of the compounds Cu_3Sn and Cu_2Sb seems fully demonstrated. Among binary alloys there are two normal types of constitution. The first presents crystals of a pure body (which may be a single metal or a definite compound of two metals) inclosed in a second constituent, which is in general a eutectic mixture formed by the juxtaposition of two finely divided elements, one of which is that which forms the crystals. The second type is that of isomorphous mixtures formed of a single species of crystals occupying the entire mass. This second type is of very frequent occurrence.

Determination of Oxygen Dissolved in Sea-water.—Albert Levy and Felix Marboutin.

Compounds of Metallic Salts with Organic Bases.—D. Tombeck.—It is known that metallic salts combining with ammonium chloride, either in the presence or the absence of water, forms compounds which have been studied by several chemists, especially by Isambert. The author proposes the study of analogous bodies in which ammonia is replaced by the bases derived from ammonia.

A Compound of Silver Chloride and Monomethylamine.—R. Irry.—The author having examined the ammoniacal silver chlorides extends his researches to compounds in which monomethylamine is substituted for ammoniacal gas.

Recognition of the Yellow of Naphthol S, and of Analogous Colouring-matters in White Wines and Liqueurs.—Alberto d'Aguiar and W. da Silva.—Already inserted.

MISCELLANEOUS.

Rheostats for enabling Street Currents to be used for Medical Purposes.—The idea of making use of large and powerful currents for operations requiring but weak currents is nothing new. M. Foveau de Courmelles has recently brought out a compact and convenient instrument for this purpose which can be readily fitted to a wall plug. It is specially adapted for use with continuous currents.

Carborundum Production and Use. — The Carborundum Company reports to the *Engineering and Mining Journal* that its works have produced during the year 1896, in round numbers, 1,191,000 pounds or 595½ tons of crystalline carborundum. Consideration at the present is given to the production in crystalline form only, but another important industry into which carbide of silicon promises to be a valuable adjunct will naturally increase the usefulness of the material. Some mention has been made of the experiments showing that carborundum can be used, and will, in all probability, take the place of ferro-silicon in the manufacture of steel. Professor Luehrmann, of Germany, recently wrote an article on this subject, indicating that in the use of carborundum there will be in Germany alone, approximately, 2500 tons consumed annually, provided its cost would not exceed 6 cents per pound. It may be used for this purpose in an amorphous form, and the Carborundum Company is prepared to furnish it at a price slightly under this figure. In the *Journal of the Franklin Institute* for February, 1897, will be found an excellent descriptive paper on the carborundum plant at Niagara Falls, from the pen of Mr. Fitzgerald, chemical engineer of the works. This industry stands as a conspicuous illustration of the possibilities of the electric furnace as the source of hitherto unknown and valuable products.

MEETINGS FOR THE WEEK.

Monday, 14th.—Society of Chemical Industry, 8. "Note on a Possible Danger from Fire involved in the Transport of Barium Peroxide in Wooden Barrels," by Dr. A. Dupré, F.R.S. "The Valuation of Commercial Nitrate of Soda," by Dr. Pauli. "Recent Improvements in Smokeless Compounds and in Processes of Manufacture," by Hudson Maxim. "Comparative Experiments on the Estimation of Phosphoric Acid," by A. Cameron. "The Strength of Commercial Formaldehyd Solutions," by W. A. Davis.

Thursday, 17th.—Chemical, 8. Ballot for the Election of Fellows. "Reduction of Perthiocyanic Acid," by F. D. Chattaway, M.A., and H. P. Stevens, B.A. "Molecular Refraction of Dissolved Salts and Acids—Part II." by Dr. J. H. Gladstone, F.R.S., and W. Hibbert. "A Space Formula for Benzene," by Dr. J. Norman Collie, F.R.S. "The Production of some Nitro- and Amido-Oxypicolines," by Dr. A. Lapworth and Dr. J. Norman Collie, F.R.S. "The so-called Hydrates of Isopropyl Alcohol," by Dr. T. E. Thorpe, F.R.S. "The Carbohydrates of the Cereal Straws," by C. F. Cross, E. J. Bevan, and C. Smith. "Further Experiments on the Absorption of Moisture by Deliquescent Substances," by H. Wilson Hake.

THE CHEMICAL NEWS.

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FURTHER NOTE ON THE INFLUENCE OF A MAGNETIC FIELD ON RADIATION FREQUENCY.*

By Prof. OLIVER LODGE, F.R.S., assisted by Mr. BENJAMIN DAVIES.

Referring to a former communication of mine, on the subject of Zeeman's discovery, printed on page 513 of the *Proceedings of the Royal Society*, for Feb. 11 this year, vol. lx., No. 367, I wish to add an observation to those previously recorded, as I have recently acquired a concave Rowland grating (3½×1½ in. ruled surface, 14,438 lines to inch, 10 feet radius of curvature, being the one used by Mr. George Higgs), of which the spectra of the first and third orders on one side are very satisfactory.

It is said on page 513, "If the focussing is sharp enough to show a narrow, dark reversal line down the middle of each sodium line, that dark line completely disappears when the magnet is excited." With the greater optical power now available the dark reversal line is often by no means narrow, and, though in some positions of the flame it does still tend to disappear or become less manifest when the flame is subjected to a concentrated magnetic field, the reason of its partial disappearance is that it is partially reversed again—*i.e.*, that a third bright line, as it were, makes its appearance in the midst of the dark line, giving a triple appearance to each sodium line.

More completely stated the phenomena are as follows:—After obtaining each sodium line with a prominently double aspect by manipulating the flame, the magnet is excited, and the dark band in the midst of each sodium line is then seen to widen out considerably in the region of most intense magnetisation, while a bright intrusion line makes its appearance. On closer examination this new line is seen to be double, by reason of a dark division down its middle; and I apprehend that with still more magnetic power this dark band might itself open out into two; but this last phenomenon I have not yet observed.

The whole sodium group is thus seen as if it were octuple. The effect is not due to a mere mechanical disturbance or re-arrangement of the gases of the flame by the agency of magnetism; because a nicol, placed in the rays emanating transversely to the magnetic lines of force, cuts off nearly all the visible magnetic effect when oriented so as to get rid of light whose plane of polarisation contains the lines of force—that is, of oscillations or revolutions whose electrical components are across or around the magnetic lines. That it does not cut off every trace of the effect appears to be due to the fact that the field of force is not strictly uniform, and so its lines are not strictly parallel.

The following is a summary of the different appearances that may be seen, according to the state of the flame and the strength of the field:—

At low temperature, and with the flame forward in the field, when each sodium line is sharp and single, magnetism widens it, and with a little more power doubles it, causing a distinct dark line down its middle. The same effect occurs with lithium and thallium lines.

At higher temperature, and with the flame partially behind the field, when each sodium line appears as a broad hazy-edged double, magnetisation greatly widens the doubling, pushing asunder the bright components very markedly; stronger magnetisation reverses the middle of the widened dark band, giving a triple appearance; stronger magnetisation still reverses the middle once more, giving a quadruple appearance to the line. In every case a nicol, suitably placed, cuts off all the magnetic effect, and restores the original appearance of the line.

A curious circumstance is that although both lines, D_1 and D_2, show the effect, D_1, *i. e.*, the less refrangible line, shows it best and most sharply. I should describe the effect on D_2 as a coarse widening of considerable amount, but without very clear definition; whereas the widening of D_1, though perhaps no greater in amount, is decidedly better defined. There is no doubt but that, with my grating, D_1 is the line at which one finds oneself usually looking in order to see the details of the change best; and I can hardly suppose this to be subjective to the grating. I hope to show the effects at the *Soirée* of the Royal Society.

(The same thing is seen when salts of lithium or of thallium are introduced into the flame, and the components of the doubled red lines are more widely separated than the components of the doubled green lines, the effect being proportional to wave-length. The most interesting line to try was the red cadmium line, since this has been proved to be of specially simple constitution by Michelson. We have recently been able to get the cadmium spectrum well developed by means of a sort of spark arc between the magnet poles, maintained by an induction coil excited by an alternating machine; and we find that the magnetic doubling of the chief lines occurs in precisely the same way with the spark spectrum as with the flame spectrum, and that the red cadmium line behaves in the same way as the others. The magnetic effect is better seen, from a direction perpendicular to the line of force, when a nicol is interposed in the path of the light, but rotation of the nicol through 90° cuts it entirely off, accurately so when a small spark is the source of light.—May 31).

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* A Paper read before the Royal Society, June 3, 1897.

SANITARY PROBLEMS CONNECTED WITH MUNICIPAL WATER-SUPPLY.*

By Prof. W. P. MASON.

This subject is in some danger of being over-written to-day; but we have about us material evidence that it is not over-studied, especially by those Boards of public officials whose responsibilities are often much greater than their knowledge of sanitary principles. The public also is far from being well posted on the matter, and one encounters all sorts of odd views, which are remarkable not only for their character, but also for the tenacity with which they are held.

Ocular evidence of purity is quite sufficient for most people. The bright and limpid water from a well which drains a grave-yard is counted a blessing by those who would shudder at the thought of a cholera-ship touching at one of our most distant ports. Nor is faith in the self-purifying power of running streams any less pronounced. The author had the following curious criticism made on his report condemning the use of a sewage-laden river-water:—"We would hint to Prof. Mason that every impurity which enters the river is either heavier or lighter than water. If it be heavier, it sinks quietly to the bottom; if it be lighter, it will remain on the surface a few hours, when it will be blown ashore by the wind.

"Water taken midway between the surface and bottom of the river will always be found as pure as the best spring water."

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* Abridged from a Lecture delivered before the Franklin Institute March 19th, 1897.

So long as such notions find expression in the daily press, so long, we may be sure, are the people ignorant and misinformed upon questions very nearly touching their safety, and so long there is direct need of suitable sanitary education.

To the writer's way of thinking, a land should be looked upon as watered by its smaller lakes, its springs, and its brooks and streams, and sewered by its great—especially its navigable—rivers. Its water sources should be protected by law with exceeding care, and no stream or river should be added to its list of drains, except after proper consideration by the State Board of Health, followed by legislative permission.

Cases such as the typhoid fever outbreak at Plymouth, Pa., impress upon us the necessity of caring for our watersheds and the ultimate ramifications of the tributaries to our sources of supply.

Many readers are probably familiar with the excellent experiments carried on at Lawrence by the Massachusetts State Board of Health, which go to show that, by carefully conducted intermittent filtration through beds of sand or gravel stones, city sewage may be converted into what may practically be called potable water. Let these two very important points be always kept in mind however:—First, the filtration must be intermittent, for if it be continuous the atmospheric oxygen necessary to the activity of the purifying organisms of nitrification becomes excluded, and purification ceases. Secondly, the "dose" of applied sewage must not be larger than that quantity which experiment has shown to be capable of disposal by the filter.

The general trend of our information goes to establish the fact that proper care of the water-shed is as necessary as it is unusual, and I firmly believe that such care should be carried even to the extent of protecting the ground-water for a reasonable distance before it enters the draining brooks of the district.

After a suitable and well-protected gathering ground has been secured, and after the water has been started on its way to the consumer, other opportunities for pollution not infrequently arise. Open channel-ways, as a means of conveying water to a town, are quite commonly seen, and care is not always taken that pollution shall not reach the water during its flow therein. We find a very noteworthy case of contamination, under just such circumstances, recorded in the history of the cholera epidemic at Messina, Sicily, in 1887. The plague lasted from the 10th of September to the 25th of October, during which time there were some 5000 cases and 2200 deaths. The Government felt that a very possible cause for the rapid spread of the scourge lay in a contaminated drinking water, and enquiry fully confirmed this suspicion. The water as it left the gathering grounds was of excellent quality, but, for the benefit of the Messina washerwomen, a portion of the water was deflected before reaching the wells, and turned into neighbouring washing-pools of stone. A fair proportion of this deflected water, after having been used for laundry purposes, found its way back into the open channel, and continued its course to the city. Further contamination occurred within the town itself; the water-mains and sewers were of unglazed tiles, very leaky, and the sewers were at times found on the top of, and parallel with, the water-mains themselves. The Government sent tank ships filled with pure "Serino" water, supplied the people therewith, and the daily number of cases immediately fell from seventy to five.

Keeping our attention upon typhoid fever, it will be remembered that two conceptions of its origin are entertained by opposing schools of bacteriologists. On the one hand, it is held that the typhoid germ is always the offspring of a bacillus of its own kind; while, on the other side, there are those who believe—and it is a very conceivable belief—that the progenitor in question is often a saprophyte which takes on its pathogenic properties by cultivation through successive generations under favourable conditions.

Many illlustrations are available, in the world of larger vegetation, of greater changes in structure due to cultivation under an altered environment.

Roux and Rodet are perhaps the leaders among those who claim a saprophytic ancestry for the typhoid germ, but they are not without a strong following in this country.

Whatever may be the final decision of the specialists upon this knotty point, it is our manifest duty to adopt for the present the saprophyte theory as our working formula, and to protect water-supplies from the infiltration of animal waste material.

Directly connected with the conveying of water in open channels comes the question of the self-purification of water under such circumstances. Agitation and aëration do certainly aid in preventing abundant growth of Algæ, and an undoubted improvement in the quality of water results from the establishment of a fountain in a too quiet reservoir; but the expectations of those who hope to thus easily eliminate pollution of a serious character will not be realised.

Sedimentation plays a part in the general purification during open flow, but it is commonly a small one, particularly small in such streams as stand in special favour with the public, because of the riffles and other interruptions in their courses.

Sedimentation, when we consider the question of drawing our supply from a lake, particularly a large one, becomes of prime importance, and, as the element of time enters largely into the consideration of these cases, material changes for the better are often noticeable in lake waters; thus the tributary of a lake may be undesirable for domestic use, while its outlet may be entirely satisfactory.

Referring to the suggestion recently published by one of our sanitary engineers, to the effect that the cleaning of storage reservoirs is all a mistake, and that it would be far better practice to leave the vegetable *débris* where Nature placed it, it must be replied that comparative experiments upon such reservoirs have shown that improved water unquestionably follows cleaning. No stripping of the soil from the bottom of the Vyrnwy reservoir, which supplies Liverpool, was done, but the water is filtered before delivery for consumption.

Filtration is so common in Europe that the same care in storage is not so necessary as in the United States, where the practice is to supply the raw water direct to the consumer.

Waters from underground sources should be distributed for use as soon as possible after they have been brought to the surface, for they are commonly well supplied with plant-food in solution, and, under the influence of light and air, there is danger of abundant development of objectionable Algæ if much time for open storage be allowed. With surface-waters the case is quite the reverse, and long storage becomes a distinct advantage, if the reservoir be clean. Bacteria often die but slowly, and, although a large percentage of their number will disappear through storage, it should not be forgotten that they are very small and very light, and consequently are very long in settling, so that it should not be expected that a reservoir could do the efficient work accomplished by a filter.

From whatever source the water may be derived, it is the common American practice to deliver it "raw" to the consumer, even when its appearance is distinctly unsightly. Such, however, is not the European custom. Public sentiment abroad demands that surface-waters should receive efficient purification before they are distributed for domestic use. As a result, filters are established, or arrangements are contemplated for their erection, to filter waters, of a degree of natural purity, equal to the best supplies America can show. We on this side of the Atlantic would consider the expenditure of money for the purpose of purifying such waters as we find at Liverpool and Zurich quite unnecessary and superfluous; Europeans think differently, however, and their notions are best expressed by Voltaire's apothegm "Le superflu, chose très nécessaire."

It is very amusing to note the care with which Americans—perhaps from Albany, Pittsburg, or Chicago—scrutinise the water offered them in foreign capitals, when what they are in the habit of drinking at home would not be tolerated for an instant in the great cities of Europe.

The day is past when we could feel a sense of superiority over the crowded millions of the old world, because of the relative magnitude and consequent initial purity of the sources of our water-supplies. Europe has, of late years, expended much labour and capital in substantial plants, that make for sanitary betterments, while we have continued upon a conservative course, forgetful that our populations and industries have been growing, and that the rivers our fathers drank from with pleasure and safety have become charged with the refuse of up-stream communities, and converted into what may be properly styled the county sewers.

There is no system of filtration so expensive but that a community can well afford to introduce it rather than to drink a dangerous water in its raw state, and this, too, from purely economic considerations, and leaving out of sight all ethical questions whatsoever.

THE VISCOSITY OF MERCURY VAPOUR.*

By A. A. NOYES, Ph.D., and H. M. GOODWIN, Ph.D.

The uncertaintity which attaches to the specific heat ratio of gases as a means of distinguishing between monatomic and polyatomic molecules has been recently made evident by the extended discussions of the significance of that property in connection with the atomic weights of argon and helium. It is therefore of great interest to investigate other properties which may be expected to be related to the atomicity of the molecule. The authors have therefore undertaken the investigation of one of these, viz., the viscosity, or internal friction, in order to determine if any marked difference in its value exists in the case of gases with monatomic and those with polyatomic molecules. To this end they have made comparative measurements of the viscosity of hydrogen, carbon dioxide, and mercury vapour, at the boiling temperature of the latter. The authors thought that monatomic molecules might prove to be much smaller than polyatomic ones, since it seems *a priori* not improbable that the spaces between the atoms of the latter are large in comparison with the atoms themselves. The experiments described show, however, that no marked distinction exists between monatomic and polyatomic gases in this respect.

The method used by them in determining the relative viscosity consisted in measuring the quantities of the different gases which, under a constant difference of pressure, passed in a given time through the same capillary kept at a definite constant temperature. The apparatus and experimental method employed were, for given reasons, quite different from the usual ones, and are briefly described. The capillary used in the most complete series of experiments consisted of a glass tube 74 c.m. long and 0·34 m.m. internal diameter (a smaller capillary, 49 c.m. long and 0·22 m.m. in diameter, was used in a preliminary series); it was compactly bent up on itself so as to form five vertical segments with, of course, four elbows, the beginning and the end of the capillary part of the tube being at the same level. To these ends were fused pieces of ordinary glass tube, one of which was bent horizontal, and provided at the point with a ground joint; to the other was fixed a vertical T-piece. This was all placed in a heavy steel cylinder, 30 c.m. high and 2·8 c.m. internal diameter, having a small orifice at the side through which the ground joint protruded for about 1 c.m., the whole being held in position by loosely-packed asbestos. Although the capillary was vertical, the influence of gravity was eliminated by reason of the fact that the ascending and descending parts were of equal length. The top of the cylinder was closed by an iron plate screwed down by a nut, both plate and nut were perforated through the centre, and into the latter was welded an iron tube, projecting vertically, 25 c.m. in length and 2·5 c.m. diameter. The cylinder was covered, except on the bottom, with a jacket of asbestos about 5 c.m. thick, and spirals of copper wire were wound round the vertical tube, which was to serve as a condenser, in order to increase the cooling surface. Pure mercury was placed in the cylinder and boiled vigorously by means of a flame underneath. The capillary was thus kept at the temperature of the boiling mercury at atmospheric pressure. No regard was paid to the variations of temperature arising from changes in barometric pressure, as their effect would evidently be entirely negligible.

Any desired difference of pressure at the two ends of the capillary was obtained by inserting a tube in the ground joint and connecting it with a large air reservoir, which was in turn connected with a suction-pump and furnished with an open mercury manometer. The gas, or vapour entered at the other end of the capillary, always under atmospheric pressure.

In making the experiments the rate of flow of the mercury vapour was first determined in the following manner:—While the cylinder was being heated carbon dioxide was forced through the capillary to prevent the condensation in it of liquid mercury and the formation of its oxide. After the mercury was boiling actively and its vapour entirely enveloped the capillary, shown by a thermometer inserted into the vertical iron tube, it was connected with the suction pump and mercury vapour drawn through for half an hour. The carefully ground end of a weighed bulb was then inserted in the ground joint, and its other end connected by means of a clamped rubber tube with the air reservoir, in which the desired reduction of pressure had been produced. At a definite moment the clamp was opened and the time noted. The mercury vapour was found to be completely condensed in the weighed tube, about 2 or 3 c.m. from the ground joint. There was a slight and unavoidable leakage* through the ground joint, and it was therefore necessary to re-adjust the pressure occasionally. It could easily be kept constant to 0·2 or 0·3 m.m. Usually after sixty minutes the clamp was closed, and at a noted instant the bulb was removed and subsequently weighed. The capillary was removed from the cylinder and the lower end of the T-piece closed by fusion. A glass tube, long enough to project above the end of the iron tube, was then fused to the upper part of the T-piece, and the capillary was then ready for the experiments with carbon dioxide and hydrogen. It was replaced in the cylinder as before, and the projecting vertical glass tube connected through suitable wash-bottles with the gas generator.

In order to maintain the gas entering the capillary at atmospheric pressure, a T-tube was inserted between the wash-bottles and the capillary, and its perpendicular arm was turned downwards and caused to dip into sulphuric acid, barely below its surface. The cock of the generator was opened sufficiently to cause the gas to bubble out steadily through the sulphuric acid.

The transpiration measurements were made as in the case of the mercury. The carbon dioxide flowing through in a definite time, was determined by absorption in weighed tubes filled with lumps of soda-lime. The hydrogen was burnt by passing it over hot copper oxide contained in combustion-tubes from which the air was previously displaced by carbon dioxide, and the water collected in weighed calcium chloride tubes.

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* Abridged from the *Technology Quarterly*, vol. x., No. 1, 1897.

* In the case of the mercury experiments no error could arise from this source, as the leakage was inward. In the case of those of carbon dioxide and hydrogen it was proved by blank experiments that the amounts of carbon dioxide and water which leaked in were less than 1 per cent of the total weight.

The results are given in the following tables. The first column gives the symbol of the substance; the second, the atmospheric pressure, p_1; the third, the difference in pressure (p_1-p_2); the fourth, the time, t, expressed in hours; the fifth, the weight, w, in grms. of the substance weighed; the sixth, the mean weight transpired in one hour as computed from the separate check experiments; and the last, the quotient obtained by dividing this weight by the molecular weight, m, of the substance, the time, and the pressure function $(p_1^2-p_2^2)$.*

Series I.—*Small Capillary.*

	p_1.	p_1-p_2.	t.	w.	$w:t$.	$\frac{w \times 10^{10}}{t\,m(p_1^2-p_2^2)}$
Hg..	753	200	1½	0·738	—	—
	753	—	1½	0·740	—	—
	756	—	1½	0·745	0·494	93·6
	755	300	1	0·685	—	—
	755	—	1	0·686	0·686	93·6
	754	400	1	0·834	—	—
	754	—	1	0·831	0·833	92·9
CO_2.	752	200	1	0·237	—	—
	752	—	1	0·239	—	—
	752	—	1½	0·357	0·238	205
	759	300	1	0·329	—	—
	759	—	1	0·327	—	—
	766	—	1	0·324	0·327	203
	766	400	1	0·400	—	—
	766	—	1	0·396	—	—
	759	—	1	0·396	0·397	202

Series II.—*Large Capillary.*

	p_1.	p_1-p_2.	t.	w.	$w:t$.	$\frac{w \times 10^{10}}{t\,m(p_1^2-p_2^2)}$
Hg..	769	150	1	1·548	—	—
	769	—	1	1·548	1·548	374
	769	300	1	2·763	—	—
	769	—	1	2·764	—	—
	769	—	1	2·739	2·755	373
CO_2.	756	150	1	0·704	—	—
	765	—	1	0·706	0·705	774
	765	300	1	1·267	—	—
	765	—	1	1·264	1·265	779
H_2..	766	150	1	0·557	—	—
	766	—	1	0·557	0·557	1517
	766	300	1	1·009	—	—
	766	—	1	1·006	1·008	1496
Hg..	766	300	1	2·728	—	—
	766	—	1	2·746	—	—
	764	—	1	2·743	2·739	371

The agreement of the values of the last column in the cases of the same substances under different pressures show that the capillaries are of sufficient length and small enough bore to give the true values of the viscosity coefficients.

The relative viscosity coefficients of the different gases were calculated from the values of the last column in the tables, and gave the following results:—

$$\frac{\eta\,Hg}{\eta\,CO_2} = 2{\cdot}17 \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ \text{(First series).}$$

$$\frac{\eta\,Hg}{\eta\,CO_2} = 2{\cdot}08 \cdot \frac{\eta\,Hg}{\eta\,H_2} = 4{\cdot}04 \cdot \frac{\eta\,CO_2}{\eta\,H_2} = 1{\cdot}94 \ \text{(Second series).}$$

The relative values for mercury and carbon dioxide agree within about 4 per cent.

The corresponding values of the mean cross-sections as calculated are—

$$\frac{q\,Hg}{q\,CO_2} = 1{\cdot}02 \ . \ \frac{q\,Hg}{q\,H_2} = 2{\cdot}48\,;$$

that is to say, the average cross-section of the mercury molecule or atom is very nearly the same as that of the carbon dioxide molecule, and is about two and a half times as large as that of the hydrogen molecule.

These results indicate that *atoms and molecules are of the same order of magnitude*, and that the spaces between the atoms within the molecule, if any exist, are not large in comparison with those occupied by the atoms themselves; and, consequently, the viscosity of gases, or any other property which, like it, is dependent only on the size or form of the molecules, is not adapted for distinguishing between monatomic and polyatomic molecules.

The mercury and carbon dioxide molecules have, as we have seen, the same cross-section, and therefore, assuming both to be of the same general form, they occupy the same volume. The mass of the former is, however, 4·55 times as great as that of the latter. The density of the mercury molecule is consequently greater in this same proportion. But this difference is not marked enough to make it necessary to attribute it to free spaces within the carbon dioxide molecule.

ON THE PURIFICATION OF CERIUM.

By MM. WYROUBOFF and A. VERNEUIL.

IN spite of the large number of researches on cerium and its compounds there still exists much uncertainty with regard to its most characteristic chemical properties.

These uncertainties come from two causes—the absence of any method enabling us to easily obtain cerium quite free from its accompanying earths, and the inadequacy of the methods used for determining its atomic weight. These two voids keep us in a circle of errors, from which we have no escape, for we recognise the purity of a body by its atomic weight, and we are fixing the atomic weight in a product we cannot recognise as pure.

Among the numerous methods for the separation of cerium, there are only two that are held in general favour —the treatment by chlorine in the presence of alkalies employed by Mosander, and fusion with nitre proposed by Debray. Both have the same fault; they are not based on any precise reaction, and exist under the most disadvantageous conditions with regard to the separation in view.

Cerium is distinguished from all similar metals by a very characteristic property,—the existence of a very stable higher oxide, capable of easily forming basic salts which are generally insoluble. It is therefore very natural to take advantage of this property to isolate the metals of its group, or of neighbouring groups. This is, in fact, what has been attempted by Mosander and Debray; but they were not aware of the existence, between the lower oxide, CeO,* and the higher oxide, Ce_3O_4, of an intermediate oxide, $Ce_6O_7 = Ce_3O_4,3CeO$, very stable, and also giving insoluble basic salts, depending in most cases on the oxidation of the CeO and the reduction of the Ce_3O_4. This oxide becomes even more stable when the cerium is in the presence of lanthanum and didymium, both more basic than itself, for it then invariably forms a complex oxide, $Ce_3O_4,3MO$, in which $M = Ce + La + Di$ in proportions varying according to circumstances. Now, in Mosander's method, even the prolonged action of chlorine

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* In the calculation of this quantity, the same mean value of p_1 was used in all the experiments of each series, namely, 760 for those with the smaller capillary, 765 for those with the larger.

* We consider cerium as being *bivalent* in its lower oxide, and we shall give, before long, the reasons which have forced us to adopt this old opinion of Berzelius.

will hardly bring about the formation of this intermediate oxide; and in Debray's process, the very first thing caused by the action of heat is precisely its production. It is for this reason that, in order to produce a body, even the purity of which is never certain, it is necessary to repeat the operation many times.

The existence of the intermediate oxide once admitted, the problem of the separation of cerium is much simplified, for it is reduced to the two following points:—we can either prevent the formation of this oxide, or else find out under what conditions it will separate into its two component parts, Ce_3O_4, forming insoluble basic salts, and $CeO+LaO+DiO$, giving neutral soluble salts. It is this latter, and far simpler, solution of the difficulty that we have endeavoured to find.

The oxides resulting from the moderate calcination of the oxalates are dissolved in warm nitric acid. There results a partial reduction, a disengagement of oxygen, and the formation of the intermediate oxide. The solution is evaporated to the consistency of a syrup, to drive off the excess of acid. The mass is then easily dissolved in water, forming a limpid yellowish solution, which should be diluted to about 4 per cent of oxide. If to this warm solution we add 5 per cent of nitrate of ammonia the intermediate oxide is completely dissociated; the whole of the oxide Ce_3O_4 is precipitated as a basic salt, $(Ce_3O_4)4N_2O_5$, and the protoxides remain in solution, which takes the violet tint of didymium salts. The precipitate deposited is washed with 5 per cent nitrate of ammonia; it contains cerium as free from didymium and lanthanum as from the yttria earths. These earths cannot be associated with cerium except when the latter is in the state of the oxide $Ce_3O_4,3CeO$, and the nitrate of ammonia—by making the salt of Ce_3O_4 insoluble—renders the existence of this oxide impossible. It is true that by this method we only get about 75 per cent of the cerium present, but there is nothing to prevent us from repeating the operation by precipitating the filtrate by oxalic acid, calcining the oxalates, and re-dissolving in nitric acid.

In cases when the mixture of oxides contains more than 50 per cent of cerium, it is no longer integrally soluble in nitric acid. It is then necessary to dissolve the oxalates in nitric acid, and add peroxide of hydrogen and ammonia. This is boiled, to transform the brown peroxide formed into yellow ceroso-ceric hydroxide; this hydroxide, after washing, is dissolved in nitric acid, and the operation continued as we have just described. The cerium thus obtained is not yet, however, pure; it contains all the thorina which was present in the mixture of the oxides.

We would further remark, however, that the thorina exists only in the 75 per cent of cerium of the first operation. If therefore we wish to obtain, without further purification, cerium completely free from thorina, it suffices to repeat the operation on the oxides remaining in solution after the first precipitation. In any case it is easy to get rid of the thorina, by treating the oxalates, or better still the nitrates, made as near as possible neutral, by a concentrated solution of carbonate of ammonia, to which is added a little caustic ammonia. The thorina is easily dissolved, at the same time as a small portion of the other earths; after two exhaustions there is not more than 1 per cent of thorina left. To remove this last trace we crystallise the sulphate at 60° in a liquor entirely free from free sulphuric acid; the thorina accumulates in the mother-liquor, forming with cerium a very soluble double sulphate.

There remains now nothing but to rid the cerium of iron, which it retains with great persistence. To do this it is necessary to precipitate it several times from its chloride and nitrate solutions, by means of oxalic acid, in hot and acid solution; we can also eliminate the sulphate by dehydration at a high temperature—400° to 450°; the iron then remains in an insoluble state.

Cerium thus purified is always identical in composition, and its atomic weight does not vary, as we shall show in a future note. Its oxide, calcined at a high temperature, is absolutely white when cold. All yellow, chamois, or rose tints indicate the presence of impurities, which can always be eliminated by known methods (*Laboratoire de Chimie du Museum d'Histoire Naturelle*).

M. **Moissan** added the following remarks *à propos* of the communication of MM. Wyrouboff and Verneuil "On the Preparation of Oxide of Cerium."

The important researches of MM. Wyrouboff and Verneuil induce me to mention the process I adopted to obtain the perfectly white oxide of cerium, which I used in the preparation of carbide of cerium.

I started with an oxide of cerium no longer giving an absorption spectrum in a concentrated solution. I transformed it into carbide in the electric furnace. By dissolving this in cold water, either pure or slightly acidulated, I obtained a complex mixture of carbides of hydrogen, the composition of which would not remain constant during the whole length of the reaction.

Three hundred grms. of this carbide, finely powdered, was then treated with a solution of nitric acid, kept very dilute in order to limit the action. The carbide remaining was taken up in a fresh quantity of weak acid, but the solution was not allowed to be complete. The solution obtained by this second treatment furnished, by simple calcination, absolutely white oxide of cerium.

The iron was found in the first liquid, and the thorina in the residue of unattacked carbide.

This method of preparation gave me a white oxide of cerium, while that from the first solution was of a rose-colour, and that from the residue of a yellowish green tint.—*Comptes Rendus*, vol. cxxiv., No. 22, p. 1230.

FOURTH ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS.
RESULTS PUBLISHED IN 1896.*

By F. W. CLARKE.

(Concluded from p. 283).

Nitrogen.—Among the ratios measured by Penny and by Stas relative to the atomic weights of nitrogen, those connecting the chlorides and nitrates of potassium and sodium were highly important. These are now redetermined by Hibbs (Doctoral Dissertation, University of Pennsylvania, 1896, by J. G. Hibbs, *Journ. Am. Chem. Soc.*, xviii., 1044) in a different way. The nitrates were heated in gaseous hydrochloric acid, and so converted easily into chlorides, with considerable accuracy. The data are as follows with vacuum weights, and reduced with $O=16$, $K=39{\cdot}11$, $Na=23{\cdot}05$, and $Cl=35{\cdot}45$.

Weight KNO_3.	Weight KCl.	Atomic wt. N.
0·11090	0·08177	14·011
0·14871	0·10965	14·010
0·21067	0·15523	14·013
0·23360	0·17223	14·011
0·24284	0·17903	14·014
	Mean ..	14·0118

Weight $NaNO_3$.	Weight NaCl.	Atomic wt. N.
0·01550	0·01066	14·011
0·20976	0·14426	14·011
0·26229	0·18038	14·014
0·66645	0·45829	14·014
0·93718	0·64456	14·008
	Mean ..	14·0116

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* *Journal of the American Chemical Society*, xix., No. 5.

These results seem to be exceedingly good, and the process has the advantage of great simplicity. The work was done under the direction of Prof. E. F. Smith.

Arsenic.—In the dissertation already cited Hibbs gives some determinations of the atomic weight of arsenic. Sodium pyroarsenate was heated in gaseous hydrochloric acid and so converted into chloride. The latter was perfectly white, unfused, and showed no trace of arsenic. I subjoin the vacuum weights, and the values found for arsenic when O = 16, Na = 23·05, and Cl = 35·45.

Weight $Na_4As_2O_7$.	Weight NaCl.	Atomic wt. As.
0·02177	0·01439	74·904
0·04713	0·03115	74·921
0·05795	0·03830	74·927
0·40801	0·26981	74·901
0·50466	0·33345	74·916
0·77538	0·51249	74·917
0·82897	0·54791	74·917
1·19124	0·78731	74·926
1·67545	1·10732	74·928
3·22637	2·13267	74·901
	Mean ..	74·9158

Magnesium.—Atomic weight determined by Richards and Parker (*Zeit. Anorg. Chem.*, xiii., 81), who studied the carefully purified chloride. First, a gravimetric series, with all weights reduced to a vacuum.

Weight $MgCl_2$.	Weight AgCl.	Atomic wt. Mg.
1·33550	4·01952	24·368
1·51601	4·56369	24·350
1·32413	3·98528	24·369
1·40664	4·23297	24·386
1·25487	3·77670	24·373
	Mean	24·369

The remaining series of experiments are of the usual volumetric character.

Second Series.

Weight $MgCl_2$.	Weight Ag.	Atomic wt. Mg.
2·78284	6·30284	24·395
2·29360	5·19560	24·379
2·36579	5·35989	24·366
	Mean	24·380

To this series the authors attach less importance than to the others.

Third Series.

Weight $MgCl_2$.	Weight Ag.	Atomic wt. Mg.
1·99276	4·51554	24·349
1·78870	4·05256	24·363
2·12832	4·82174	24·268
2·51483	5·69714	24·372
2·40672	5·45294	24·369
1·95005	4·41747	24·377
	Mean	24·365

Fourth Series.

Weight $MgCl_2$.	Weight Ag.	Atomic wt. Mg.
2·03402	4·60855	24·360
1·91048	4·32841	24·364
2·09932	4·75635	24·362
1·82041	4·12447	24·362
1·92065	4·35151	24·363
1·11172	2·51876	24·363
	Mean	24·362

These values are computed with O = 16.

When O = 15·88, Mg = 24·179. The last series outweighs all the others.

Cadmium.—Hardin's determinations of the atomic weight of cadmium resemble those which he made upon silver. First, the chloride, in solution with potassium cyanide, was electrolysed in a platinum dish. The weights in this and the other series are all reduced to a vacuum. Computations made with Cl = 35·45 and O = 16. Data as follows:—

Weight $CdCl_2$.	Weight Cd.	Atomic wt. Cd.
0·43140	0·26422	112·054
0·49165	0·30112	112·052
0·71752	0·43942	112·028
0·72188	0·44208	112·021
0·77264	0·47319	112·036
0·81224	0·49742	112·023
0·90022	0·55135	112·041
1·02072	0·62505	112·002
1·26322	0·77365	112·041
1·52344	0·93315	112·078
	Mean	112·038

Secondly, the bromide was treated in the same way. The data were reduced with Br = 79·95.

Weight $CdBr_2$.	Weight Br.	Atomic wt. Cd.
0·57745	0·23790	112·031
0·76412	0·31484	112·052
0·91835	0·37842	112·067
1·01460	0·41808	112·068
1·15074	0·47414	112·053
1·24751	0·51392	112·019
1·25951	0·51905	112·087
1·51805	0·62556	112·076
1·63543	0·67378	112·034
2·15342	0·88722	112·041
	Mean	112·053

In a third series of experiments cadmium was thrown down simultaneously with silver in the same electric current. Weights and results as follows, with Ag = 107·92.

Weight Ag.	Weight Cd.	Atomic wt. Cd.
0·24335	0·12624	111·928
0·21262	0·11052	111·991
0·24515	0·12720	111·952
0·24331	0·12616	111·916
0·42520	0·22058	111·971
	Mean	111·952

Mean of all the twenty-five experiments, Cd = 112·027.

Mercury.—Atomic weight also determined electrolytically by Hardin, in the same paper with his work upon silver and cadmium. With the oxide he obtained unsatisfactory results; but with the chloride, bromide, and cyanide he did better. With the chloride, when Cl = 35·45, his data, with vacuum weights, are as follows:—

Weight $HgCl_2$.	Weight Hg.	Atomic wt. Hg.
0·45932	0·33912	200·030
0·54735	0·40415	200·099
0·56002	0·41348	200·053
0·63586	0·46941	199·947
0·64365	0·47521	200·026
0·73281	0·54101	199·988
0·86467	0·63840	200·038
1·06776	0·78825	199·946
1·07945	0·79685	199·912
1·51402	1·11780	200·028
	Mean	200·006

With the bromide, when Br = 79·95, Hardin found these weights and values:—

Weight HBr_2.	Weight H_5.	Atomic wt. H_5.
0·70002	0·38892	199·898
0·56430	0·31350	199·876
0·57142	0·31750	199·938
0·77285	0·42932	199·832
0·80930	0·44955	199·814
0·85342	0·47416	190·911
1·11076	0·61708	199·869
1·17270	0·65145	199·840
1·26186	0·70107	199·899
1·40142	0·77870	109·952
	Mean	199·883

With the cyanide, when C = 12·01 and N = 14·04, Hardin found—

Weight HgC_2N_2.	Weight Hg.	Atomic wt. Hg.
0·55776	0·44252	200·063
0·63290	0·50215	200·092
0·70652	0·56053	200·038
0·80241	0·63663	200·075
0·65706	0·52130	200·057
0·81678	0·64805	200·103
1·07628	0·85392	200·077
1·22615	0·97282	200·071
1·66225	1·31880	200·057
2·11170	0·67541	200·077
	Mean	200·071

Finally, Hardin made use of Faraday's law, throwing down mercury and silver simultaneously in the same electric current. The equivalent weights are as follows, reduced with Ag = 107·92 :—

Weight Hg.	Weight Ag.	Atomic wt. Ag.
0·06126	0·06610	200·036
0·06190	0·06680	200·007
0·07814	0·08432	200·021
0·10361	0·11181	200·011
0·15201	0·16402	200·061
0·26806	0·28940	199·924
0·82808	0·89388	199·929
	Mean	199·996

The general mean of all four series is—

Hg = 199·989.

Tellurium.—In all determinations hitherto made of the atomic weight of tellurium, the material has been derived from metallic tellurides. Chikashige (*Journ. Chem. Soc.*, lxix., 881) now gives a series of experiments upon tellurium obtained from Japanese native sulphur, using Brauner's method. The tetrabromide was titrated with solutions of silver, and the following data were obtained. Computations were made upon the basis of O = 16.

Weight $TeBr_4$.	Weight Ag.	Atomic wt. Te.
4·1812	4·0348	127·57
4·3059	4·1547	127·61
4·5929	4·4314	127·58
	Mean	127·587

Tungsten.—Schneider (*Journ. Prakt. Chem.*, [2], liii., 288) objects to the determinations published by Pennington and Smith, regarding them as too high. He attributes their highness to the fact that very small quantities of material were handled, and thinks that there may have been mechanical losses of small particles during the long heating of the substance weighed. He now gives new determinations of his own, with tungstic oxide carefully freed from molybdenum, and made partly by reduction of the oxide, partly by oxidation of the metal. Results as follows, with the percentage of tungsten in tungsten trioxide stated in a third column :—

						W in WO_3. Per cent.
2·0728	grms.	WO_3	gave	1·6450	W	79·323
4·0853	,,	,,	,,	3·2400	,,	79·309
6·1547	,,	,,	,,	4·8811	,,	79·307
1·5253	,,	W	,,	1·9232	WO_3	79·311
3·1938	,,	,,	,,	4·0273	,,	79·304
3·7468	,,	,,	,,	5·9848	,,	79·314
					Mean	79·311

Hence with O = 16, W = 184·007.

On the other hand, Shinn (Doctoral Thesis, University of Pennsylvania, 1896), working in Smith's laboratory, obtains some data corroborative of Pennington and Smith. In this series tungsten was oxidised to tungsten trioxide. Results as follows, computed with O = 16 :—

						Atomic weight.
0·22297	grm.	W	gave	0·28090	grm. WO_3	184·720
0·17200	,,		,,	0·21664	,,	184·964
0·10989	,,		,,	0·13844	,,	184·753
0·10005	,,		,,	0·12598	,,	185·206
					Mean	184·910

The cause of the difference between the values found and those of Schneider is yet to be made out.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 3rd, 1897.

Professor Dewar, F.R.S., President, in the Chair.

Messrs. Thomas Tickle and Thomas Girtin were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Ball, Ph.D., 18, Redshaw Street, Derby; Alec Alfred Beadle, Beadonwell, Belvedere, Kent; James Walter Horseman, 5, South Parade, Chelsea, S.W.; Charles John Jodrell Mansford, B.A., Lady Manners Grammar School, Bakewell, Notts.; Thomas Southern, jun., 2, Cherry Mount, The Cliff, Higher Broughton, Manchester; Francis Samuel Young, M.A., Mill Hill School, N.W.

Of the following papers those marked * were read :—

*67. "*On the Thermal Phenomena attending the Change of Rotatory Power of Freshly-prepared Solutions of certain Carbohydrates; with some Remarks on the Cause of Multirotation.*" By Horace T. Brown, F.R.S., and Spencer Pickering, F.R.S.

During an investigation of the thermal changes attending hydrolysis under enzyme action, whose results are described in the next paper, it became necessary to enquire whether the change in the multi-rotation of certain sugars is attended with any heat disturbance, as it is now well-known that, at any rate, dextrose and maltose are liberated by hydrolysis in the "birotatory" state. The authors find that the changes of rotation experienced by dextrose, lævulose, and milk-sugar in passing from the optically unstable α- to the optically stable β-form, are accompanied by distinct thermal effects which, although taking place slowly in the solutions under ordinary conditions, can be produced, like optical stability, almost instantaneously by the addition of traces of an alkali. A full account is given of the apparatus employed, of the method of experiment, and the nature of the corrections to be applied. In the cases of dextrose and milk-sugar, there is a liberation of heat accompanying the change of rotatory power; with lævulose there is a very decided absorption; and with maltose no thermal disturbance is recognisable. The following are the values obtained :—

	Per grm. of sugar.	Per grm.-molecule.
Dextrose	+0·588 cal.	+106 cal.
Lævulose	−4·64 cal.	−835 cal.
Milk-sugar	+0·19 cal.	+ 34 cal.
Maltose	0	0

The authors discuss the various explanations which have been given from time to time to account for multirotation, and consider that their experiments favour the view that it is conditioned by chemical rather than physical causes, and that Fischer is probably correct in his suggestion that dextrose, for instance, in passing from the optically unstable to the optically stable modification in solution, passes from the aldehyd, $C_6H_{12}O_6$, to the heptahydric alcohol, $C_6H_{14}O_7$. They believe, however, that the analogy which Fischer suggested, of the change of a lactone into its acid, is less close than that afforded by the gradual change of acetic aldehyd, in contact with water, into ethylidene glycol where the CHO group becomes $CH(HO)_2$.

*68. "*On the Thermo-chemistry of Carbohydrate Hydrolysis.* (I.) *The Hydrolysis of Starch by Vegetable and Animal Diastase.* (II.) *The Hydrolysis of Cane-sugar by Invertase.*" By Horace T. Brown, F.R.S., and Spencer Pickering, F.R.S.

The attempts made to determine the thermal effects of hydrolysis have hitherto been confined to indirect methods, based on the heats of combustion of the hydrolysable substance and its products. Such methods, it is shown, cannot give results of any real value, as the thermal changes to be measured are considerably within the experimental errors of the combustion values.

The paper describes the results obtained by direct measurement of the heats of hydrolysis of starch and of cane-sugar. Lintner's soluble starch was for the most part used, as there are certain mechanical difficulties in employing starch paste in the calorimeter, owing to its viscidity. The hydrolytic agents used for starch were (1) malt-diastase, (2) pancreatic diastase, (3) Taka-diastase, and (4) saliva. With malt-diastase, the heat of hydrolysis was found to be +2·60 calories per grm. of amylin converted into maltose. The amount of heat is proportional to the water fixed, and is independent of the molecular complexity of the amylin attacked. The breaking down of the starch molecule prior to hydrolysis does not appear to be attended with any thermal disturbance.

With pancreatic diastase, the heat liberated per grm. of amylin hydrolysed amounts to +1·8 cal., a value sensibly less than that deduced from the action of the malt diastase. With Taka-diastase, the heat disturbance is still less than with the other two agents. The possible causes of these differences are discussed.

Cane-sugar was hydrolysed with invertase, and was found to give a thermal effect of +11·21 cal. per grm. of cane-sugar inverted when the products were in the optically stable β-form, and 13·34 cal. per grm. at the moment of liberation of the products, *i.e.*, when they are in their "birotatory" or optically unstable form. It is the larger number which correctly represents the heat of hydrolysis of cane-sugar.

Discussion.

Mr. Pickering made a statement as to some additional work which had been done in connection with the subject since the paper had been sent in to the Society. The nature of the change produced by water on the sugars has been suggested to be the conversion of the aldehyd groups present into aldehydrol groups, an action which there is every reason to believe occurs in the case of acetic aldehyd itself, and experiments were, therefore, made to ascertain whether the action in the case of aldehyd exhibits the same peculiarity as in the case of the sugars, of being greatly accelerated by the addition of alkali. This was found to be the case, and the analogy of the two actions is, therefore, greatly strengthened. In both cases, also, the ammonia combines directly with the substance—the sugar or the aldehyd—with evolution of heat, but the results with aldehyd show that the formation of these compounds is not the cause of the hydrating effect of the alkali, for, although the alkali renders the hydration instantaneous, the formation of the aldehyd ammonia proceeds gradually, and with the quantities used is complete only after seven or eight minutes, the action evidently being independent of, and posterior to, the hydration. The accelerative action of the alkali on the hydration is probably due to its increasing the number of free molecules of water present in the liquid, by forming continually dissociating compounds such as NH_4OH, $NaOHxH_2O$, &c., and a free molecule of water would be a far more active hydrating agent than the average water aggregate constituting the bulk of liquid.

Mr. A. R. Ling said he was under the impression that Béchamp, and subsequently Tollens, were the first to point out that the multirotation of carbohydrates was correlated with thermic phenomena, but neither had made the exact measurements now presented. He wished to know if the authors had observed any change in the density of the solutions before and after the transition from the abnormal to the normal rotatory power.

Dr. Kipping said that although it seems to be generally understood that the phenomenon of birotation is not the result of a purely physical change, the assumption that it is due to the mere hydration of the aldehyd group might be objected to as involving the apparent contradiction that a very considerable change in specific rotation is brought about, not by increasing or diminishing the number of asymmetric carbon atoms in the molecule, but by merely altering to a comparatively slight extent the asymmetry of the groups already present. Important data in support of the chemical or hydration explanation of birotation were afforded, however, by some experiments made at the suggestion of Emil Fischer, as it had been found (Jacobi, *Ann.*, 1892, cclxxii., 170) that the rapidity of the formation of a hydrazone from a sugar which showed birotation varied with the time which had elapsed since the sugar had been dissolved.

Mr. Horace Brown, in reply, said that he believed Mr. Ling was mistaken in his statement that Béchamp or Tollens had done anything to correlate multirotation with thermic phenomena. So far as he knew, the only previous work on this subject was that of Berthelot, who had indirectly determined, for the solid state, the heats of transformation of α- and γ-dextrose into the β form.

Up to the present time, the authors had been unable to discover any change of density in solutions of multirotatory sugars.

Whilst fully admitting the force of Dr. Kipping's objections, it must be remembered that, so far as our knowledge goes at present, we are not justified in denying that comparatively small changes in the asymmetry of groups may be attended with a considerable change in rotatory power. The experiments of Jacobi are fully described in the paper, and are regarded by the authors as strongly confirmatory of their views.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, June 11th, 1897.

Mr. Shelford Bidwell, President, in the Chair.

A mathematical paper was read by Mr. C. S. Whitehead, on "*The Effect of Sea-Water on Induction Telegraphy.*"

If a secondary circuit containing a telephone is rightly placed with respect to the field of a primary circuit traversed by an alternating current, signals may be transmitted over considerable distances. The author investigates the effect of filling the intervening space with sea-water; and, generally, the effect of a spherical conducting shell on the induction, at a point in a dielectric, due to an alternating current in a circular circuit, when the axis of the conductor passes through the centre of the shell. In the mathematical treatment two cases are considered:—(1) To find the normal magnetic induction at any point in the dielectric outside the shell when a circular circuit carrying an alternating current is placed in the dielectric inside a spherical conducting shell. (2) To find the normal magnetic induction at any point on the remote side of an infinite conducting plate, due to a circular circuit parallel to the plate. In both cases the following result is arrived at:—

$$\frac{v_0}{u_0} = e^{-q\eta},$$

where v_0 is the maximum value of the normal magnetic induction at any point outside; u_0 the maximum normal magnetic induction due to the current in the primary, supposing the conducting shell or plate absent, at the same point; η the thickness of the shell or plate; and—

$$q = \left(\frac{2\pi\,\mu p}{\sigma}\right)^{\frac{1}{2}}$$

where μ is the permeability of the conducting shell or plate; σ its specific resistance, $p = 2\pi$ times the frequency. If the frequency is 300, $p = 1885$. For sea-water, σ is taken as 2×10^{10} C.G.S. units, and $\mu = 1$. The sea-depth at the North Sand Head corresponds to $\eta = 2000$ c.m. Hence, in this case,—

$$\frac{v_0}{u_0} = 0{\cdot}21,$$

or 79 per cent is lost. Similarly, when $\eta = 1000$, the loss is 54 per cent. The method employed in the investigation is that suggested by Lamb and Niven; the author adds an expression for Ω, the solid angle subtended by the circuit at any point, in terms of Bessel's functions.

Mr. **Evershed** referred to some experiments of his own, from which he concluded that the author's formula gave too low an estimate of the attenuation; the discrepancy indicated that some term had been neglected.

Mr. **Yule** doubted whether the equations given by the author were quite applicable to sea-water. There was need, apparently, of a term involving the polarisation of the medium.

Mr. **Heaviside** communicated a criticism of the paper. It was not necessary to investigate the problem for any particular form of circuit from which the waves proceed. The attenuating factor for plane waves, due to Maxwell, was sufficient. Taking the best-known value for the conductivity of sea-water, there was no reason why the conductivity should interfere with signalling. A considerably greater conductivity must be proved for sea-water before it could be accepted that the failure of experiments on telegraphic communication with light-ships from the sea-bottom was due to that factor. It was unlikely theoretically, and Mr. Stevenson had contradicted it from a practical stand-point. For some reason, the account of the light-ship experiments had not been published, so that there was no means of finding the real cause of failure.

Mr. T. H. **Blakesley** read a paper on "*A New Definition of Focal Length, and an Instrument for Determining it.*"

The author asserts the principle that the focal length of a lens-combination is an abstract quantity, not necessarily the distance between two particular points. It is a quantity best defined in terms of some function of the two distances of object and image from their appropriate focal centres. Such a function is the magnification factor, m, the linear ratio of image to object, positive if the image is erect with regard to the object. Consider a particular pair of conjugate foci on the axis of a lens-system. Let one of these foci be at distance v from some fixed point on the axis, measured positively, in the direction of the rays. Then—

$$\frac{dv}{dm}$$

is constant, and is the focal length, f. If v_0 is the value of v when $m = o$, $v - v_0 = f.m$.

Let u be the position of the other focus, and u_0 its value when $m = \infty$. Then $u - u_0 = f.m^{-1}$; and—

$$\frac{v - v_0}{u - u_0} = m^2.$$

The last expression, m^2, may be called the "areal magnification"—it is important in determining photographic exposure. The author describes an optical bank, which enables—

$$\frac{dv}{dm}$$

to be measured by a very simple operation; it gives also a record, on a paper strip, of the magnification factor corresponding to various relative positions of object and image.

Dr. S. P. **Thompson** said the paper was the most important contribution to geometrical optics that had appeared for many years. The introduction of the magnification function was a most useful device, leading to exceedingly simple results. The important thing to measure was not so much the focal length as the reciprocal of that quantity.

Dr. **Chree** said the photographic method at present used at Kew for determinations of focal length gave greater security than any more direct method. The colour of the light had to be taken into account.

Mr. **Blakesley**, in replying, called attention to the use of his strip diagrams of magnification, for enlarging purposes in photography. When the magnification along some definite line was known, the focussing-cloth might almost be dispensed with.

Dr. J. A. **Fleming** read a paper on "*A Method of Determining Magnetic Hysteresis Loss in Straight Iron Strips.*"

The author's process is based upon the use of the bifilar reflecting Watt-meter. The samples of iron, large or small, in the form of straight strips are inserted in a long solenoid. The solenoid is traversed by an alternating current, and the square-roots of the mean-square values of the current are determined by a Kelvin balance. A flat bobbin of fine wire may be slided along the strip; an electrostatic voltmeter connected to the ends of this exploring coil gives the square-roots of the mean-square values of the electromotive force in that coil. From these measurements, and the known dimensions of the solenoid and coil, the induction-density, B_1, can be found at any point of the length of the strip. From these results a curve is drawn, co-ordinating the values of B to corresponding distances along the half-length of the strip. Assuming the hysteresis loss per cycle, per c.c. of iron, to vary as the 1·6th power of the maximum induction density, and then raising all the B ordinates to the 1·6th power, and plotting a new curve over the first, another curve is obtained which represents the variation of hysteresis loss per c.c. of iron from point to point along the half-length of strip. Now at some point along the half-length of strip there must be a section where the induction density is B_1, such that the true *mean* hysteresis loss for the *whole* bar is proportional to $B_1^{1{\cdot}6}$. Let this value of the induction density be called the "*effective value*" and the corresponding point in the strip the "*effective point.*" Let $M.B^{1{\cdot}6}$ stand for the mean ordinate of the curve representing the varying values of $B^{1{\cdot}6}$ all along the half-length. Then, evidently,—

$$B_1 = \sqrt[1{\cdot}6]{M.B^{1{\cdot}6}}.$$

The following curious experimental result is found:—Whatever may be the length or section of the iron strip, the point at which the actual induction density has a value equal to the "effective" value always comes at the same proportional distance from the centre of the strip. This distance is very exactly equal to 0·56 of the half-length, as measured from the middle, or 0·22 of the whole length from one end. If, therefore, the secondary coil is placed at that spot, and the secondary voltage then observed is used to calculate the induction density, the value so obtained corresponds to the true mean value of the varying hysteresis loss per c.c. all along the strip.

Mr. Carter asked whether roots other than the 1·6th gave a similar constant value of the induction density.

Dr. Fleming said it seemed to be the result of accident that the 1·6th root gave a constant value for iron.

The President proposed a vote of thanks to the authors, and the meeting adjourned until June 25th.

THE ROYAL SOCIETY.

The Conversazione held on Wednesday, the 16th inst., at the Royal Society's Rooms, Burlington House, was in every respect a most brilliant and interesting gathering.

Apart from the purely social side of the entertainment, there were a number of exhibits which could not fail to attract attention. On entering, the eye was immediately caught by Prof. Ramsay's Argon and Helium Tubes, arranged to form the words "Vivat Victoria Regina."

In the Office upstairs, some of Lord Kelvin's Experiments on the Quasi-perpetual Motion Action, of Uranium-Zinc Contact were shown.

One of the most striking exhibits was that of Dr. Alex. Muirhead, who had an actual working instrument receiving, by means of a Kelvin syphon recorder, the signals transmitted from a distant room through the surging crowd, and being recorded on the tape in dots and dashes without the help of any intervening wires.

Prof. Roberts-Austen showed some Photographs and Microscopic Slides of Diamonds separated from carburised iron, made, with certain modifications, according to the method described by M. Moissan.

The Shadow Photographs illustrating the absorption of X rays by certain elements and their compounds, exhibited by Dr. J. H. Gladstone and Mr. Walter Hibbert, were of peculiar interest. The "photographs" were obtained by subjecting various tubes, containing equal parts of certain elements, but in different compounds, to the action of the X rays, and it was noted in the case of carbon that the absorption was the same whether the tubes contained charcoal, anthracene, or naphthalene; the different forms of combination of the carbon having no influence whatever on the result.

A beautiful example of the work of our almost prehistoric forerunners was shown by Sir John Evans. It consisted of a collection of flint knives and lance-heads from Egypt, dating back to 4000 B.C. These exquisitely fluted blades have been polished all over by grinding before the flakes were removed; the edges were subsequently re-touched and serrated with minute teeth at intervals of about 35 to the inch.

Medals, struck in gold, silver, and bronze, to commemorate the 60th year of the reign of Her Majesty the Queen, were exhibited by Mr. Horace Seymour, Deputy Master of the Mint. These attracted a good deal of attention.

At 9.45 and 11 o'clock Demonstrations of Signalling through Space without Wires were given by Mr. W. H. Preece, C.B.; and at 10.30 Photographs illustrating the arrangements of the 1896 Eclipse Expedition at Kiö and Novaya Zemlya, were exhibited by Mr. J. Norman Lockyer, C.B., in the meeting room on the ground floor.

NOTICES OF BOOKS.

Electro-chemical Problems for Practice and for Self-instruction. Collected by Dr. Felix Oettel. With 20 Woodcuts in the Text. Halle-on-Saale: W. Knapp. 1897. 8vo., pp. 53.

An unusual degree of attention seems to be at present directed to electro-chemistry.

The work before us opens with generalities on the necessary arrangements. As a source of current the preference is given to accumulators which may either be charged by means of a small dynamo or from a central station. For electro-metallurgical investigations a tension of 4 volts (= 2 accumulators) is generally sufficient. For regulation, a crank regulator with 15 to 20 contacts is considered convenient.

As measuring instruments the author recommends those of Meyer, form E, which are accurately gauged notwithstanding their cheapness (25 marks), though the Weston instruments (made apparently by a Berlin firm) have advantage of rapid adjustment, but are decidedly more expensive than the apparatus above mentioned.

The electro-chemist is strongly advised to test the accuracy of his measuring instruments.

All the instruments above mentioned are unaffected by currents in their neighbourhood, even by dynamos in action. But the instruments which work with magnetic needles are much less widely useful. They must be placed at least at the distance of some metres from other circuits.

A galvanometer on the system of Deprez d'Arsonval is not affected by neighbouring currents, and may be set up anywhere.

The most important voltmeters are the copper voltmeter and the detonating-gas instrument. The solution for the former is made up of 150 grms. blue vitriol, 50 grms. sulphuric acid, 50 grms. alcohol, and 1000 grms. water. The liquid must be agitated during use.

The detonating-gas voltmeter, which is permanently inserted in the circuit, is the most convenient instrument for gauging and checking ammeters. This apparatus, as usually constructed, consists of a stout glass cylinder with two concentric sheets of nickel, the internal one serving always as anode.

In a section on testing and guaging measuring appliances, there is first a comparison between the silver and the copper voltmeters, the former of which is universally regarded as the most accurate. Then follows the checking of the ammeter respectively with the detonating-gas voltmeter and the copper voltmeter, the comparison of the ammeter with the tension galvanometer, the duplication of the measuring scope of an ammeter by a by-connection.

The gauging of a galvanometer respectively as ammeter and as voltmeter forms the subject of two short but clearly written sections.

We next come to the dependence of the tension of the bath upon the following factors: density of current concentration and temperature of the solution, and mutual distances of the electrodes. There is a special discussion on the influence of density of current and concentration upon the course of electro-chemical reaction.

Oxidation is most favourable in a concentrated solution, and with a low density of anodic current.

Reduction is promoted in a concentrated solution, but with a low kathodic current.

Oxidation is slightest in a dilute solution, and with a high density of anodic current.

The slightest reduction ensues in dilute solutions, and with a high density of current at the kathode.

In accounts on electro-chemical work a statement of the density of the current at each pole is therefore necessary. We quote this statement literally, as a short time ago it was the subject of a discussion.

Next follow the oxidation of oxalic acid; the electrolysis of a mixed ferrous and ferric solution; the formation of hypochlorites and chlorates; and the electrolysis of hydrochloric acid without a diaphragm.

The last sections of the work treat of the precipitation of metals with soluble and insoluble anodes; the introduction of auxiliary reactions of experiments with pyroliquid electrolytes; the separation of copper with bipolar electrodes; the electrolysis of sodium acetate, and other organic electrolyses.

Dr. Oettel has favoured the chemical world with a very useful, compact, and well-illustrated work.

CORRESPONDENCE.

ESTIMATION OF CARBON IN FERRO-CHROME.

To the Editor of the Chemical News.

Sir,—I have neither time nor inclination to follow Mr. R. L. Leffler into the details of his letter. Mr. Leffler stated that my method gave only half the carbon present in ferrochrome: this statement was inaccurate. That Mr. Leffler has been putting up men of straw to somewhat ostentatiously knock them down again will be seen from Mr. Saniter's letter. As till quite recently Mr. Leffler was a student of mine, it would seem that the dictates of common courtesy would have led him to ask personally for an explanation of his low results before making the rash assertion in the article. No amount of ingenuity of argument on Mr. Leffler's part will alter the fact that other students have obtained from 8 to 9 per cent of carbon from ferro-chrome by the method which in his hands failed.—I am, &c.,

J. O. Arnold.

The Technical Dept., University College,
Sheffield, June 12, 1897.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 19, May 10, 1897.

The President announced two severe losses which the Academy has experienced. The illustrious mineralogist M. des Cloiseaux, one of the oldest members of the Academy, is dead. He was born in 1817, and was elected a Member of the Academy in 1869. His principal researches were devoted to crystallography and to the optical properties of minerals. The Duc d'Aumale was indirectly one of the victims to the terrible catastrophe of the Rue Jean Goujon, in which his niece, the Duchess d'Alençon, perished. He bequeathed to the Institute his estate of Chantilly, formerly the residence of the Princes de Condé, which he had fitted up as a library and museum of art.

Explanation of some Experiments of G. le Bon's. H. Becquerel.—Already inserted.

The Solutions of Acetylene, and on their Explosive Properties.—MM. Berthelot and Vieille.

Remarks on the Explosive Decomposition of Solutions of Acetylene.—MM. Berthelot and Vieille.

Some Conditions of the Decomposition of Pure Acetylene.—MM. Berthelot and Vieille.

Solubility of Liquids.—A. Aignon.—One litre of the ether examined can dissolve 33 c.c. of water, whilst one litre of water can dissolve 132 c.c. of the same ether.

On Multiple Resonance.—L. Deconté.—This paper requires the two accompanying figures.

Diurnal Variation in the Direction of the Wind.—Alfred Angot.—This memoir also necessitates the accompanying illustration.

Basic Salts of Cadmium.—M. Tassilly.—The action of metallic oxides upon the corresponding haloid salts has yielded two novel cadmium compounds, an oxybromide and an oxyiodide. These bodies have been obtained by heating to 200°, in a sealed tube, a concentrated solution of bromide or iodide along with cadmium oxide. The yields are exceedingly small. The bodies obtained are distinctly crystalline, and act upon polarised light. The oxyiodide gave on analysis the formula $CdI_2CdO.3H_2O$. It is little acted on by water. At 120° it does not vary in weight either in a current of nitrogen or of air deprived of carbonic acid and watery vapour. In parallel light the crystals present an extinction parallel to the longitudinal axis. In converging light we observe a lemniscate. The crystal is bi-refringent at axes widely remote from each other. The oxybromide appears in very small crystals, answering to the formula $CdBr_2CdO.3H_2O$, and acting upon polarised light. In conclusion it is well to observe that the basic salts of cadmium are always formed of equal molecules, contrary to what takes place with the salts of zinc, which are capable of fixing a variable number of mols. of oxide to form salts which do not answer to a general type.

Researches on Strontium Sulphide, and a Method of Rendering it Highly Phosphorescent.—José R. Movelo.—After many trials I had the idea of modifying the procedure previously adopted, and I had recourse to a method by which I obtained a strontium sulphide possessing a magnificent phosphorescence of a greenish blue and so intense that, after insolation for less than a second, it was perceptible by its shade without the necessity of placing the substance in the dark. I took 285 grms. of impure commercial strontium carbonate, 62 grms. flower of sulphur, 4 grms. crystalline sodium carbonate, 2·5 grms. sodium chloride, and 0·4 grm. bismuth subnitrate. The mixture, finely powdered, was placed in an earthen crucible, pressed down and covered with a layer of tinder in coarse powder: this stratum does not exceed 2 c.m. in depth. The crucible, set in a furnace, is heated to bright redness by a coke fire for five hours, and is then allowed to cool slowly for ten or twelve hours. After this we extract from the crucible an agglomerate, nearly white, granular, and friable, possessing a phosphorescent power which the diffused light of the laboratory is sufficient to excite in the shade and behind the windows of the cupboard in which the bottle was inclosed. Like M. Verneuil I have observed that most of the strontium sulphides which I have prepared lose their phosphorescent power if powdered, but these pulverised sulphides, if mixed with tinder and heated to bright redness for five hours, resume their phosphorescent power.

Thermic Study of Mono- and Di-sodic Acetylenes.—Camille Matignon.—A thermo-chemical paper, suitable neither for abstraction nor for insertion in full.

Contribution to the Study of the Preparation of Common Ether.

Action of Chlorine Hydrate upon Phenylhydrazindiphenylglyoxazol and its Derivatives..—H. Causse.—The compounds here described are trichlorethylidenediphenylhydrazin, chlorodiphenylglyoxazol, hydroxydiphenylglyoxazol, oxydiphenylglyoxazol antimonite, and the barium derivative.

Intervention of Manganese in the Oxidations induced by Laccase.—G. Bertrand.—Already inserted.

No. 20, May 17, 1897.

On the Cathodic Rays and on certain Phenomena in Vacuum Tubes.—The tube used by the authors was pear-shaped; the electrodes terminating in two aluminium discs, one of which was placed at the narrow extremity of the tube, whilst the other was placed in the expanded part, the surfaces of the two discs being respectively perpendicular. At the anti-cathode there is formed a luminous ring and a central spot. If the disc in the narrow part serves as a cathode, the following phenomena have been observed:—If we touch with the finger the tube near the cathode disc we observe an attraction of the cathodic rays. The glass under the finger is rendered luminous and all the cathodic bundle is deflected towards the hand. We observe at the same time that under the anticathodic ring the phosphorescence becomes stronger towards the finger and the central spot undergoes a transformation from circular towards elliptical, as if subjected to pressure. There is in front of the anode a bluish light which, if examined with the spectroscope, gives the line-spectrum of nitrogen. If we touch the tube with the finger at a point of the expanded portion, the anodic light is energetically repelled.

Transparence of Ebonite.— M. Perigot. — The phenomena ascribed to "black light" are explained by the well-known fact of photographic inversion.

Lithium Borate.—The composition of this salt is $Bo_2O_3,LiO,16H_2O$. Its specific gravity at 14·7° is 1·397. Its crystallisation in the rhombohedric system is distinctly uniaxial. Its heat of hydration is +43·4 cal. Its solution heat is −28·4 cal. Crystalline lithium borate effloresces slowly if left in contact with the air, and at the same time absorbs small quantities of carbonic acid.

Alloys of the Silver and Copper Group.—F. Osmond.— M. Charpy, on examining microscopically different groups of alloys, has established that the structure of the eutectics recalls generally that of the perlite of steels, and the comparison is justified from all points of view. Micrography confirms absolutely the indications of the curve of fusibility, and leaves no doubt concerning the non-existence of Ag_3Cu_2 as a definite compound.

Researches on the Colouration of Glasses by the Direct Penetration of Metals or Metallic Salts.—Léon Lémal.—The author applies upon glass a salt of silver and raises the temperature to 500—550°. The glass, when cooled and freed by washing from excess of salt, has a yellow colour. The shade obtained may range from straw-colour to an orange-red. Glasses thus coloured present phenomena of dichroism always yellow by transmitted light, but having by reflected light fluorescent tints, from yellowish green to violet-blue.

Action of Water upon Phosphoryl Chloride.—A. Besson.—The limited action of water upon $POCl_3$ yields the series of products $P_2O_3Cl_4,PO_2Cl$ and PO_4H_3, in virtue of the reactions $2POCl_3+H_2O=2HCl+P_2O_3Cl_4$.

Certain New Aromatic Synthetic Ureas.— P. Cazeneuve and M. Mar.—A description of dipseudocumyl urea, dixyl urea, dipara-aminyl urea. These results lead to the conclusion that all the primary bases yielding with guiacal carbonate corresponding symmetrical ureas are very easy to obtain.

Amidised Amidines.—Charles Lauth.—The hydrochlorates of these two amidines are easily diazotised. The diazoïcs obtained yield, on conjugation with the phenols and the amines, azo-pigments which dye cotton directly, in shades ranging from yellow to red and black. They resist well the action of chemical reagents, but they are not very fast.

Rôle of the Tannins in Plants and especially in Fruits.—C. Gerber.—In fruits containing tannins—such as the kakis, these tannins disappear by complete oxidation without giving rise to carbohydrates.

Royal Institution. — A General Monthly Meeting of the Members of the Royal Institution was held on the 14th inst., Sir James Crichton-Browne, M.D., F.R.S.. Treasurer and Vice-President, presiding. The following were elected Members:—Dr. Tempest Anderson, M.D.; Mr. Samuel Pope, Q.C.; and Major Clifford Probyn.

MEETINGS FOR THE WEEK.

Friday, 25th.—Physical, 5. "A New Theory of the Earth's Magnetism," by Mr. Sutherland. "Experiments in Critical Phenomena," by Dr. Kuenen. "Attenuation of Electric Waves in Wires," by Dr. Barton. "The Steady Motion of an Electrified Ellipsoid," by G. F. C. Searle.

IMPORTANT NOTICE.

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DIAMONDS.*

By WILLIAM CROOKES, F.R.S., M.R.I.

It seems but the other day I saw London in a blaze of illumination to celebrate Her Majesty's happy accession to the throne. As in a few days the whole Empire will be celebrating the Diamond Jubilee of our Queen, who will then have reigned over her multitudinous subjects for sixty years, what more suitable topic can I bring before you than that of Diamonds! One often hears the question asked: "Why *Diamond* Jubilee?" I suppose it is a symbol intended to give a faint notion of the pure brilliancy and durability of the Queen's reign; and in thus associating Her Majesty with the precious Diamond, to convey an idea of those noble qualities public and private which have earned for her the love, fealty and reverence of her subjects.

From the earliest times the diamond has occupied mens' minds. It has been a perennial puzzle—one of the riddles of creation. The philosopher Steffans is accredited with the dictum that "Diamond is quartz which has arrived at self-consciousness;" and an eminent geologist has parodied this metaphysical definition, saying—"Quartz is diamond which has become insane!"

Professor Maskelyne, in a lecture "On Diamonds," thirty-seven years ago,† in this very theatre, said:—"The diamond is a substance which transcends all others in certain properties to which it is indebted for its usefulness in the arts and its beauty as an ornament. Thus, on the one hand it is the hardest substance found in nature or fashioned by art. Its reflecting power and refractive energy, on the other hand, exceed those of all other colourless bodies, while it yields to none in the perfection of its pellucidity"—but he was constrained to add "The formation of the diamond is an unsolved problem."

Recently the subject has attracted many men of science. The development of electricity, with the introduction of the electric furnace, has facilitated research, and I think I am justified in saying that if the diamond problem is not actually solved, it is certainly no longer insoluble.

In the early part of last year, accompanied by my wife, I visited some of our Colonies in South Africa, and spent a considerable time in the neighbourhood of the famous Diamond Mines of Kimberley, where I had an exceptionally good opportunity of studying the peculiar geological formation, and of noting interesting facts connected with the occurrence of the precious stone which forms the subject of this evening's lecture.

Although the experiments I wish to bring before you are chiefly connected with the physical and chemical properties of diamonds, and of the light that recent researches throw upon their probable formation, it will possibly act as a kind of compensation for the dryness of some of the theoretical points if with the help of a few photographs taken on the spot, I bring before your very eyes the general character of the famous mines and their surroundings.

The most famous diamond mines are Kimberley, De Beers, Dutoitspan, Bulfontein, and Wesselton. They are situated in latitude 28° 43′ South, and longitude 24° 46′ East. Kimberley town is 4042 feet above sea-level. Other mines in the district, as yet unimportant, are worked for diamonds. Kimberley is practically in the centre of the present diamond-producing area. Besides these mines, there are in the Orange Free State, about 60 miles from the Kimberley diamond region, two others of some importance known as Jaggersfontein and Coffeefontein.

River Washings.

Before describing the present mode of diamond extraction followed in the leading mines, I will commence with the so-called "River Washings," where, in their original simplicity, can be seen the methods of work and the simple machinery long since discarded in the large centres. These drifts or "river-washings" present an interesting phase of Diamond industry. The work is carried out in the crude fashion of early diamond discovery, every man working on his own little claim, assisted by a few natives, and employing primitive machinery. The chief centre of the river washings is at Klipdam No. 2, about 30 miles to the north-west of Kimberley. The road to Klipdam No. 2 involves a journey of about a dozen miles in one of the old African coaches now becoming obsolete through the spread of railways. Road there is none—only a track across the veldt made by countless teams of oxen and mules.

Diamonds from the "river washings" are of all kinds, as if every mine in the neighbourhood contributed. The samples are much rolled and etched, and contain a fair proportion of stones of very good quality, as if only the better and larger stones had survived the ordeal of knocking about.

Diamonds from the drift fetch about 40 per cent more than those from Kimberley: taking the yield of the Kimberley and De Beers mines as worth, all round, large and small, 26s. 6d. a carat, the drift diamonds are worth 40s.

Kimberley.

The town of Kimberley is a remarkable instance of rapid growth. It has an excellent club and one of the best public libraries in South Africa. Parts of the town, affectionately called "the camp" by the older inhabitants, are still in the galvanised iron or "tin shanty" stage, and the general appearance is unlovely and depressing. Reunart reckons that over a million trees have been felled to supply timber for the mines, and the whole country within a radius of 100 miles has been denuded of wood with most injurious effects to the climate. The extreme dryness of the air, and the absence of trees to break the force of the wind and temper the heat of the sun, probably account for the dust storms so frequent in summer. The temperature in the day frequently rises to 100° in the shade, but in so dry a climate this is not unpleasant, and I felt less oppressed than I did in London the previous September. Moreover, in Kimberley, owing to the high altitude, the nights are always cool.

The Pipes.

The five noted diamond mines are all contained in a circle $3\frac{1}{2}$ miles in diameter. The mines are irregularly-shaped round or oval pipes, extending vertically downwards to an unknown depth, retaining about the same diameter throughout. They are said to be volcanic necks, filled from below with a heterogeneous mixture of fragments of the surrounding rocks, and of older rocks such as granite mingled and cemented with a bluish-coloured hard clayey mass, in which famous blue the diamonds are hidden.

The breccia filling the pipes, usually called "blue ground," is a collection of fragments of shale, eruptive rocks, boulders, and crystals of many kinds of minerals.

The Kimberley mine for the first 70 or 80 feet is filled with what is called "yellow ground," and below that with "blue ground." This superposed yellow on blue is common to all the mines. The blue is the unaltered ground, and owes its colour chiefly to the presence of lower oxides of iron. When atmospheric influences have access to the iron it becomes peroxidised, and the ground

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* A Lecture delivered at the Royal Institution, Friday, June 11th, 1897.

† Chemical News, vol. i., p. 208.

assumes a yellow colour. The thickness of yellow earth in the mines is therefore a measure of the depth of penetration of air and moisture. The colour does not affect the yield of diamonds.

The diamantiferous clay or blue ground shows no signs of passing through great heat, as the fragments in the breccia are not fused at the edges. The eruptive force was probably steam or water-gas, acting under great pressure but at no high temperature. According to Mr. Dunn, in the Kimberley mine, at the depth of 120 feet, several small fresh-water shells were discovered in what appeared to be undisturbed material.

Let me cite a description of a visit to Kimberley in 1872, by Mr. Paterson, taken from a paper read to the Geologists' Associaton, which gives a graphic picture of the early days of the Kimberley mine:—

"The New Rush diggings (as the Kimberley mine was first called) are all going forward in an oval space enclosed around by the trap dyke, of which the larger diameter is about 1000 feet, while the shorter is not more than 700 feet in length. Here all the claims of 31 feet square each are marked out with roadways about 12 feet in width, occurring every 60 feet. Upon these roadways, beside a short pole fixed into the roadway, sits the owner of the claim with watchful eye upon the Kafir diggers below, who fill, and hoist by means of a pulley fixed to the pole above, bucketful after bucketful of the picked marl stuff in which the diamonds occur."

Soon came the difficulty how to continue working the host of separate claims without infringements. A system of rope haulage was then adopted. This mode of haulage continued in vogue during the whole of 1873, and if the appearance of the mine was less picturesque than when roadways existed, it was by moonlight, particularly, a weird and beautiful sight.

But the mine was now threatened in two other quarters. The removal of the blue ground undermined the support from the walls of the pipe, and frequent falls of reef occurred, not only burying valuable claims, but endangering the lives of workers below. Moreover, as the workings deepened, water made its appearance, necessitating pumping.

It soon became evident that open workings were doomed, and by degrees the present system of underground working was devised.

During this time of perplexity, individual miners who might have managed one or two claims near the surface could not continue work in the face of harassing difficulties and heavy expenses. Thus the claims gradually changed hands until the mine became the property first of a comparatively small number of capitalists, then of a smaller number of limited liability companies, until the whole of the mines have practically become the property of the "De Beers Consolidated Mines, Limited."

The areas of the mines are:—

Kimberley	33 acres.
De Beers	22 ,,
Dutoitspan..	45 ,,
Bulfontein	36 ,,

The contents of the several pipes are not absolutely identical. The diamonds from each pipe differ in character, showing that the upflow was not simultaneous from one large reservoir below, but was the result of several independent eruptions. Even in the same mine there are visible traces of more than one eruption.

The blue ground varies in its yield of diamonds in different mines, but is pretty constant in the same mine. In 1890, the yield per load of blue ground was—

From the Kimberley mine	from 1·25 to 1·5	carats.
,, De Beers mine	,, 1·20 ,, 1·33	,,
,, Dutoitspan mine	,, 0·17 ,, 0·5	carat.
,, Bulfontein mine	,, 0·5 ,, 0·33	,,

Underground Workings.

In the face of constant developments I can only describe the system in use at the time of my visit. Shafts are sunk in the solid rock at a sufficient distance from the pipe to be safe against reef movements in the open mine. Tunnels are driven from this shaft at different levels, about 120 feet apart, to cross the mine from west to east. These tunnels are connected by two others running north and south, one near the west side of the mine and one midway between it and the east margin of the mine. From the east and west tunnels offsets are driven to the surrounding rock. When near the rock, the offsets widen into galleries, these in turn being stoped on the sides until they meet, and upwards until they break through the blue ground. The fallen reef with which the upper part of the mine is filled sinks and partially fills the open space. The workmen then stand on the fallen reef and drill the blue ground overhead, and as the roof is blasted back the *débris* follows. When stoping between two tunnels the blue is stoped up to the *débris* about midway between the two tunnels. The upper levels are worked back in advance of the lower levels, and the works assume the shape of irregular terraces. The main levels are from 90 to 120 feet apart, with intermediate levels every 30 feet. Hoisting is done from only one level at a time through the same shaft. By this ingenious method of mining every portion of blue ground is excavated and raised to the surface, the rubbish on the top gradually sinking and taking its place.

The scene below ground in the labyrinth of galleries is bewildering in its complexity, and very unlike the popular notion of a diamond mine. All below is dirt, mud, grime; half naked men, black as ebony, muscular as athletes, dripping with perspiration, are seen in every direction, hammering, picking, shovelling, wheeling the trucks to and fro, keeping up a weird chant which rises in force and rhythm when a titanic task calls for excessive muscular strain. The whole scene is more suggestive of a coal mine than a diamond mine; and all this mighty organisation, this strenuous expenditure of energy, this costly machinery, this ceaseless toil of skilled and black labour, goes on day and night, just to win a few stones wherewith to deck my lady's finger.

(To be continued).

ON THE ACTION EXERTED BY CERTAIN METALS AND OTHER SUBSTANCES ON A PHOTOGRAPHIC PLATE.

By W. J. RUSSELL, Ph.D., F.R.S.,
Lecturer on Chemistry at St. Bartholomew's Hospital.

Having some years ago prepared for the purpose of spectroscopic examination several uranium compounds, it was of interest to make further use of them by repeating some of the very important experiments which Becquerel has made with these compounds. He has shown that if the metal or some of its salts be placed on a photographic plate in perfect darkness, and allowed to remain there for some days, the plate becomes acted on, the action being rendered evident by the ordinary photographic process of development. This action is readily produced, and belongs apparently to all the salts of this metal, and, as Becquerel has shown, to uranous as well as uranic salts. It is very remarkable that this power belongs also to the salts when in solution, and, as the action passes through glass, solutions of the double chloride or of the nitrate contained in a thin glass bottle, when placed on a photographic plate, act readily upon it. While speaking of these compounds it may be well to record some experiments which have been made to determine whether they lost their peculiar activity on being kept in the dark.

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* A Paper read before the Royal Society, June 17, 1897.

On the 10th August last, specimens of yellow oxide, recrystallised nitrate, and chloride, the latter in solution, were each divided into two equal portions, and all placed in similar clean thin glass bottles. One sample of each was then placed in total darkness, and the other kept in the light. These samples have from time to time been tested by placing them on a photographic plate for a week and then developing the plate in the usual manner. Seven such examinations have been made at about one month's interval. No very marked difference between the samples in the light and the dark has occurred; on the whole the samples preserved in the dark have proved slightly the most active, and this was decidedly the case with all three specimens at the last examination on March 26. Another experiment was begun a little later with the black oxide of uranium, which appears to be one of the most active of the uranium compounds. Equal weights of a sample of this body were placed in two similar pill-boxes with a glass bottom; one has been kept in the dark, and the other in the light; after five months there was no difference in the effect which they produced on the photographic plate. The experiments are being continued. When repeating these different uranium experiments and using a card painted with the yellow oxide, perforated zinc was made use of simply as a screen to show the activity of the uranium compound by the density of the picture of the pattern formed; but in place of obtaining in all instances a negative of the perforated zinc, *i.e.*, the action occurring where the plate was exposed, and none where covered by the zinc, the reverse took place, and the greatest amount of action occurred underneath the zinc. This happened over and over again, and even when the experiment was varied in different ways, so that the only explanation of the action was that the zinc itself must be able to effect a change of the same kind as the uranium, at all events, to act on a photographic plate; and further experiment with zinc alone proved this to be the case; later on it became known to me that M. Colson had already described this action of zinc in a paper in the *Comptes Rendus* in January last, and had also found that similar results could be obtained with cadmium and with magnesium. He explains this remarkable action as due to vapour given off by these metals.

Both before and after seeing the account of Colson's work a large number of experiments have been made with zinc under different conditions, and there is no doubt of the ease and certainty with which the results can be obtained. The zinc, as Colson states, must be bright; if well rubbed with coarse sand-paper it is most active: probably this may, to some extent, arise from increase of surface; if cleaned with acid or with caustic alkali it is not so active, and zinc in its ordinary condition after exposure to the air ceases to be active. The salts also have no power of acting in this way. A polished piece of zinc laid on a highly sensitive photographic plate will, under certain conditions, even in four or five hours, so act on it that on development a complete picture of the zinc is produced, showing the scratches or any ruled lines or faint pattern drawn on it, or if flaws in the metal exist they are clearly seen. A slight pattern produced on zinc by pressing on it a piece of white net, and then rubbing it down with fine emery or sand-paper, will give a picture in which the pattern is very evident. In fact, such a pattern forms a satisfactory test of this action of the zinc. Very slight alterations of the surface are shown in the picture. Absolute contact of metal and plate is not necessary. If screens of different thicknesses of any inactive substance be interposed between plate and metal, thus preventing contact, the action still occurs; if the screen be very thin, a picture of the zinc surface is still obtained, but if thicker only a dark cloudy patch is formed. Still further, if a thick piece of glass tubing an inch long be placed on a photographic plate, and the upper end covered with a piece of polished zinc, in a week to a fortnight distinct action will be found to have taken place below the zinc. Since the action then is not one of mere contact, the next point was to ascertain whether it would be transmittted through different solid or liquid media. Glass, even of the thinnest kind, was found to stop the action, but many other substances allow of its transmission. For instance, the action takes place readily through celluloid, sheet gelatin, gutta-percha tissue, collodion, vegetable parchment, real parchment, gold-beater's skin, tracing-paper, and no doubt many other bodies. With all these bodies experiments have been made by placing the medium first in contact with the zinc and the photographic plate, then by introducing a screen so as to prevent the medium from touching the zinc, and then placing a second screen so that neither zinc nor plate were in contact with the medium. The screens were made of different materials, most commonly of either white cardboard or sheet indiarubber, and of different thicknesses. The details of each experiment need not be here described; but the general results obtained are that with thin sheet gelatin, either red, green, or blue, when laid on the zinc, the action readily passes through, and a good clear picture of the surface of the zinc is obtained, and even with two sheets of gelatin a similar effect is produced. With thick sheet gelatin interposed the action on the plate still takes place, but of course the exposure must be longer. Warm solutions of gelatin were painted on polished zinc and allowed to harden; the action took place through such layers as readily as through the films. With screens used as before described to prevent contact the gelatin still allowed the action to take place through it. Thin sheets of celluloid, about 0·28 m.m. in thickness, allowed the action to take place through them, and sheets 0·81 m.m. in thickness also allowed the action to be transmitted. Again, gutta-percha tissue was found to act in the same kind of way as the gelatin and celluloid. The other media experimented with, although possibly not so uniform and continuous in structure as the foregoing, also allow this action to be transmitted to them.

Gold-beater's skin and tracing-paper both allow the action readily to pass through, and pictures of the zinc are readily obtained. If either of these bodies be placed between a piece of perforated zinc and the plate, the perforations are very distinctly shown, or if they be placed between a double screen with corresponding holes cut, a picture of the holes is readily obtained.

Both vegetable and real parchment are also transparent to this action, but not so much so as the previously-mentioned substances; the vegetable parchment is more transparent than real parchment. When in contact with the zinc, a picture of the zinc surface is obtained, but this is somewhat modified by the substance of the parchment.

If different kinds of ordinary papers, such as writing and drawing papers, be interposed between polished zinc and a photographic plate, interesting results are obtained, for the pictures formed show clearly the structure of the papers, and also show that papers have very different powers of transmitting this action. Certain writing papers are quite opaque to the action; with others, pictures of the structure and the water-mark are easily obtained.

The painting a paper with India ink does not destroy its transparency. Obviously pictures of bodies, such as skeleton leaves or dried flowers, &c., are easily obtained in this way.

A mere difference of colour does not appear to alter the absorptive power of a medium; at least, this is the case with gelatin. The thin sheets of gelatin, whether red, green, or blue, have no difference in their absorptive power, and when gelatin, coloured with aniline dyes, is painted on polished zinc, the colour does not affect the amount of action which takes place. The same thing happens if demy paper be painted with different coloured solutions of gelatin. With ordinary pigments different results are obtained, but these results need not be discussed on the present occasion.

In addition to the metals cadmium and magnesium, mentioned by M. Colson, there are certainly many others which are able to produce effects similar to that produced by zinc. There are also certain alloys which can act in the same way. The following is a rough list of active metallic bodies approximately in the order of their activity:—Mercury, magnesium, cadmium, zinc, nickel, aluminium, pewter, fusible metal, lead, bismuth, tin, cobalt, antimony.

The above order, even if not absolutely correct, is sufficiently so to indicate that, although mercury is the most active, the other metals do not follow in the order of their fusibility or exactly according to any obvious physical property, but most nearly according to their position in the electrical series. Mercury is, then, at ordinary temperatures the most active metal, and its action is exercised not only when the photographic plate is placed half an inch or so above the metal, but when gelatin, gutta-percha, tracing-paper, vegetable parchment, are interposed. It appears, however, that the action of the mercury does not take place as readily through gelatin, but more readily through gutta-percha than is the case with zinc.

Magnesium is also a very active metal, and very good pictures, showing every scratch on its surface, is easily obtained, and also very marked effects are produced when both single and double screens are used. Cadmium also produces very good pictures, and is rather more active than zinc; nickel and aluminium are not quite so active, but give good pictures; then follow lead, bismuth, and tin. The last metal is by far the least active. Only a few alloys have at present been experimented with; brass gives no action, but ordinary pewter, and fusible metal, consisting of lead, bismuth, and tin, were found to have considerable activity, and are placed in the list between aluminium and lead. That certain alloys should act in the same way as the metals is certainly of interest, and probably of considerable importance. The oxide and sulphate, both of zinc and cadmium, were found to be devoid of any power of acting on the photographic plate. Iron, gold, and platinum are not active, and copper only very slightly. All the above results are founded on experiments in which the exposure lasted for one week; with longer exposure other metals will probably produce some action.

In order to determine whether moisture was an active agent, either directly by affecting the medium or indirectly by affecting the photographic plate, experiments were made by exposing the plates under bell-jars, in which in one case there was water, and in the other sulphuric acid or calcium chloride, and even in these extreme cases no appreciable difference was found to occur, and even if the membrane was purposely damped it did not appear to aid the action except by bringing it closer to the metal, so that aqueous vapour is not apparently an active agent in producing these reactions. In an atmosphere of hydrogen the action takes place as it does in air. Carbon dioxide, under ordinary conditions, does produce an effect, but this probably arises from its action on the zinc plate. Alteration of temperature, on the other hand, produces very marked effects; increase the temperature, and the action of the zinc is greatly increased; for instance, two similar plates, both wrapped in tinfoil and the plates separated from the zinc by means of a cardboard frame. One was placed on a water-bath and exposed to a temperature of about 70° C., and the other placed in a vessel of ice at 0° C. After five hours the one which had been exposed to the high temperature had given a black picture, while the one at the low temperature gave a picture barely visible. A similar experiment was also made with nickel, and this gave, after heating to about 70°, a good dark picture, but the corresponding experiment, when the metal was kept at 0° for five hours, gave no picture at all. Aluminium, when treated in the same way, gave at the higher temperature only a faint picture, but at the lower temperature, even after two days, no picture at all. It has already been mentioned that this action of the metals cannot pass through even thin glass, nor can it pass through selenite, nor a layer of gum arabic, nor one of paraffin. Glass being impervious to the action, renders it somewhat difficult to try satisfactorily the action exerted by liquids, but celluloid may be used for this purpose; also mercury may be covered with a thin layer of water, and then its action entirely ceases. The action of certain salts in the dry state has, however, been tried by soaking non-glazed paper in different solutions, drying it, and then placing it, either with or without a screen, between the zinc and the photographic plate. These experiments have given some interesting results; for instance, paper soaked in the following solutions, alum, potassium chromate, zinc sulphate, and quinine sulphate, renders the paper quite opaque to the action of the zinc.

No doubt this action of alum accounts for certain papers not allowing the action to pass through them. Some singular developments of this subject have arisen from experiments made while examining the metals. A piece of polished zinc was coated with copal varnish with the object of ascertaining whether the action would take place through such a medium, and in case it did, as it was thought at the time, of demonstrating that the action could not arise from metal vapour. The experiment was quite successful; the photographic plate, notwithstanding the varnish, was strongly acted on. The experiment was repeated several times, and always with the same result; but the pictures seemed rather too good, darker than those given by the zinc alone, and on trying the copal on plain glass instead of on zinc it proved that effects apparently similar to those obtained with zinc were produced. What is known as picture copal answers very well for these experiments. That prepared by Winsor and Newton has been used. This is painted or poured on a clean, warm glass plate, and allowed to harden completely. The plate can then be used in the same way as the zinc plates. If a photographic plate be laid on the hardened varnish for two to seven days, a picture of the varnish, showing the streaks it happens to have dried in, is produced. If screens be interposed so as to prevent contact between the copal and the plate, the action still occurs, and, in fact, readily passes down a tube 1 inch long. Therefore, as with the zinc, any figure cut out in an inactive screen is readily produced on the photographic plate. Substances which are transparent or opaque to the action of the metals seem to act in the same way towards copal. It is rather more active than zinc. Glass is perfectly impervious to its action, but celluloid, gutta-percha tissue, and gelatin it permeates more readily than zinc does. The activity of the copal varies considerably under different conditions. If gum be sprinkled on a glass plate and then fused, it is not so active as when picture varnish is used. If the solid gum be dissolved in pure alcohol and ether, and applied to a glass plate as before described, it is far more active than after fusion. Heating it in a water-bath for a considerable length of time certainly deprives it of a considerable amount of its activity; but this can be revived by wetting it with ether and allowing it again to dry at ordinary temperatures. As with zinc, increase of temperature increases its activity to a great extent. Experiments similar to those with zinc were made with copal. A coated glass was exposed to a heat of about 70°, and a similar one was kept at 0°. This one after five hours gave only a faint picture, whereas the heated one gave a dark picture, and a considerable amount of action took place even through the cardboard screen. Many other bodies of the same nature as copal act in the same way. This has been proved to be the case with Damar and with Canada balsam, but copal seems to be the best representative of the class. Certain gums, such as gum arabic, gum senegal, have not the property of acting in this way. There are, however, a large number of bodies which have the power of acting in a manner similar to the copal; one of these is wood, and it possesses a very considerable amount of activity. Any ordinary smooth piece of wood laid on a photographic plate will act like zinc in impressing its picture on the plate.

A section of a young larch tree gave a good picture, showing clearly the different rings and the layer of bark, which was the darkest part of the picture. The same section, when a film of gelatin was interposed between it and the plate, still gave a good picture. Wood which is thoroughly dried and hardened is also able to act in the same way.

A piece of mahogany 3·5 m.m. thick, which had been in this form for at least thirty-five years and been carefully preserved in a dark cupboard, gave after a week's exposure a good picture, and the bottom of an old cigar-box acted equally well. Bodies such as straw, hay, bamboo, oiled silk, and, no doubt, many others, act in the same way. If wood, however, be painted with melted paraffin, it is no longer active. Ordinary charcoal also depicts itself on a photographic plate, but if it be heated for some hours in a covered crucible it loses this property. An ordinary piece of wood, if it be charred on one side by heating it with a Bunsen lamp, becomes remarkably active, as shown by placing it behind a screen with a pattern cut out. The action passes readily through different media, such as gelatin, tracing-paper, &c., vegetable parchment, &c., and the structure of the charcoal is shown, when the action has taken place, even through a sheet of vegetable parchment. Coal and coke, sulphur, sugar, on the other hand, exert no action of this kind. When trying whether a copy of a lithographic picture could be obtained by placing behind it a plate of zinc, some curious results occurred. It would seem that printer's ink in most cases is not capable of acting, like copal, on a photographic plate, but that there are many cases in which it is a remarkably active substance. Specially so is the ink used in printing many of the newspapers. The *Westminster Gazette*, for instance, is printed with an ink which very readily acts on a photographic plate. A portion of this paper with printing on only one side, laid with the blank side on the photographic plate, in a few days gives a remarkably black and distinct picture. If there be printing on both sides, then two pictures are obtained, the darker printing becoming most evident on whichever side it may be. Interpose a sheet, for instance, of gold-beater's skin, and still the picture is obtained. The *Standard* and *Daily Graphic* are also very active, and the *Times* only a little less so. The *Evening News* is only slightly active, and the *Morning Post*, *Pall Mall*, *Echo*, and *Daily News* have not the property of acting in this way; at least, those copies experimented with had not. An admission ticket to the Society of Arts laid on a photographic plate, the ink away from the plate, also gave a very distinct picture.

Another singular case of an action of this kind was met with when experimenting with the uranium salts. Not having a sufficient number of small clear glass bottles for a certain set of experiments, one of the compounds, the black oxide, was placed in a pill-box, believing that the action of the uranium would take place through the bottom of the box, and on developing the plate a dark circular space where it had stood was visible. The experiment was therefore considered very satisfactory, and, with different salts and for different objects, it was several times repeated. Ultimately it was forced upon one that the uranium salts acted more strongly when in pill-boxes than in any other way, and on placing a pill-box without any uranium salt in it on a photographic plate it was found that action had occurred, as shown by the dark circular space produced.

The experiment was repeated over and over again, with the result that most pill-boxes have the power of acting on a photographic plate. Both new and old pill-boxes from different sources were experimented with, and almost all of them found to be active. There are, however, exceptions, and these, it was noticed, were always the more expensive and elaborate boxes. On examining the structure of a pill-box it was found that it is usually made of what is known as strawboard, covered with a thin white paper; on separately testing these two materials it was apparent that the white paper was without action on the plate, and that the strawboard was very active and produced exactly similar effects to those produced by the active pill-boxes. The inactive ones proved to be made of white cardboard, which is not an active substance. Samples of strawboard from several different sources have been tried, and all found to be active, and when separated from the photographic plate by means of screens, like the copal and the zinc, it gives a clear action. Different substances of a like nature have been tried, such as brown papers, &c. Some of them are more or less active, but none more so than common strawboard. Mr. Bevan was good enough to examine a piece of this active strawboard, but was unable to find any material other than straw present. Writing paper and, as mentioned before, white cardboard, have not this power of acting on a photographic plate, but many kinds of brown paper and no doubt many other bodies have the property. Many of the boxes in which photographic plates are packed are made of strawboard, but as the action does not pass through glass, the plates are but little or not at all acted on; but if a plate be laid face upwards in one of these boxes and left there for a week, it will be very appreciably affected. If a small piece of glass be laid on the plate, it protects the film beneath, and shows clearly the amount of action which has occurred. If a box of this kind be painted inside with melted paraffin, this action does not take place. It happened that a few months before making the above experiments others were in progress in which black net was placed on a photographic plate simply to show clearly whether the plate had been acted on, and continually a reversed picture was obtained; this at the time could not be accounted for, but now the experiment was made of simply placing the black net on the photographic plate and leaving it there for some days; then on development a clear picture of the net was produced. The action is due to some material in the black dye, for white net does not act in the same way.

The action of the vapour from a few liquids on a sensitive plate has been tried. The plate was placed about half an inch above the liquid, and a screen, with holes cut in it, was fastened against the plate. Methylated spirit acted slightly on the plate; pure alcohol and ether had no action; benzene, coal-tar, crude wood spirit, linseed oil also, had no action, but turpentine and oil of cloves produced a slight amount of action.

Such, in outline, is an account of the experiments which have already been made on this subject. One point has led on to another, and some of the results were so unexpected that the experiments had to be repeated many times before full credence could be given to them. On the present occasion it is desired to do little more than record facts; further experiments, it is hoped, may lead to explanations not now evident. The supposition that all these active substances, the metals as well as organic bodies, give off a vapour capable of acting on a photographic plate, naturally suggests itself, and that copal does give off a vapour which directly or indirectly is active there can be no doubt. At the same time, it is at least difficult to suppose that the activity of such a body as strawboard should, after the treatment it has undergone, give off at ordinary temperatures sufficient vapour to produce the effects described, and the same applies to old dry wood, &c. Still more interest attaches to the action of the metals; do they emit a vapour so delicate in constitution and in such a quantity that it can readily permeate celluloid, gelatin, &c., and produce a picture of the surface from whence it came, or is it a form of energy (possibly what has been called dark light) that these bodies emit? Zinc kept and polished in the dark loses none of its activity. An experiment has been made with the object of reflecting the zinc action from glass. This did not succeed; whether this arose from the glass not being capable of effecting such a reflection, or whether a fortnight was not sufficient time to produce in this way a visible effect, is not known, but the experiment is being repeated. A photographic plate, suspended film upwards, over a copal plate, was acted on round the edges in the way one would imagine a vapour to act. A similar experiment is being made over a zinc plate. The action of glass proves that there is at least a marked difference between the action exerted by metallic uranium and that by zinc and other metals.

It should be stated that it is only the most sensitive photographic plates which, without extremely long exposures, give the results described. The Mawson plate has generally been used in the foregoing experiments, but the Ilford special rapid plate acts equally well, and Edwards's isochromatic snap-shot plates are particularly sensitive to the action of the uranium salts. Lumière's extra rapid are not so sensitive as the Mawson and Ilford plates, and still less sensitive are the same firm's plates for yellow and green, and for red and yellow. Other sensitive plates have not been experimented with.

ANALYSIS OF A RECENTLY DISCOVERED TOXINE SPRING.

By A. LIPP.

The spring occurs at Seeg, near Füseen, in the Bavarian Algau district, and has the local name Marienquelle. Since 1891 it has been successfully used for medicinal purposes. It is clear and colourless and has a temperature of 7° to 8° throughout the year.

A litre of the water contains :—

	Grm.
I	0·01487
Br	0·01178
Cl	1·45660
SiO_2	0·00650
N	0·09140
CaO	0·16050
MgO	0·06150
Fe_2O_3	0·00250

Sodium, lithium, aluminium, and potassium sulphates, borates, and phosphates occur in traces.—*Berichte*, xxx., p. 309.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending May 31st, 1897.

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

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

London, June 10th, 1897.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the past month was 0·85 inch; the average fall for the past 30 years is 1·83 inches, showing a deficiency of 0·98 inch, reducing the total excess for the year to 1·04 inches on an actual fall of 9·67 inches. All the rain this month fell on the last five days, with the exception of 0·12 inch, which was divided between the 4th, 5th, and 11th.

The results of our bacteriological examinations of 258 samples are recorded in the following table; we have also examined 69 other samples taken from special points either at the different filter beds, or at stand-pipes :—

	Microbes per c.c.
Thames water, unfiltered (mean of 26 samples)	2937
Thames water, from the clear water wells of five Thames-derived supplies (mean of 128 samples)	40
Ditto ditto .. .. highest	233
Ditto ditto .. .. lowest	10
New River, unfiltered (mean of 26 samples) ..	388
New River, filtered (mean of 26 samples) ..	44
River Lea, unfiltered (mean of 26 samples) ..	791
River Lea, from the clear water well of the East London Water Company (mean of 24 samples)*	68

* Two additional samples abnormal.

Instead of, as formerly, examining bacteriologically each water supply once a fortnight, we are now examining samples from each water supply daily. This is therefore a much more severe test of the adequate nature of the filtration from day to day, and the mean results of our microbial estimations cannot properly compare with results obtained at periods of a fortnight apart. Further, the samples we collect from the clear water wells of the Companies are immediately cooled to the temperature of melting ice, and this temperature is maintained till the plate cultivation is commenced not later than five hours afterwards, and it is continued at 21° C., for forty-eight hours, when the colonies are counted. Such a severe examination of the process of filtration at once enables us to warn the companies if any of the filter beds are working abnormally, and already we are in a position to say that the average bacteriological quality of all the London waters has been greatly improved since the commencement of this year.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 3rd, 1897.

Professor Dewar, F.R.S., President, in the Chair.

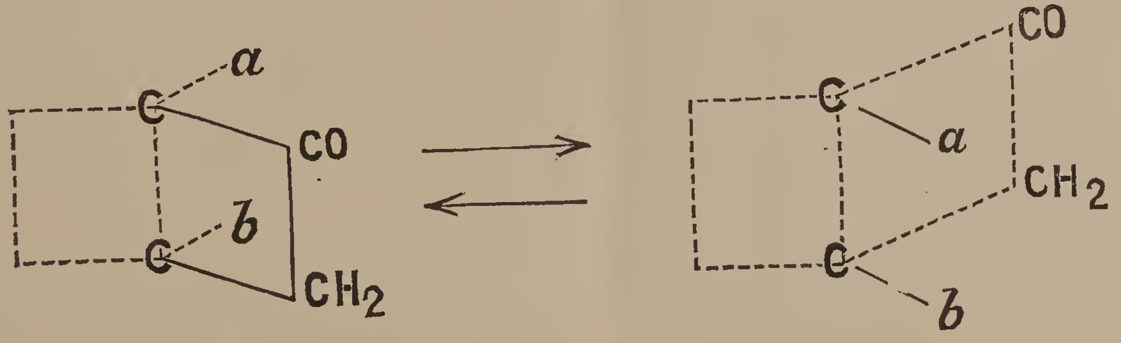
(Concluded from p. 296).

*69. "*Optical Inversion of Camphor.*" By Frederick Stanley Kipping, Ph.D., D.Sc., and William Jackson Pope.

It was shown some time ago (*Trans.*, 1896, lxiii., 548) that two optically active isomeric sulphonic chlorides of the composition $C_{10}H_{15}O\cdot SO_2Cl$ could be obtained from the product of the action of anhydrosulphuric acid on ordinary *d*-camphor; these two compounds differed only in optical and crystallographic properties, and it was therefore concluded that they must be regarded as optical antipodes.

This conclusion has been fully borne out by some recent work, in the course of which the properties of a considerable number of inactive compounds, prepared from inactive camphorsulphonic chloride, have been examined; it has thus been proved beyond doubt that these inactive compounds are composed of equal quantities of two enantiomorphous camphor derivatives, and that, consequently, either before or during sulphonation, the original *d*-camphor must be partly converted into its optical antipodes, *l*-camphor.

In the present paper, particular attention is drawn to this interesting case of optical inversion, as the intramolecular changes which take place appear to be entirely different from those which occur in the case of substances which contain asymmetric carbon atoms as constituents of an open chain. Although the constitution of camphor is still a matter for further investigation, it is now almost universally admitted that the skeleton of this substance consists of two closed carbon chains having two or more carbon atoms in common; further, a study of the chemical and optical properties of the various modifications of camphoric acid leads to the conclusion that each of the carboxyl groups in camphoric acid is united to an asymmetric carbon atom (Aschan, *Acta Soc. Scient.*, xxi., [5], 1—227). Admitting these two apparently well-founded assumptions, the conversion of *d*- into *l*-camphor requires that part of one of the closed chains, for example, the group —CH_2—CO—, should change places with the two atoms *a* and *b*, as shown in the following scheme.



As this view is based upon the two assumptions already stated, the matter is discussed from other standpoints, and it is finally concluded that the changes which occur in the optical inversion of camnhor are of the nature already suggested.

*70. "*Derivatives of Camphoric Acid.* Part II. *Optically Inactive Derivatives.*" By F. Stanley Kipping, Ph.D., D.Sc., and William Jackson Pope.

The optically inactive, externally compensated derivatives of camphoric acid described in this paper were prepared initially from ordinary *d*-camphor by first converting this substance into the approximately inactive camphorsulphonic chloride (*Trans.*, 1893, lxiii., 547) or camphorsulphonic bromide (*Trans.*, 1895, lxvii., 354), from which inactive π-chlorocamphor and racemic π-bromocamphor were then obtained by the method previously employed (*Trans.*, 1895, lxvii., 371).

Inactive π-chlorocamphoric acid, $C_{10}H_{15}ClO_4$, prepared by oxidising inactive π-chlorocamphor with nitric acid, crystallises in flat plates or in prisms, and melts at about 194—195°; its *anhydride*, $C_{10}H_{13}ClO_3$, melts at 193—194°.

Inactive π-bromocamphoric acid, $C_{10}H_{15}BrO_4$, obtained in a similar manner from racemic π-bromocamphor, is a crystalline powder melting at about 203—204°; its *anhydride*, $C_{10}H_{13}BrO_3$, melts at 155—156°.

These four externally compensated substances resemble the corresponding active compounds (Kipping, *Trans.*, 1896, lxix., 913; Lapworth and Kipping, *Trans.*, 1897, lxxi., 1) very closely in general properties, but the inactive anhydrides are not easily obtainable in large crystals, active π-bromocamphoric anhydride forms large monosymmetric crystals, measurements of which are given.

Inactive trans-*π-camphanic acid*, $C_{10}H_{14}O_4$, is obtained by the decomposition of the sodium salt of π-chloro- or π-bromocamphoric acid. It crystallises from water in monosymmetric prisms, which contain one molecule of water of crystallisation, but from ethylic acetate it is deposited in anhydrous, monosymmetric, six-sided plates; the anhydrous crystals change in crystalline form at about 130° and melt at 164—165°, namely, at the same temperature as the anhydrous active acid.

Active trans-π-camphanic acid (*Trans.*, 1896, lxix., 929) has been further investigated, and has been found to exist in a number of different crystallographic modifications; it separates from cold water in hydrated prisms, very similar to those of the inactive acid in all respects, and it is also deposited in hydrated monosymmetric prisms from its solution in ethylic acetate; when crystallised from benzene, it affords either well-defined orthorhombic needles which contain one molecule of water of crystallisation, or a microcrystalline powder of the anhydrous acid, according to the conditions of the experiment. From a mixture of chloroform and light petroleum, it is deposited in large, transparent, anhydrous orthorhombic prisms which change in crystalline form at 100°.

The conclusions to be drawn from these and other facts bearing on the relation between the active and inactive trans-π-camphanic acids are discussed in the following paper.

Inactive cis-π-camphanic acid, $C_{10}H_{14}O_4$, is the principal product of the distillation of trans-π-camphanic acid. It crystallises in large, transparent, hexagonal plates, which are indistinguishable from those of the corresponding active acid (*Trans.*, 1896, lxix., 943) except in optical behaviour; the crystals of the active acid are circularly polarising, and all of one kind, whereas those of the inactive substance show either right- or left-handed circular polarisation. It is thus possible to separate this externally compensated cis-π-camphanic acid into its *d*- and *l*-isomeric components.

Inactive trans-*camphotricarboxylic acid*, $C_{10}H_{14}O_6$, is obtained when inactive trans-π-camphanic acid is oxidised with nitric acid; it crystallises from water in lustrous, transparent, monosymmetric prisms, which differ from those of the active acid (*Trans.*, 1896, lxix., 951) deposited under similar conditions in being anhydrous, and consequently also in crystalline form. It melts at 224—225°, whereas the active acid melts at 196—197°.

Inactive trans-*camphotricarboxylic anhydride*, forms transparent monosymmetric crystals which are remarkably similar to those of the active anhydride; it melts at 253—254° whether heated alone or with an approximately equal quantity of the active substance.

*71. "*Racemism and Pseudoracemism.*" By F. Stanley Kipping, Ph.D., D.Sc., and William Jackson Pope.

The data afforded by a comparison of the physical and crystallographic properties of the optically inactive substances described in the preceding paper with those of the corresponding active compounds (*Trans.*, 1896, lxix., 913), and a number of other facts collected during the investigation of various active and inactive π-derivatives of camphor, have led the authors to the conclusion that the present classification of externally compensated substances into (*a*) mere mixtures and (*b*) racemic compounds, requires modification.

It has been found that optically inactive substances which are not mere mixtures of individual crystals of each of the enantiomorphous components are either very similar to, or extremely different from, their isomeric constituents in all those properties more immediately connected with crystalline structure; no intermediate degree of similarity is, in fact, observable in any case where these properties have been thoroughly examined.

Such externally compensated substances fall, therefore, into two groups. Those which closely resemble the corresponding active compounds are called *pseudoracemic*, the name racemic compound being reserved for those of the other group, of which racemic acid is the classical example.

The subdivision of optically inactive compounds has, not only an experimental, but also a theoretical basis. It can be shown that, in accordance with the present theory of crystalline structure, optically active and racemic compounds cannot assume the same type of homogeneous crystalline structure, but that an externally compensated substance may form crystalline individuals extremely similar to, but still not identical with, those of its active isomerides; in the latter case, the crystals consist of mere intercalations of those of the active modifications, and the non-identity is the result of the disturbance set up by intercalation. It is to these substances that the term pseudoracemic is applied.

Definitions of pseudoracemic and of racemic compounds based on these considerations are given, and some of the properties of the two classes of substances are then discussed. It is pointed out that the melting point of an externally compensated substance does not afford conclusive evidence as to its nature at ordinary temperatures, inasmuch as changes in crystalline form frequently occur with a change in temperature, and a mere mixture may become a racemic compound, and *vice versâ* before the melting-point is reached; numerous experiments are quoted in support of this view. It is also concluded that solubility determinations are valueless as a means of deciding between the three classes of externally compensated substances.

The properties of a number of inactive substances described by Aschan, Emil Fischer, Liebisch, Wallach, and others are briefly discussed, and reference is made to a recent paper by Walden, which deals with the characteristics of optically active and racemic compounds.

DISCUSSION.

Dr. BONE enquired what was the practical criterion between a mixture of two optically active substances and a racemic compound proper, and whether there is any difference between the readiness with which the racemic and pseudoracemic forms can be resolved.

Dr. KIPPING said that, in the majority of cases, it is very difficult to distinguish between mixtures and racemic compounds except by crystallographic examination, but Liebisch's rule, that the density of a racemic compound is different from that of its optically active isomeride, if confirmed by further experimental data, might be made use of in many cases. Theoretically a racemic compound would probably be resolved into its components less readily than a pseudoracemic substance, but when using the methods at present known for the separation of externally compensated substances, it seems improbable that any general difference in this respect would be noticed.

*72. "*Note on some New Gold Salts of the Solanaceous Alkaloids.*" By H. A. D. JOWETT, D.Sc.

When hyoscine hydrobromide and auric chloride are mixed, either in concentrated, dilute, neutral, or acid solution, a red precipitate is formed which can be crystallised from a hot aqueous solution acidulated with hydrochloric acid. On analysis, the salt is found to be an additive compound of auric chloride with hyoscine hydrobromide [$B \cdot HBr \cdot AuCl_3$. When this experiment is conducted in the presence of a large excess of hydrobromic acid, a chocolate-coloured precipitate is formed which can be re-crystallised from hot dilute hydrobromic acid and forms chocolate-coloured prisms, which, on analysis, prove to be the auribromide of the base [$B \cdot HBr \cdot AuBr_3$]. Even when excess of hydrochloric acid is present the aurichloride is not formed. The analogous compounds of hyoscyamine and atropine were formed by similar reactions and resemble the corresponding salts of hyoscine in chemical and physical properties.

Experiments were made to determine whether the bromaurichloride of formula $B \cdot HBr \cdot AuCl_3$ was an isomorphous mixture of aurichloride and auribromide, in view of the evidence adduced by Hertz (*J. Am. C. S.*, xviii., 130) regarding the composition of the salt formed by mixing solutions of platinic chloride and potassium bromide ($K_2PtCl_4Br_2$). It was proved, however, that this view could not be adopted for the constitution of the gold salt, which must therefore be considered a true chemical compound.

*73. "*Production of Camphenol from Camphor.*" By J. E. MARSH, M.A., and J. A. GARDNER, M.A.

The authors have described (*Trans.*, 1897, lxxi., 285) the production of an isomeride of camphor, camphenol. This substance was obtained by the action of strong sulphuric acid on chlorocamphene, $C_{10}H_{15}Cl$. Camphenol is produced by the action of the same reagent on camphene dichloride, $C_{10}H_{16}Cl_2$, which is the immediate product of the action of phosphorus pentachloride on camphor. The same camphenol is apparently produced from both the isomerides of the formula $C_{10}H_{16}Cl_2$, obtained from ordinary camphor, and a satisfactory yield is obtained in both cases. The action of strong sulphuric acid on other chloro-derivatives of terpenes has been examined. In particular, turpentine dihydrochloride behaves in a manner very similar to the camphor derivative, but the nature of the product of the reaction has not yet been determined.

*74. "*Preliminary Note on the Oxidation of Fenchene.*" By J. A. GARDNER and G. B. COCKBURN.

Fenchene prepered from the fenchone of fennel oil by a modification of Wallach's method was oxidised on the water-bath by moderately dilute nitric acid (1 part strong acid to 1 part water). The oxidation was complete in three days. After distilling with steam, the acid liquid was neutralised with sodium carbonate and extracted with ether, to eliminate some insoluble oily matter. The alkaline liquid was now acidified and repeatedly extracted with ether. On evaporating the ether a syrup was obtained which gradually crystallised. The crystals were purified from oily matter by washing with chloroform, and after re-crystallisation from water melted at 207°; they proved to consist of cis-camphopyric acid. The oily substance, separated by chloroform, was distilled under diminished pressure. A considerable amount of decomposition took place, and an oil and a solid distilled over. The solid was crystallised from alcohol, and proved to be camphopyric anhydride (m. p. 187°).

The yield of camphopyric acid was about 9—10 per cent of the fenchene taken.

75. "*Apiin and Apigenin.*" By A. G. PERKIN.

In a preliminary notice upon this subject (*Proc.*, 1897, xiii., 53), some derivatives and decomposition products of apigenin were described; these, together with an account of further work upon this colouring-matter, are included in the present paper. The formation of phloroglucol and parahydroxyacetophenone, as the principal products of the gentle action of alkali upon apigenin, have been confirmed, and it is now shown that, at 200°, protocatechuic acid, parahydroxybenzoic acid, and phloroglucol are obtained in the same way. These results confirm those of Gerichten (*Ber.*, 1876, ix., 1124), except as regards the production of parahydroxyacetophenone, which is not mentioned by him. On methylation, apigenin forms a dimethyl ether, $C_{15}H_8O_3(OCH_3)_2$, yellow needles, m. p. 171—172°, which furnishes with alcoholic potash a potassium salt, decomposed by water, and with acetic anhydride a monacetyl derivative, $C_{15}H_7O_3(OCH_3)_2C_2H_3O$, colourless needles, m. p. 195—196°. The diethyl ether, $C_{15}H_8O_3(OC_2H_5)_2$, yellow needles, melts at 161—162°, and its monacetyl derivative, $C_{15}H_7O_3(OC_2H_5)_2C_2H_3O$, colourless needles, at 181—182°. As previously shown, apigenin contains three hydroxyl groups, consequently one is in the ortho-position to a carbonyl group. Decomposed with alcoholic potash, the dimethyl ether yields anisic aldehyd, anisic acid, and a phloroglucol derivative, ethylparahydroxybenzoic acid being formed from the diethyl ether under similar conditions.

These results, with the exception of the production of protocatechuic acid by means of alkali, point to a close relationship between apigenin and chrysin, $C_{15}H_{10}O_4$, the colouring-matter of poplar buds, which yields on decomposition phloroglucol, benzoic acid, and acetophenone. It is probable that apigenin is a hydroxychrysin.

This suggested relationship is borne out by the dyeing properties of the two colouring-matters, which show a close similarity. The formation of protocatechuic acid from apigenin appears to be the result of an oxidising action, for there is no evidence of a catechol nucleus in this substance. Further experiments upon its constitution are in progress.

In the previous communication (*loc. cit.*) the author erroneously assigned the discovery of the glucosoidal nature of apiin and the preparation of pure apigenin to Gerichten, instead of to Lindenhorn ("Inaug. Diss.," Würzburg, 1867).

76. "*Rhamnazin.*" By A. G. Perkin and H. W. Martin.

Rhamnazin was isolated from Persian berries by one of the authors and J. Geldard (*Trans.*, 1895, lxvii, 496), and shown to be a quercetindimethylether. The present investigation was instituted to determine the position of the methoxyl groups. On methylation it yielded quercetintetramethylether, and from this result, and other experiments described in the paper, it evidently contains no methoxyl group in the phloroglucol nucleus in the ortho-position relatively to the carbonyl group. By fusion with alkali at 200°, rhamnazin yielded phloroglucol and protocatechuic acid, and digestion with boiling alcoholic potash gave vanillin, vanillic acid, and a non-crystalline phloroglucol derivative. Oxidised by air in alkaline solution, vanillic acid and a similar phloroglucol derivative were obtained. No free phloroglucol resulted from either of these decompositions. Taking into consideration that though the dyeing properties of rhamnazin are extremely feeble, it must still be considered a colouring-matter, these results indicate that it has the constitution of a rhamnetinmonomethylether.

77. "*Experimental Verification of van 't Hoff's Constant in Very Dilute Solutions.*" By Meyer Wilderman, Ph.D.

In van 't Hoff's thermodynamic argument the solutions are assumed to be very diute, and the same assumption is made in the deductions from it of Planck, Riecke, Lorentz, Bolzmann, and others. The experimental verification in dilute solutions of van 't Hoff's law is therefore especially important. The freezing-point method has been worked out with greater accuracy for the purpose of this investigation (*Trans.*, 1895, lxvii., 1; Lewis, "On the Real and Apparent Freezing-point and the Freezing-point Methods," *Proc. Roy. Soc.*, 1896; *Zeitsch. fur Physik. Chemie*, 1896, xix., 233).

The author has determined van 't Hoff's constant in dilute solutions with thermometers graduated to 1/100th and 1/1000th of a degree respectively, simultaneously for a series of compounds, cane-sugar, alcohol, urea, acetone, aniline, phenol, dextrose, resorcin, maltose, milk-sugar, at converging temperatures above and below the freezing-points, using different parts of the scale of both thermometers. Small deviations only, from the theoretical value of 1·87, are found, due to the different sources of experimental error, van 't Hoff's constant being thus confirmed in dilute solutions.

78. "*The Isomeric Dibromethylenes.* By Thomas Gray, B.Sc.

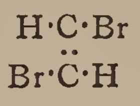
This paper contains a record of an attempt to prepare the stereo-isomeride of symmetrical dibromethylene. The following reactions are discussed:—(1) the reduction of tribromethane by sodium ethoxide; (2) the union of acetylene with bromine; (3) the reduction of acetylene tetrabromide; and (4) the addition of hydrogen bromide to bromacetylene.

By the first of these methods Tawildarow (*Ann.*, 1875, clxxvi., 22) obtained, in addition to $CH_2{:}CBr_2$, a liquid boiling at 157°, and having the formula $C_2H_2Br_2$. The author confirms the observation of Michael (*Amer. Chem. Journ.*, 1883, v., 192), and finds that the only product of this reaction, under varying conditions of concentration, is $CH_2{:}CBr_2$, and he attributes Tawildarow's observation to the formation of bromacetyl bromide by oxidation during the process of distillation.

The product of three other reactions is shown to be in every case the same symmetrical dibromethylene—

$$(CHBr{:}CHBr),$$

boiling at 110°. The author considers that the formation of this substance by the fourth method, and the probable instability of the *cis*-modification, which should result from the second reaction, point to the formula—



$$\begin{array}{c} H{\cdot}C{\cdot}Br \\ \ddot{} \\ Br{\cdot}C{\cdot}H \end{array}$$

as representing the structure of the symmetrical dibromethylene at present known.

SOCIÉTÉ D'ENCOURAGEMENT POUR L'INDUSTRIE NATIONALE.

May 14, 1897.

President, M. Mascart.

"*Art Bronze Castings.*" By M. Maglin. By using a mixture of gelatin, glycerin, and glucose, M. Maglin is able to make a complete mould of a statue in two pieces, owing to the flexibility of this substance. Perfect castings can be reproduced giving all the minute detail of the original.

M. Emilio Damour presented to the Society a laboratory form of regenerative furnace enabling temperatures of 1300° and 1400° C. to be attained. The furnace burns gas, and is made to heat muffles as large as 35 c.m. × 14 c.m. × 10 c.m. up to this high point.

May 28, 1897.

This meeting was also held under the presidency of M. Mascart.

The thanks of the Society were given to the various donors of books.

M. Joly was nominated a member of the Council.

A paper, accompanied by numerous experiments, was read by M. H. Le Chatelier, on "*Grisou*," its nature, and the means of preventing accidents. This paper will be published in full in the *Bulletin.*

CHEMICAL AND METALLURGICAL SOCIETY, JOHANNESBURG.

April 17, 1897.

At the adjourned discussion on Prof. Christy's paper on "*The Solution and Precipitation of Cyanide of Gold,*" Mr.

Butters criticised the method of precipitation proposed. He found it very difficult, he said, to make a University man realise the difficulty of carrying on, on a commercial scale, the operations which may be successfully done in the laboratory; he himself dealt with very many tons of ore per month, nearly 100,000, and he got his gold all right, but he could not succeed with this process.

Mr. L. Ehrmann then read a paper on the "*Precipitation of Gold from Cyanide Solutions*," in which he describes a series of experiments carried out by him with zinc, and zinc coated with copper, for precipitating the gold, and in every case he found that the return was higher when the zinc-copper couple was used. Hot treatment accelerated the precipitation to a very considerable degree, but the practical difficulty of heating 1000 tons of liquor a day up to 175° F. will probably prevent its adoption.

A paper on "*Liquation in Cyanide Bars*" was then read by Dr. Stockhausen. He finds that samples taken from different parts of the same bar of gold from the MacArthur cyanide process give widely different results, owing to liquation or want of homogeneity of the mass. This very unsatisfactory result is due to the neglect of stirring the molten metal before casting the ingot; dip samples and drillings also give very different results, and he comes to the conclusion that, to arrive at correct results in assaying "cyanide" gold, the only way is to take samples, after stirring, when the metal is in the molten state.

OBITUARY.

PROFESSOR FRESENIUS.

The present month must be viewed as an epoch in the history of chemistry. Dr. C. Remigius Fresenius has joined the majority. To estimate what we owe to the late head of the Wiesbaden School, we need merely imagine ourselves engaged in estimating phosphoric or even sulphuric acid by the methods of the present day, as compared with those of forty years ago as laid down by experts of high and well-earned reputation. We are far from asserting that all the niceties and improvements which have been latterly introduced into the practice of the laboratory are due to the work of Fresenius; but we know to what an extent he has been, year by year, our guiding soul. He and his pupils have taught us how to find, in a specimen submitted for examination, what really exists, and—what is certainly in many cases not less important—to avoid finding what is not present, and thus to escape founding erroneous theories.

Still we must gratefully own that Fresenius had to a great extent completed his work. For the last few years his labours had mainly ceased. His sons, Dr. Heinrich Fresenius, Dr. W. Fresenius, and his son-in-law, Dr. Ernst Hintz, have been carefully trained to follow in his steps, and we feel confident that the Wiesbaden School of Chemistry will continue to do good and useful work. To the best of our knowledge the *Zeitschrift für Analytische Chemie* will continue to enjoy the co-operation of the numerous able chemists who have heretofore contributed to its pages.

NOTICES OF BOOKS.

City and Guilds of London Institute for the Advancement of Chemical Education. Report to the Governors. March, 1897. Gresham College, Basinghall Street, London, E.C.

This Report is minute, and on the whole satisfactory.

The constitution of the Institution is somewhat complex. There is a list of Governors, including the President (H.R.H. the Prince of Wales); a body of Vice-Presidents, some of whom hold their position *ex officio*, such as the Presidents of the Royal and the Chemical Societies and the Chairman of the Society of Arts, a number nominated or appointed by the Corporation and by the principal Companies. As the nominees or representatives of the Goldsmiths' Company, we notice the names of Mr. G. Matthey, F.R.S., F.C.S.; Sir F. Bramwell, F.R.S.; Sir Frederick Abel, Bart., K.C.B., D.C.L., F.R.S.; and many other gentlemen widely known in scientific and technical circles.

The Council is a distinct body, though including not a few of the same names.

Then follow the Executive Committee, in which we meet—we may say welcome—not a few of the members of the former bodies.

Lastly, comes the Staff of the Institute's Colleges, including, on behalf of the Central Technical College, Prof. H. E. Armstrong, Ph.D., F.R.S.; F. S. Kipping, Ph.D., D.Sc., Assistant at the Research Laboratory; G. S. Moody, D.Sc.; and W. L. Pope, Instructor in Crystallography.

In the department of applied chemistry we find Prof. Raphael Meldola, F.R.S., F.C.S., beside three assistants.

It does not appear with quite sufficient clearness what are the duties or functions of these Boards.

It appears that on April 22nd, 1896, a communication was received from the Mercers' Company requesting the Governors to appoint a Special Committee to inquire into the expenditure of the Central Technical College of the Institute, with especial reference to the results attained. The Special Committee appointed consisted of the Lord Chancellor, six engineers, six chemists (using the latter term in the acceptation which it bears in France, Germany, &c.), four members of the Technical Education Board of the London County Council, one member of the last Royal University Commission, and twelve others. The results of the Report were very satisfactory. The conclusion was that the work in the College had been eminently successful and fully commensurate with the expenditure, and that its objects are well deserving of every support and encouragement that the Corporation and City Companies of London can give them.

The various Companies and other bodies who support the Institute have distinctly expressed themselves satisfied with the work as carried on. The gross cost per student for the years 1894 and 1895 has been £54, whilst the cost per student at the Zürich Polytechnic is about £59; at the American Institutions from £60 to £63, and at the Royal College of Science about £67.

Alumni Report of the Philadelphia College of Pharmacy. May, 1897, vol. xxxiii., No. 8.

The contents of this number begin with a short biographical sketch of the *honour* students of 1897. Then follows a brief account of the sixth Pharmaceutical Meeting of the Session 1896-1897, at which there were discussions on ointment of mercuric nitrate, the analysis of "Gelsemium," and a contribution on "The Presence of Starch and Strontium Sulphate in Opium, and their Influence on Assaying," in which we find the curious statement that, though starch has been often found in opium in quantities varying from a trace to 8 per cent, it should not be considered as an adulterant.

The rest of the number contains accounts of the annual meeting, reception, &c., and a list of the graduates of the year.

A Text-book of Chemistry. Translated into Chinese by Jas. B. Neal, M.D.

We have received from the English author, Prof. Clowes, a most interesting publication, hailing from the Flowery Land. It is a text-book of chemistry, printed throughout in Chinese characters, being for the most part a translation of Clowes's "Analytical Chemistry," the only exception being the third chapter, which has been taken mostly from Fownes's "Manual of Chemistry." The book is intended simply for laboratory use. It is the translator's firm conviction that only by practical work in the laboratary can a knowledge of chemistry be gained, which will be more than a mere learning by *rote*, and especially so in the case of Chinese students.

The elements are, with four exceptions,—viz., potassium, calcium, zinc, and arsenic—called by the names or characters adopted by Dr. Fryer: these four exceptions are so frequently met with in Chinese medical works that it was thought best to adhere to the terms used by Dr. Kerr, to prevent the confusion which would inevitably arise through the use of two sets of names.

CORRESPONDENCE.

THE DISCOVERY OF OXYGEN AND THE "ENCYCLOPÆDIA BRITANNICA."

To the Editor of the Chemical News.

Sir,—In spite of the indisputable fact that oxygen gas was first isolated and recognised as a supporter of combustion by the Rev. Dr. Joseph Priestley, on the 1st of August, 1774, French writers on the history of chemistry have persistently claimed the honour of this discovery for Lavoisier. This unhappy attempt to transfer credit from an English man of science to a French one would not have received the support of Lavoisier himself, whose immortality in the annals of chemistry does not need to be magnified by mendacious claims.

I have grown accustomed to this perversity on the part of the French; but imagine my surprise when I found that peculiarly English work the "Encyclopædia Britannica" coolly perpetuating this inaccuracy for the benefit of its Anglo-Saxon readers. In the ninth edition, under the caption "Alchemy" (vol. i., 1878), are the following paragraphs:—

"Lavoisier, who by discovering oxygen destroyed the theory of Stahl."

. . . "and finally in disengaging from the red-oxide of mercury oxygen gas, that Proteus which so often eluded the grasp of the alchemists, till at last it was held fast by the subtle analysis of Lavoisier" (page 462).

After I had recovered from the shock at seeing these statements in that monument of English erudition, I turned to the end of the article on alchemy to ascertain the authorship; it is signed "J. A.," which the key at the close of the volume interprets "Jules Andrieu." *Hinc illæ lacrymæ!* Why the Editor-in-chief sought for a Frenchman to write the article in question it is difficult to conceive. Were there no Englishmen in 1878 competent to compile such an essay? And, having secured the article, were there no members of the editorial staff who had heard of Priestley and his discoveries in chemistry? Unfortunately for the staff, the articles "Chemistry" and "Priestley," in which the fact is correctly given, only appeared in later volumes.

Those curious in the matter will find the whole article on alchemy of interest, but not because it is judiciously written.—I am, &c.,

H. C. B.

ESTIMATION OF CARBON IN FERRO-CHROME.

To the Editor of the Chemical News.

Sir,—A complete and accurate analysis of ferro-chrome is not an easy thing to do. I am pleased, therefore, to notice Mr. Saniter's letter, because he has long been interested in the matter. The letter, however, indicates that he has confused the preliminary experiments and temporary method with the procedure finally adopted, viz., combustion with lead peroxide.

On page 243, col. 1 (Chemical News, vol. lxxv.) it is stated that "the mixture [PbO_2 and ferro-chrome] fuses, and there is the same need to quicken the oxygen to supply the absorption in the boat, but all else goes on *with comparative quietness and at ordinary temperatures*." The covered boat, previously mentioned, is necessary only with the lead chromate or copper oxide at the higher temperatures.

I have just finished a duplicate determination on 1·00 and 1·25 grms. respectively, and, on unwrapping the asbestos from the glass tube, find only a faint deposit immediately over the boat. With such large amounts of peroxide and ferro-chrome the reaction is, of course, more vigorous than it would be with Mr. Saniter's proportions. That his assays do not spurt causes no surprise, and one may justifiably suspect that the copper oxide is not greatly concerned in the matter when, under less favourable circumstances, assays do not spurt without it. The copper oxide may preserve the porcelain from the attack of the litharge by diluting it, as it were; but this is a very minor point: only the boat can be attacked, and with the peroxide alone we use them over and over again after re-heating in the muffle and pouring away the melt.

The complication then narrows itself down to this:—Mr. Saniter uses a mixture of copper oxide and litharge, and I use lead peroxide alone.

It should be noticed that Mr. Saniter's ferro-chrome must needs be ground fine in an agate mortar—a labour he has elsewhere endeavoured to avoid. It may be seen (p. 243, col. 2) that PbO_2 much more readily than CuO—or presumably than a mixture of CuO and and PbO—attacks the ferro-chrome. In this respect, then, it would be less troublesome to use the single reagent.

The comparative advantage of using litharge or the peroxide would favour the former if—to use Mr. Saniter's expression—it were "free from substances which might be given off and absorbed by the potash." So far we have found that, having once determined the blank of the peroxide, it may be relied upon to remain unchanged. The reaction $2PbO_2 = 2PbO + O_2$ seems to be nearly, if not altogether, completed before the subsequent reaction, $2PbO + C = CO_2 + 2Pb$,* is begun. It would be a slight advantage, then, if PbO could be used straightaway, but unfortunately PbO—perhaps the litharge variety in a less degree—absorbs CO_2 from the air, and particularly so if damp. It would be necessary, therefore, on using this reagent, to prepare it immediately before use, and to take the troublesome precaution to keep it perfectly dry, and practically out of contact with the air. Thus the complications, if great accuracy is a vital consideration, would seem to hamper the use of the mixed reagents.

I ought to state that I have not largely experimented with litharge. The previous considerations, founded on known properties of lead protoxide, and the fact that the peroxide as received from the dealers gave a small constant blank, led me to prefer the latter.—I am, &c.,

H. Brearley.

June 14, 1897.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxiv., No. 21, May 24, 1897.

Tools and Arms of the Age of Pure Copper in Egypt.—Prof. Berthelot.—The author gives a list of antique

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* The third reaction in the tube, which explains the need to quicken the oxygen, may be written $2Pb + O_2 = 2PbO$. An attempt is being made to substantiate these equations by direct experiment.—H. B.

articles sent him by M. de Morgon. They belong to the most remote ages of the Egyptian empire. They all consist of copper nearly pure, sometimes containing arsenic, but no tin, lead, or zinc. They were then succeeded by bronze and then by iron.

On various Liquids contained in Antique Vases.—Prof. Berthelot.—Two of these liquids have been forwarded to the author by Th. Hubert, custos of the Archæological and Ceramic Museum of the city of Reims; they seem to belong to the Gallo-Roman epoch. They have been extracted from a glass bottle, and consisted of an aqueous liquid covered by fatty matter, chiefly liquefied. The solid portion consisted of stearic and palmitic acids accompanied by a neutral fatty matter. The aqueous matter consists of a mixture of volatile acids with watery vapour ($C_n{\cdot}H_{2n}O_2$), and of fixed acids ($C_nH_{2n-2}O_4$), mixed with acids ($C_nH_{2n-2}O_3$?). A perfectly distinct specimen was obtained from a Syrian tomb. It was merely water with small quantities of calcium bicarbonate chloride and traces of nitrates. It is apparently water of infiltration. Observers should mistrust the accidental introduction of water by infiltration into antique vessels.

Action of Light upon Gaseous Mixtures, especially Mixtures of Chlorine and Hydrogen.—Armand Gautier and H. Helier.

On the Sojourn of General Poncelet at Saratow.—Germain Babst.—This paper, though placed under the heading "History of the Sciences," is merely a fragment of the history of the retreat of the Grande Armée.

New Improvement of the Grisometer.—M. Grehont.—The new model is constructed of stout glass cylinder, with two concentric plates of sheet nickel. It is charged with soda-lye free from Cl at about 15 per cent NaOH. The silver-voltameter is universally recognised as the most accurate voltmeter.

The External Surface of Cast-iron Raised to a Red Heat Converts Carbonic Acid into Carbon Monoxide.—M. Grehont.—The author infers from his researches that we must abandon heating rooms by walls of cast metal heated to redness.

Reflection of Light by a Long and Narrow Surface.—M. Gouy.—MM. Nichols and Rubens, when operating with thermic rays of great wave-length (24μ) have found that a long narrow band of silver reflects these radiations whilst polarising them perpendicularly to the length of the band, whence there results an interesting approximation to electric waves.

An Antianodic Phosphorescent System, and on the Anodic Rays.—C. Maltézos.—The phenomena observed indicate the existence under certain conditions of anodic rays which provoke the phosphorescence of glass, visible and invisible, and which most generally are diffused or which do not reach the glass.

Properties of certain Radiations of the Spectrum.—Gustave Le Bon.—A reply to the paper by Prof. Becquerel, and his objections to his hypothesis of "black rays."

Precipitation of Zinc Sulphide for the Determination of that Metal.—J. Meunier.—All chemists who have been concerned themselves with the determination of zinc know the difficulties of collecting on a filter zinc sulphide precipitated by ammonium sulphide. The filtrate is turbid and the filtration is soon stopped. To the solution of zinc, which is properly luke-warm, he adds ammonia, and when the precipitate of zinc oxide is formed he continues to add this reagent, but cautiously, and passing in sulphuretted hydrogen bubble by bubble, ceasing as soon as the precipitation of the zinc is complete.

Remarks on the Formation-heat of Sodic Acetylene.—M. de Forcrand.—A thermo-chemical paper, not suitable for abstraction.

New Compounds of Pyridine, Piperidine, and Quinoleine with the Metallic Salts.—Raoul Varet.—The compounds described are pyridine, bromocuprite, iodozincate, cyanozincate, bromocadmiate, and bromonickelate.

Solubility of Ecgonin.—Oechsner de Coninck.—The author gives the solubilities of ecgonin in 25 solvents.

Comparative Study of the Quotients of Acids and of Fermentation observed during the Ripening of Fruits.—C. Gerber.

Denaturation of Alcohol.—Ernest Barillot.

MISCELLANEOUS.

The Philadelphia Museums.—This institution is in a measure similar to the Imperial Institute. It is divided into several departments—that of Foreign Manufactures has for its object the showing to the American manufacturers what their foreign competitors are exporting. There is a large collection of all kinds of goods, each sample being accompanied by the manufacturer's price. One great innovation which we should be very sorry to see introduced into England, is the analysis and reporting on of all raw products sent, entirely free of charge, the Institution being supported by the public funds. We hope the city also helps to support the analytical chemists who must be adversely affected by this action on its part.

Inauguration of the Monument Erected to the Memory of Jean Servais Stas.—After the death of Stas an international commission was constituted, and an appeal was made to the scientific men of all countries, with the object of perpetuating the name and works of this illustrious chemist. With the funds collected the committee have already raised one imperishable monument to his memory—a complete edition of his works. But the three volumes of which this consists appeal more or less to the *élite*; so it was decided that a monument of this man, who by his genius rose from the ranks, should be erected, accessible to all. J. S. Stas first studied at the Faculté de Medicine at the University of Louvain, and from there went to Dumas' laboratory. It was here that, under the direction and with the collaboration of his illustrious master, he made his researches on the atomic weight of carbon, and wrote his "Memoire sur les types chimiques." Some years afterwards he was appointed professor of chemistry at the Military School at Brussels, but he worked under great difficulties. The Government refusing even to complete the laboratory, Stas was constrained to defray the expenses out of his own pocket. In 1860 he wrote to an intimate friend: "To continue my researches I have to make such sacrifices that I am reduced to a condition bordering on poverty." He was offered help by Liebig, but was too patriotic to accept it from Germany, till at last his own Government, recognising the value of his work, made him a grant of 6000 francs, and it is to him and his persistent efforts that the present position of Science in Belgium is due. We cannot now follow him through his long and great career; by his nobility of character, his rare intellect and intelligence he inspired affection and commanded respect from all who knew him, and his work, better than empty titles, will keep his memory green.

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.

Marking Inks.—I should be greatly obliged for information as to whether there is a chance of obtaining a book, or one or a series of reports upon the subject relating to manufacture of the latest marking inks, especially vegetable ones. There are one or two societies in France dealing with the subject, but I do not know whether they issue any reports or books on that subject; if so, I should be glad to learn how they are to be obtained.—Sulpho.

INDEX.

END OF VOLUME LXXV.