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VOLUME LXI.

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No. 1571.—JANUARY 3, 1890.

THE LONG-CONTINUED ACTION OF THE ELECTRIC DISCHARGE ON IODINE.*

By C. LUEDEKING, Ph.D. (Leipzig).

SOME time ago, the author attempted the study of the effects of the electric discharge on iodine vapour, when continued over a long space of time. The researches of V. Meyer showed that with increasing temperature the vapour density of iodine becomes rapidly less than what is demanded by theory, finally reaching two-thirds of the theoretical value; a fact explained by the supposed partial dissociation of molecular into atomic iodine.

Later, J. J. Thomson (*Proc. Royal Soc.*, vol. xlii., pp. 343—345) showed that the silent discharge produces the same phenomena of anomalous densities that were observed by V. Meyer for higher temperatures. Several hours of time were necessary for the vapour to regain its normal density.

It was desired by the author to act upon the vapour of iodine, through a long period of time, by means of the electric discharge, and subject the result to analysis, with a view to establishing, if possible, any changes brought about.

Four Grove cells, of Browning's make, were used as electro-motive force. The circuit was passed through a Ruhmkorff coil, capable of giving sparks two inches long by this arrangement; the wires of the coil were connected with heavy platinum wires, sealed in a small heavy glass tube, with their ends opposite, and $\frac{1}{2}$ inch apart from one another. In this tube, 0.036 gm. of iodine was sealed hermetically. By gentle heat it was then vapourised, in part; the contents assuming the appearance of an intensely deep violet colour. The spark was now passed incessantly for three weeks, day and night, and the character of the light phenomena watched as carefully as possible. As the experiment advanced, the colour of the contents of the tube gradually changed, losing the rich deep violet tint that it had at first, very much resembling bromine vapour in appearance, and passing through this stage, becoming more and more faint, until, at the end of the afore-mentioned time, the tube was entirely colourless, and evidently all iodine had disappeared. What had become of it?

When reading Mr. C. P. Smyth's Address before the British Association, I recalled these experiments of mine, that had been made some time ago. His experiences are quite analogous to my own. In 1880, his iodine truly showed 148 iodine lines, and 3 exceedingly faint reproductions of the chief hydrogen lines; "Yet, in the present

year," he goes on to say, "there is not one iodine line left in that tube, and its spectrum range is filled with nothing but both high and low temperature hydrogen lines of astonishing brilliancy, while of the large amount of iodine granules hermetically sealed into the tube in 1878, only a very small amount of apparently inert dust is now left." Further, he states:—"Whether this change is an infinitesimally small part of the progress of everything to turn into hydrogen, and for assisting thereby the whole solar system to explode some day into a so-called and spectroscopically bright lined hydrogen star, I will by no means weary the Section by enquiring now."

It is clearly expressed that iodine has disappeared from a certain tube; that, whereas this tube contained at first only faint indications of hydrogen, it, after the disappearance of the iodine, showed the presence of this element in remarkable brilliancy or amount. The inference must be that iodine has been decomposed and that hydrogen is present as product of decomposition.

As our experimental results are similar in respect to disappearance of iodine, it will be of interest for me to describe my analytical manipulations of the contents of my iodine tube, and to show what my conclusions necessarily were.

As stated, the iodine had disappeared entirely from my tube. The platinum poles in the tube were much corroded and roughened; during the discharge, the ends were constantly at a bright red heat; the spark itself had a livid appearance, was uncertain in its course, changing frequently. The sides of the tube were affected as if by hydrofluoric acid, and there was in the tube what seemed to me also only a small amount of dust.

The tube was opened under water by nipping off the end; there was a partial vacuum, the water entering and filling it about one-fifth, by a rough estimate. I inferred at the time that the oxygen of the air, originally contained in the tube, had disappeared, and that what was left was nitrogen. This result is contrary to what we should expect had hydrogen been formed by dissociation of the iodine. The confined gases would have been under a pressure.

The contents of the tube were thoroughly extracted by water, the solution so obtained made slightly alkaline, and sulphuretted hydrogen passed to saturation. After expulsion of the gas, and slightly acidifying with nitric acid; nitrate of silver was added, and the precipitate filtered, washed, dried, and weighed. The quantity of precipitate produced was nearly equal to what theory requires for iodide of silver; it weighed 0.061 gm.

Evidently, then, in my experiment the disappearance of the element iodine was not due to any other cause than its uniting with the constituents of the glass. Under

* A Paper presented before the St. Louis Academy of Science.

the influence of the electric discharge, iodine certainly acquires superior chemical affinities, attacking the substance of the glass, and forming iodides, and, from the disappearance of one-fifth of the volume of gas, I should say, also some iodates. To meet this eventuality, I reduced by sulphuretted hydrogen previous to precipitation.

The changed brilliancy of the spectral hydrogen lines that Mr. Smyth observed must, then, it seems to me, be attributed to another cause than a generation of hydrogen by a decomposition of iodine. First of all, it is certain that the changed condition of the tension in the tube has something to do with it.

I determined to decide the matter experimentally. An excess of iodine was sealed up in the same kind of tube that I used above. On passing the discharge at the ordinary temperature, only faint indications of hydrogen were observed in the spectroscop. The tube was then heated gently, so that a great part of the iodine was volatilised. As the temperature rose, and the iodine vapour became more and more dense, to my surprise the hydrogen blazed in the spectrum with remarkable brilliancy. On cooling, the spectrum slowly changed back to its original appearance; hydrogen was again only faintly perceptible. It was clear then why the hydrogen lines in Mr. Smyth's tube should become so brilliant after the disappearance of the iodine. This latter is capable of binding hydriodic acid, which is the form in which the hydrogen is introduced into the tube. When by the process of action of the iodine on the walls of the glass tube it becomes united with alkalis, this hydrogen, finally, is liberated entirely, and, *instead of an iodine tube, we have a hydrogen tube developed.*

On taking a tube containing iodine in an atmosphere of hydrogen, I found that at first the hydrogen lines were very bright at ordinary temperatures. However, after a short time, and on continued passage of the spark, the lines became more and more faint, and finally scarcely perceptible. On then heating the tube, the hydrogen lines became very brilliant, and on cooling again disappeared almost entirely. On opening such a tube, dense fumes of hydriodic acid were emitted.

These experiments I think show conclusively: firstly, *the cause of disappearance of iodine in tubes on long-continued sparking*; and, secondly, *why the iodine lines are replaced by hydrogen lines during that process.*

I shall probably be in a position to make further communication on the sparking of iodine in the near future.

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THE ACTION OF ACIDS ON LITMUS.

By J. E. MARSH.

THE nature of the change which blue litmus undergoes when treated with acids has not been very satisfactorily explained. The change from blue to red is supposed to be due to the freeing of a red-coloured acid from a blue-coloured alkaline salt. Whatever the cause may be, there are some phenomena in connection with the reaction which are not without interest.

It has been noticed by occasional observers that some acids, under certain conditions, do not affect blue litmus. These observations have not received any special notice, since they are not generally mentioned in modern standard works. From these observations, and others which I have made myself, it appears that in general an acid, to affect blue litmus, must be more or less dilute; in other words, water is necessary for the particular reaction, whatever it may be, which occurs when blue litmus becomes red.

Sir H. Davy, in his well-known investigation of chlorine, states that gaseous hydrochloric acid instantly reddens

the driest litmus-paper. On the other hand, Gore found that liquefied hydrochloric acid did not redden litmus. It is possible that Davy did not dry his gas as well as his litmus, for I have found that dry litmus-paper in hydrochloric acid, dried with phosphorus pentoxide, does not appreciably alter in colour for some time. Ordinary concentrated sulphuric acid does not redden litmus-paper, but imparts a more or less bluish purple tint to it; and the Nordhausen acid acts similarly. Pelouze, some fifty years ago, stated that acetic acid does not redden blue litmus. In fact, dry litmus-paper immersed in glacial acetic acid remains practically as blue as it was before. Propionic, butyric (normal and iso-), and valeric acids behave in precisely similar manner. On the other hand, fuming nitric acid and this acid, mixed with strong sulphuric acid, immediately redden litmus-paper. A striking lecture experiment consists in placing a piece of blue litmus-paper in distilled water, and another piece, after having been dried in a desiccator, in glacial acetic acid. The paper in the acid is then taken out and dropped into the water, when both the papers rapidly change from blue to red. Another experiment of even a more striking character, but less visible to a large audience, consists in writing with water on a piece of dried litmus-paper made from writing-paper. The superfluous water is removed by blotting-paper, leaving the writing perfectly invisible. On now plunging the paper into glacial acetic acid, the writing appears at once as a bright red on the blue ground of the rest of the paper.

These experiments serve to show that water is necessary for the action of acid on litmus. The apparent exception in the case of nitric acid is easily explained. Nitric acid is, of all ordinary acids, the one which most readily attacks organic matter, the action consisting in the introduction of the nitroxyl (NO₂) group, with elimination of water. Here, then, we have water liberated in the immediate neighbourhood of the colour, which is thus acted upon by a dilute acid.

THE APPLICATION OF DOUBLE PYROPHOSPHATES FOR THE ELECTROLYTIC SEPARATION AND DETERMINATION OF METALS.

By Dr. ALBANO BRAND.

THE consistence of a metal reduced electrolytically is greatly dependent upon the state of combination in which it is present in the electrolyte. The double salts of organic acids, especially oxalic acid, are peculiarly suited for the production of good deposits, as well as for the quantitative separation of many metals.

The double pyrophosphates, as G. Vortmann has shown, behave with dilute acetic acid very much like the double oxalates. The double salt in solution is split up by the acid, and a crystalline, probably acid, salt separates out in the faintly acid liquid. This similar behaviour of the two series of salts, to which Prof. A. Classen has drawn attention, induced the author to study the electrolytic behaviour of the double pyrophosphates.

Hitherto only the double salts of nickel, tin, and gold have been applied in galvanoplastics. Concerning the electrolytic behaviour of the phosphates the only existing document is a paper by Thomas Moore (CHEMICAL NEWS, 1886, p. 209).

General Behaviour of the Double Pyrophosphates in the Formation of Electrolytes.

On the addition of an alkaline phosphate to a metallic salt dissolved in water, there is formed, with few exceptions, a phosphate insoluble in an excess of the precipitant. But if a neutral solution of a metallic salt is mixed with sodium or ammonium pyrophosphate, there is

formed a precipitate which is more or less soluble in an excess of the precipitant, forming a double pyrophosphate. The behaviour of acid sodium pyrophosphate is similar. A portion of a recently precipitated phosphate is also re-dissolved by a solution of alkaline pyrophosphate.

The solution of sodium pyrophosphate, and consequently the solution of the double salt, have a basic reaction. If the latter is submitted to electrolysis, and if the metal is deposited, pyrophosphoric acid is set free and the solution becomes acid, *i.e.*, it approximates to the initial condition of a solution prepared with the acid sodium pyrophosphate. Some metals separate from this acid solution as readily as from a neutral liquid; in others, the nature of the deposit is altered or the separation of the metal ceases, and can be renewed only on a corresponding re-inforcement of the current.

The application of the double pyrophosphates would, in consequence, be limited to the first-mentioned cases if the solution could not be kept neutral or basic. But this is practicable, as the solutions of the double salts (with few exceptions, which will be mentioned below) bear the addition of ammonia or ammonium carbonate to any extent without becoming precipitated. Soda-lye generally occasions precipitation.

In consequence of the possibility of keeping the electrolytes, neutral alkaline chlorides can be used as well as sulphates or nitrates. The metals reduced from a strongly alkaline solution, and from a pyrophosphate, are generally of an equally good condition.

The addition of ammonia or ammonium carbonate is further important, as it renders an excess of sodium pyrophosphate superfluous. If to a neutral saline solution there is added so much solution only of sodium pyrophosphate as is required for the formation of the pyrophosphate, the salt which has been separated dissolves on the addition of ammonium or ammonium carbonate in all cases where the solution, in an excess of the precipitant, supported the addition of these reagents without becoming precipitated.

The soluble double pyrophosphates bear also, without precipitation, the addition of ammonium oxalate—a behaviour which is of value in some cases.

Dilute acids precipitate probably acid pyrophosphates from the solutions of the pyrophosphates in an excess of the precipitant; these precipitates are now under examination. Some of them (*e.g.*, those of cadmium, manganese, zinc, cobalt, and iron [ferrous]) are completely insoluble in dilute acetic acid. If dilute mineral acids are employed the precipitate first formed is re-dissolved on the further addition of the acid. If the acid is first neutralised with ammonia or ammonium carbonate the precipitate re-appears, but dissolves again on a further addition of the reagent. It is to be assumed that a double ammonium salt is here formed. The same appearance is repeated if the solution of the alkaline pyrophosphate is added to a saline solution with an excess of acid so that no precipitation of a double salt takes place. By reason of this behaviour we may prepare a solution of a double salt suitable for electrolysis by setting out from an acid solution.

This behaviour of an acid salt, *i.e.*, solubility in an excess of an alkaline pyrophosphate, and bearing the addition of ammonia or ammonium carbonate without precipitation, has been, for the sake of brevity, designated in the following memoir as *normal*.

Sodium pyrophosphate is relatively sparingly soluble. A solution saturated at 18° contains in 10 c.c. about 1 grm. of the salt ($\text{Na}_4\text{P}_2\text{O}_7 + 10\text{H}_2\text{O}$). Ammonium pyrophosphate is considerably more soluble, since 1 c.c. of water takes 1 grm. of the salt. There is scarcely any advantage to be recognised in the use of the latter, and as it is about ten times as costly as the former on account of the difficulty of its preparation, and as it is not regularly crystallised, the use of the sodium salt is to be recommended.

As some of the double salts are deposited on heating

is advisable to keep solutions of sodium pyrophosphate ammonium carbonate, and ammonium oxalate in store.

The alkaline pyrophosphate is not affected by the electric current; at least, the author has not been able to observe any change.

Behaviour of Metals on the Electrolysis of their Double Pyrophosphates.

1. *Nickel*.—The behaviour of the nickel salts in the preparation of the electrolyte is in all respects normal. The whitish green precipitate of the pyrophosphate readily dissolves in an excess of the precipitant with a yellowish green colour, which turns green on the addition of ammonium carbonate and blue if ammonia is added.

Nickel is deposited from pyrophosphoric or alkaline solution as a greyish-white metal of excellent quality, compact, and adhering closely to the cathode. In a pyrophosphoric solution a powerful current is needed, especially towards the end of the process, and the deposit must be washed without interrupting the current. Of the alkaline solutions, that mixed with ammonium carbonate is preferable to one to which free ammonia has been added.

In a solution containing ammonium carbonate great latitude is permissible as regards the strength of the current. The deposition begins with currents yielding less than 0.1 c.c. of detonating gas per minute. With a current of 2–3 c.c., from 0.2 to 0.3 grm. of nickel can be quantitatively deposited in twenty-four hours. But the same quantity, and equally good in quality, can be deposited in a few hours with a current giving off 20 c.c. and upwards of detonating gas per minute. The reduction can be further accelerated by the application of heat.

The end of the decomposition may be recognised when no darkening is produced in a few c.c. of the electrolyte on the addition of pale ammonium sulphide.

The treatment of the metal at the close of the reduction, in ordinary cases, is that commonly followed. The liquid is poured off, the deposit is rapidly washed with distilled water, and then rinsed with absolute alcohol; the tared capsule is then dried at about 100°, let cool in the exsiccator, and weighed. If the current is very feeble, and if the solution has been mixed with ammonium carbonate, there is formed on the anode a slight brown deposit, which disappears spontaneously if the current is interrupted for a short time. In one instance its weight after drying is 0.0016 grm. This does not occur in ammoniacal solutions.

2. *Cobalt*.—Cobaltous pyrophosphate is pale red, and dissolves with a violet colour in an excess of the precipitant. The addition of ammonium carbonate does not affect the colour, but ammonia turns it first brown and then violet. On the electrolysis of its double pyrophosphates, cobalt behaves similarly to nickel, and separates out with its peculiar brownish colour. In other respects it behaves like iron, as the metal is slightly dissolved by the electrolyte. For the precipitation of the last traces a current of 10–15 c.c. is necessary, and it must be washed without interruption of the current. The brown colour, which traces of the metal give with ammonium sulphide, is more intense than that of nickel, and consequently the end of the reaction is more distinctly perceptible.

3. *Iron*.—In the preparation of the electrolyte ferric salts behave normally. Ferric pyrophosphate is white, and gives with an excess of sodium pyrophosphate an almost colourless solution. On the addition of ammonia it becomes yellowish brown to brown-red, according to the degree of concentration.

Ferrous salts also behave normally; they give a white precipitate, and in an excess of the precipitant a light green solution. On the addition of ammonia the solution becomes darker as the iron is peroxidised. If the colour becomes a red-brown there begins the separation of a basic salt of the colour of ferric hydroxide,

For electrolysis, in which iron behaves like nickel and cobalt, the solution mixed with ammonium carbonate is alone suitable. If the ammoniacal solution of the ferric double salt or that of the ferrous salt recently prepared is submitted to electrolysis there is deposited at the anode at first a reddish brown salt, which is strongly adhesive and which contains ferric oxide and pyrophosphoric acid. Metallic iron is deposited at the same time at the cathode. As long as the coating on the capsule is thin the colour of the reduced iron is a slate-blue; afterwards it appears iron-grey.

The reduction of iron begins with feeble currents, but for its rapid separation a current of 20 to 30 c.c. of detonating gas per minute is required. It is especially difficult to eliminate the last traces, so that if large quantities of iron have to be precipitated the decomposition may be conveniently begun with the current of two Bunsen elements connected in series, and towards the end the enfeebled current is reinforced by the introduction of a third element.

After completion of the reduction it is necessary to wash without interrupting the current, as the electrolyte has a distinctly solvent action upon the deposited metal. This is the reason why the reduction of the last traces is so difficult.

4. *Manganese.*—Manganous salts yield with sodium pyrophosphate a white precipitate which re-dissolves in a large excess of the precipitant. In ammonia the precipitate is very easily soluble; it dissolves also in ammonium carbonate, but a white salt here soon separates out. The double ammonium salt behaves like the sodium salt. On the application of heat precipitates appear which do not disappear on cooling.

The double pyrophosphates of those metals which form peroxides behave electrolytically different from the salts hitherto examined.

If we electrolyse the solution of a manganous salt in an excess of sodium pyrophosphate, we obtain, with currents of about 20 c.c. detonating gas per minute, a brown solution, but no manganese peroxide is separated. The solution (remaining at first clear) contains a double salt in which the manganese exists in a higher state of oxidation. Subsequently, especially if much manganese is present, there appears a brown flocculent precipitate of manganic hydroxide. With a weaker current (10 c.c. detonating gas per minute) some manganese peroxide is separated and adheres firmly to the anode. If the strength of the current decreases this separation of peroxide predominates, though the formation of the brown solution does not cease. At the cathode is seen, more or less, according to the strength of the solution, the characteristic colour of permanganic acid.

(To be continued).

ELECTRICITY IN CHEMICAL MANIPULATIONS.

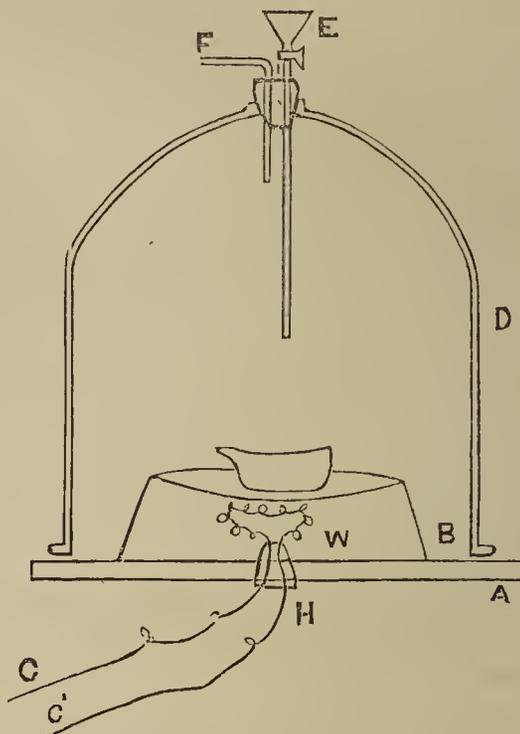
By REGINALD FESSENDEN,
Chemist, Edison Laboratory, Orange, New Jersey.

A DESCRIPTION of a few pieces of chemical apparatus in which electricity is employed may be of interest.

The current is derived from a simple primary battery, described below.

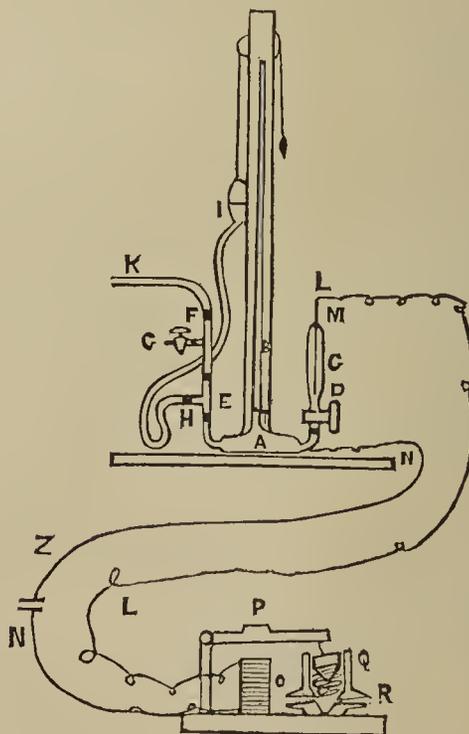
1. *For Rapid Evaporation in Vacuum.*—A, is a piece of plate-glass, through the centre of which a hole is bored by means of a brass tube and emery; in the hole a cork, H, is inserted, and two wires, G G, run through it, each connected to one end of the platinum loop, W, which latter is packed with magnesia or any such material. The operation is as follows:—The dish, C, containing the substance to be evaporated, is placed on the stand, B, and the bell-jar placed over all. The tube, F, is connected to the filter-pump, and the wires, G G, to the terminals of the battery. Evaporation proceeds with extreme rapidity.

More liquid is added from time to time through the separatory funnel, E. Where the current is obtainable,



electric incandescent lamps may be used, in place of wire, with advantage.

2. *Automatic Heat Regulator and Air Thermometer.*—A is a piece of glass tube, 4 inches long and 1 inch in diameter, having three nipples, one connected to a piece of thermometer tubing, B, one to a short piece of tubing, C, drawn out very fine at D, and having a cock at its lower extremity, and the third to the T-piece, E. K is a tube connecting with the air bulb, which may be of Bohemian glass; I is a bottle of mercury, connecting by a rubber



tube with H; N is a platinum wire, fused into A; M is a thin carbon rod, resting on the capillary portion of C, and connected to the wire, L. There are cocks at H and T. O is an electro-magnet, connected to the wires L and M; Q is a plunger, held up by a spring in a piston, so that the gas can pass freely through the opening, R, to the

burners so long as the magnet is not acting. The operation is as follows:—Cocks H and T open, cocks G and D shut; it is a simple air thermometer, readings being taken on the tube D. To use it as a regulator, the bath is raised to the required temperature, cocks G and D are opened, and the mercury adjusted so that it nearly touches the carbon rod, M; cocks G, H, and T are then closed. It will be seen that if the temperature rises ever so slightly the mercury will touch M, and the current from the battery, Z, flowing through the wires L and N, will pull down the armature, P, driving the cylinder, Q, down, and shutting off the gas, except so much as may be necessary to keep the burners lighted.

This apparatus will maintain the temperature constant for days to half a degree; hence it is of use in accurate and long fractional distillations. It works with any kind or pressure of gas, and one cell will keep it going for months.

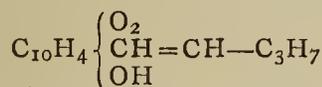
(To be continued).

ON THE
CONSTITUTION OF LAPACHIC ACID
AND ITS DERIVATIVES.*

By SAMUEL C. HOOKER and WILLIAM H. GREENE.

IN 1857, Arnoudon† described, under the name Taiguic Acid, a yellow colouring matter existing in the Taigu wood of Paraguay; nine years later, Stein‡ described as greenhartin a similar matter which he had extracted from the greenheart of Surinam. In 1879, Paterno§ proved the identity of these substances with the lapachic acid obtained by Siewert from the Lapacho tree of South America. Finally, we have recently found the same substance in a South African wood, the Bethabarra.||

Paterno,¶ in an admirable research published in the *Gazzetta*, 1882, has assigned to lapachic acid, with a very great degree of probability, the following constitutional formula:—



Oxy-amylenenaphthaquinone.

The results from which this formula is mainly deduced are the following:—

Lapachic acid gives a series of stable salts, but all experiments failed to reveal the true acid group, COOH.

On distillation with zinc dust, naphthalene and isobutylene were obtained.

On oxidation with nitric acid, phthalic acid was formed.

By reducing agents, a hydrolapachic acid was obtained, which rapidly absorbed oxygen, becoming re-converted into lapachic acid.

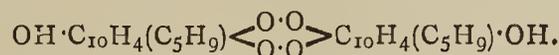
A monacetyl derivative was obtained.

Hydriodic acid and phosphorus gave a liquid hydrocarbon, which was taken to be amylnaphthalene.

In the course of the study of this acid, Paterno prepared several compounds, which he was only able to explain satisfactorily by the assumption that two molecules of the acid had taken part in the formation of each of their molecules.

By the action of concentrated sulphuric acid on lapachic acid, a compound crystallising in beautiful red needles is formed, which has precisely the same percentage composition as lapachic acid. This compound, which is known

as lapachone, was assigned the following formula by Paterno:—



Lapachone is insoluble in alkaline carbonates; it is soluble in caustic alkalies only after boiling for some time. According to Paterno it separates from the alkaline solution on cooling, and is almost completely precipitated unchanged on the addition of acids.

While recently engaged on the study of the colouring matter of Bethabarra wood, subsequently proved by us to be lapachic acid, we obtained an orange-red quinone-like substance. In the course of our experiments with this compound we observed a number of reactions which, when we had afterwards identified the compound as lapachone, did not agree with Paterno's view of its constitution.

We found that lapachone shows many of the characteristics of a chinone. It gives a white crystalline compound with acid sodic sulphite, which is re-converted by acids and alkalies into the original substance. It forms compounds with hydroxylamine and ammonia with great readiness, and gives the quinone colour reaction of Bamberger.

These reactions are obviously not reconcilable with the formula given above, and point to the probability that lapachone is $C_{15}H_{14}O_3$, and not $C_{30}H_{28}O_6$.

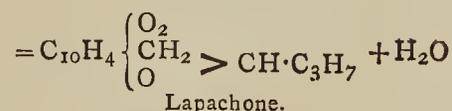
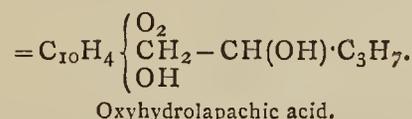
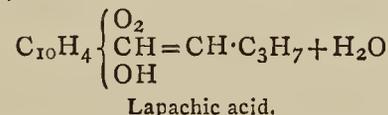
A determination of the molecular weight of lapachone, by Raoult's method, gave figures confirming this supposition, thus proving that only one molecule of lapachic acid is concerned in its formation, a result borne out by other facts.

Calculated for Paterno's formula $C_{30}H_{28}O_6$.	Calculated for $C_{15}H_{14}O_3$.	Found.
484	242	255

It remains, therefore, to explain how a substance having such strong acid tendencies as lapachic acid, dissolving with ease in alkaline carbonates, can be converted into an indifferent compound like lapachone, and yet retain the same percentage composition.

Although Paterno's formula of lapachic acid cannot be considered in any way proved, it lends itself well to the explanation of the formation of lapachone, and in this way considerable indirect proof is furnished of the probable correctness of Paterno's views in regard to lapachic acid.

It seems lawful to assume that under the influence of strong mineral acids (concentrated nitric acid in the cold acts similarly to concentrated sulphuric acid as shown by Paterno) lapachic acid takes up a molecule of water, giving rise to an intermediate compound, which is at once decomposed by the acid, again splitting off water, but in a different direction. This is shown in the following equation:—



The fact that phthalic acid is produced by the oxidation of lapachic acid would appear to furnish proof that all the side groups are situated in the same benzene nucleus, and consequently whether lapachic acid be a derivative of α - or β -naphthaquinone the (OH) group must be in the ortho

* Read at the Chemical Section of the Franklin Institute, May 21, 1889.

† *Comptes Rendus*, xli., 1152.

‡ *Journ. Prak. Chemie*, xcix.

§ *Gaz. Chim. Ital.*, ix., 506.

|| *American Chem. Journal*, xi., 26

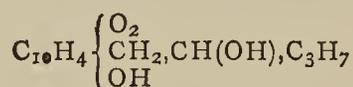
¶ *Gaz. Chim. Ital.*, xii. 337-392.

position to the amylene chain: this favours the probability of the occurrence of the above condensation.*

This view of the constitution of lapachone, *i.e.*, regarding it as a derivative of naphthofurfuran, agrees very thoroughly with all its properties and reactions so far observed. It has, moreover, received direct confirmation from the result of an experiment which was made to obtain, if possible, corroboration of our views.

Paterno states, as already mentioned, that lapachone is insoluble in caustic alkalies in the cold, but dissolves on heating, and is, in part, deposited from the filtered solution unchanged as it cools.

This observation seemed at variance with our idea of the constitution of lapachone, and we consequently carefully repeated Paterno's experiment. The insolubility of lapachone in alkaline carbonates and caustic alkalies in the cold is readily explained by the constitution we have assigned to it, and its solubility on boiling is best accounted for by the supposition that the furfuran ring is split by the action of potash, that one molecule of water is taken up with the formation of a salt of the compound—



Oxyhydrolapachic acid.

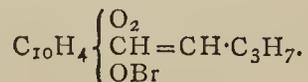
which we had previously supposed to exist as an intermediate product in the formation of lapachone. This explanation proved quite satisfactory, for on neutralising with acetic acid, a red oil was obtained which, in the course of an hour or so, solidified to a yellow crystalline mass.

Analysis proved it to have the expected composition. The tendency of the new substance to pass into lapachone under the influence of dilute mineral acids is very great, and hence if dilute HCl acid be used for the precipitation, either a mixture of lapachone and the new compound or lapachone only is obtained.

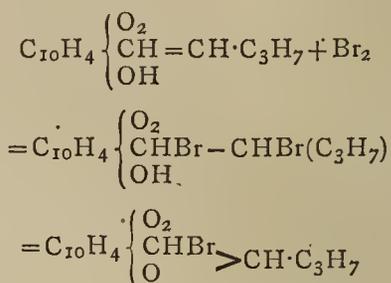
We have not yet succeeded in preparing the potassium salt of the new substance in a crystalline form, but as its barium salt, which crystallises very readily in bright orange needles, closely resembles lapachone, it is not improbable that the potassium salt may have a similar appearance, which would account for Paterno's supposition that the crystals deposited on cooling and before the addition of hydrochloric acid were crystals of lapachone. It is right to add that the fusing-point of these crystals was found by Paterno to be almost identical with that of lapachone.

The salts of the new compound, as might be expected, dissolve to the same intense red colour as those of lapachic acid. It melts at 125°, and is very readily soluble in most ordinary solvents. It may be obtained in comparatively large crystals by spontaneous evaporation of its solution in alcohol or acetic acid.

By the action of bromine on lapachic acid in acetic acid solution, Paterno obtained a compound which he regarded as monobrom-lapachic acid, and to which he assigned the formula—



Considering the properties of this compound and the probable constitution of lapachic acid, its formation would seem to be better explained by the supposition that an addition product is first formed, and that this, by splitting off hydrobromic acid, gives rise to the formation, not of brom-lapachic acid, but of brom-lapachone, thus—



We are at present endeavouring to prove the truth of this supposition, and have already observed some important facts tending to show the correctness of our views.

The formation of several of the other compounds obtained by Paterno would appear to be better explained in a similar manner to the foregoing than by the formulæ he has assigned to them. We prefer, however, to leave the discussion of these until our work has progressed further. In the meantime, we wish to say that, although we are hopeful further experiments will justify our present conclusions, we do not regard them as of necessity final, and have only been induced to make this preliminary communication to ensure to ourselves the undisturbed continuation of the work, which, owing to many causes, can not, unfortunately, proceed with as great rapidity as we could desire.

ON LAPACHIC ACID AND ITS DERIVATIVES.*

By E. PATERNO.

IN the *American Chemical Journal*, April, 1889, p. 267 I have read an important note by W. H. Greene and S. C. Hooker, in which is proved the identity of the colouring-matter of Bethabarra wood with lapachic acid. In ending their note the authors propose to study lapachone, and suggest that certain reactions observed by them lead to the belief that this compound has not the constitution provisionally assigned by me in 1882.†

I must draw the attention of these two chemists to the fact that in my memoir, after having stated that the constitution of lapachone was perhaps the most difficult and important point to determine, I terminated by saying that all my considerations had a very limited value, and I dwelt on it but a moment, with the sole design of showing the importance and the range of the argument of which I had undertaken the study.

It is indeed true that since 1882 I have published nothing on lapachic acid. I have been occupied with other matters, it has been difficult for me to obtain first materials, and I did not desire to publish the results in parts, especially when I had reserved the right of continuing the research. However, that I have never abandoned the work is shown by the fact that in my research on Raoult's law, published conjointly with Nasini in 1886,‡ we proved that lapachone is not a polymeride of lapachone, as I at first supposed, but that it corresponds to the simple formula $C_{15}H_{14}O_3$, and I said that while the polymeric quinones so far studied are brown substances, only slightly soluble, and having fusing-points much higher than the corresponding quinones, these great differences in external characters are not observed between lapachic acid and lapachone. Since that time, as I have besides announced a few months ago,§ I have continued this research with greater industry, and, by applying Raoult's method I have shown that the acetyl derivative of lapachic acid fusing at 131—132°, for which I had ad-

* Read at the Chemical Section of the Franklin Institute, June 18, 1889.

† *Gazzett Chimica*, xii., 337.

‡ *Ibid.*, xvi., 262.

§ *Ibid.*, xix, 3.

It is, of course, possible, though scarcely probable, that lapachic acid is derived from $\beta\beta$ -naphthaquinone, in which case the relative positions of the amylene chain and the hydroxyl group would be the para.

vanced a complex formula, corresponds rather to that of a diacetic derivative of lapachic acid or of lapachone, or more probably another isomeride of this substance; and in a series of researches that I may say are complete, and which were in part made together with Sig. Minimi, I have entirely re-considered the study of those derivatives of lapachic acid of whose constitution I entertained doubts, and, in particular, lapachone, the diacetyl derivative and the magnificent substance crystallising in splendid bronze-red laminæ. Of lapachic acid and lapachone we have studied the oxime and hydrazin compounds, we have obtained the quinone corresponding to the diacetyl derivative, we have prepared and studied the triacetyl derivative, corresponding to the reduction derivative of lapachic acid, the compound of lapachic acid with thiophen has been prepared, and in this manner we have collected together a considerable number of facts which completely elucidate the constitution of lapachone and many other derivatives of lapachic acid.

I am sure that Messrs. Greene and Hooker will, after what I have exposed, allow us time to publish our labours, and desist from the further investigation of lapachic acid derivatives, at least until after the publication of our researches.

A DESCRIPTION OF SEVERAL YTTRIA AND THORIA MINERALS FROM LLANO COUNTY, TEXAS.*

By W. E. HIDDEN and J. B. MACKINTOSH.

History.—In July, 1886, the first piece of gadolinite (a mass of about 1½ lbs.) was accidentally discovered, by Mr. J. J. Barringer, in Llano County, Texas. It was noticed projecting from an outcropping of granite, and was detached therefrom and preserved merely because of its peculiar appearance. Later, Mr. Barringer commenced digging at the locality, and in a short time he unearthed a pocket of huge crystals and masses of this rare mineral aggregating not less than 500 kilos. This remarkable quantity was obtained by digging with pick and shovel, in the partly decomposed surface rock, and all came from a space not over 4 ft. deep, 3 ft. wide, and 8 ft. long.

Until August, 1888, the true nature of the mineral remained unknown, and meanwhile it received such local names as "tin-ore," "black-jack zinc," "volcanic glass," &c. Later the name "samarskite" was given to it, and as such it was known until Mr. Barringer, upon sending it to New York in an endeavour to find a market for it, received the information that it was gadolinite. About this time it came under the notice of one of us, and an effort was made to develop the locality thoroughly. Thus far, only the gadolinite had been found, and no value having been attached to it, the mineral had been free to all who desired "a few pounds of it." Of the large quantity obtained in 1886, only about 100 kilos. then remained, the greater portion having been gradually distributed among local visitors. In January of this year, realising that a locality that could produce the rare mineral gadolinite in such unprecedented masses as had already come under our notice was worthy of careful investigation, we sent Mr. Wm. Niven, of New York, on a special visit to the region, and it was the series of specimens collected by him that induced one of us to personally visit the locality. This was done during the past summer, two months being spent in prospecting the whole region; the results of this investigation are embodied in this announcement.

Description of Locality.—The spot where the gadolinite has been found is nearly five miles southward from Bluffton, in Llano Co., Texas, and on the west bank of

the Colorado River. The whole surrounding region for many miles is Archæan* (with occasional cappings of limestone), and granite, in various shades of colour and texture, is the common country rock. A coarse textured deep red granite is most abundant, and through it numerous and extensive quartz veins extend to the surface. Only in these veins have the ores of yttria, &c., been found, and only in the wider swellings of these veins or where they have assumed the character of bold uplifts, have masses of large size been found. Here is to be seen a mound-like elevation, 100 × 150 feet in area, projecting boldly from the surrounding granite, and 27 feet in elevation above the river terrace. It is made up of huge blocks and masses of quartz and red felspar, all tightly massed together. The mound is nearly circular in form, and the contact with the country granite is sharply defined. It is plainly seen to be a widening of a vein that can be traced in a south-westerly direction for some distance and one of a series to be seen at several locations in the near neighbourhood.

The quartz masses are from 5 to 20 feet thick, with the interstices filled completely with a highly crystalline red felspar. Between these irregular masses are found at times thin seams of a black iron-mica, and with this mica, and in the adjacent felspar, are found the various ores of the rare earths hereinafter to be noticed.

From all sides this mound has been entered with trenches, and one or more of the yttria minerals have been found at every opening. At this writing it has been so much cut into by trenching that it is difficult to trace the original boundary. On the river side the mound is rather steep, but in other directions its sides slope gradually. Its top is flat and consists of pure white quartz (bleached by weathering), and it is only on the slopes and at the base that the several rare minerals show themselves. The quartz and felspar are very much stained with red oxide of iron and some yellow and green uranium compounds at the points where at present the larger mineral masses have been found, and these stains have constituted a good guide to their discovery.

Up to the present time we have identified the following mineral species, but we will describe in detail only the more important in the present paper. The list of species includes quartz, hyalite, orthoclase, albite, biotite, muscovite, magnetite, martite, gadolinite (several varieties due to alteration), fergusonite (three varieties of hydrous species), allanite, molybdenite, molybdite, cyrtolite (several varieties), fluorite, gummite (two varieties), a carbonate of the rare earths (tengerite?), a thorium-yttrium-lead uranate, a hydrous uranium thoro-silicate, an yttrium-thorium silicate, a fetid gaseous compound (which we first observed upon breaking some of the material for analysis), and several minerals, found in small quantities, which we have not had the opportunity to identify with certainty.

Quartz is rarely found crystallised at this locality. Only one pocket of smoky crystals (coated with ferric oxide), of noteworthy size and transparency, having been as yet found. Small druses of quartz-caps are often met with in the seams of the larger quartz masses.

Hyalite, in mammillary forms, was observed coating the seams of the felspar and quartz, in very small patches.

Orthoclase occurs massive and finely crystallised and in great variety of form. Twin crystals, of curious complexity, and simple forms are very common. Crystals of huge dimensions, a foot or more in length, more or less perfect, and smaller sizes, abound; especially are they abundant on the contact of the vein with the granitic walling.

Albite is rare, and occurs coating small cavities in the massive orthoclase. Crystals not above 1 inch diameter were observed.

* From the *American Journal of Science*, Third Series, vol. xxxviii., No. 228, December, 1889.

* See "Geologic Story of the Colorado River," R. T. Hill, in *American Geologist*, vol. iii. No. 5, pp. 291-2.

Biotite (?) is very abundant, and occurs in broad folia in the seams between the quartz and felspar masses. Diagonal prismatic cleavage surfaces were common. It was intimately mixed with much magnetite, and was often the matrix or foundation upon which the rarer minerals rested. Many alteration products were noticed.

Muscovite is quite rare, and occurs as hexagonal implanted prisms only in the albitic cavities. These prisms seem to be made up of 3 or 6 sectors on a basal section. No examination, chemical or optical, has been made.

Magnetite is quite abundant, both massive and crystallised. It is always associated and intermixed with the biotite. Octahedral crystals with planes of the cube, rhombic-dodecahedron and of a trapezohedron were found abundantly, though superficially they were coated with a thin micaceous layer and some uranium hydrate.

Martite was very common, being an alteration from the magnetite. Crystals having a black colour interiorly and preserving the cleavages of magnetite, but having no magnetic properties, were very commonly observed.

Gadolinite.—We have already detailed the events surrounding the discovery of this mineral in Texas. For a description we would refer to the paper by Dr. Genth,* in the *American Journal of Science*, September, 1889. As Dr. Genth as stated, this gadolinite, when unaltered "has a black colour; in thin splinters it is translucent with a dark bottle-green colour; the fine powder is greenish grey; fracture conchoidal to splintery. Specific gravity 4.201—4.254."†

Most of the gadolinite is altered into a brownish red mineral of waxy lustre; some of the masses are entirely so altered, while in others the change has only taken place superficially. A further alteration has been to a yellowish brown earthy (ochreous) substance, which upon drying in the open air becomes a very light powder. The average size of the masses of this Texas gadolinite has been, in our experience, about half a pound; though embedded crystals (hydrated) were noticed not above half an inch long by one-quarter inch wide (very acutely terminated), and as to large masses there were many of 5, 10, and 15 lbs. each. One double crystal weighed forty-two pounds, and was nearly free from matrix. Another huge pointed mass, in reality a crystal, weighed fully sixty pounds.‡ All of the gadolinite had, at some time in the past, presented smooth crystal surfaces (as the hydrated crust often gave evidence of), but very few masses were found without more or less exterior alteration. This alteration had roughened the underlying surface and had given a dark brick-red colour to all the changed mineral.

On only three crystals were we enabled to find sufficiently smooth surfaces to give us even approximate angles, and these we here append:—

$$\begin{array}{ll} I \wedge I = 115^\circ - 117\frac{1}{2}^\circ & O \wedge \frac{1}{2}i = 145^\circ - 146^\circ \\ I,, I = 156^\circ - 158\frac{1}{2}^\circ & \frac{1}{2}i,, \frac{1}{2}i \text{ (ov. } O) = 111 - 112^\circ \\ I,, I = 119^\circ - 119\frac{3}{4}^\circ & O,, I = 90^\circ - 91^\circ \\ I,, O = 113^\circ - 113\frac{1}{2}^\circ & I,, I \text{ (ov. } \frac{1}{2}i) = 77^\circ - 79^\circ \\ -I,, +I \text{ (ov. } O) = 46^\circ & \frac{1}{2}i,, I = 123^\circ - 126^\circ \end{array}$$

All the crystals observed were lengthened in the direction of the vertical axis (in one instance, ten inches long), and the plus and minus 1 and 2 pyramids are present often to the total extinction of the basal pinacoid, making acute forms difficult to extract from the matrix in perfect condition. A distinctly monoclinic habit was apparent in many of the masses, and the pyramid 2 was often developed only upon the plus or minus side. The basa,

plane was only noticed in one instance. At another vein, one mile south, two crystals of gadolinite, of rare beauty and perfection, were found on the land of Mr. Hiram Casner; this goes to show that other discoveries of the rare minerals are possible in the neighbourhood.

YTTRIALITE, a new Thorium-Yttrium Silicate.

The mineral, which we have named Yttrialite, was discovered associated with, and often upon, the gadolinite, and but for its characteristic orange-yellow surface alteration (that of gadolinite immediately alongside of it being invariably of a dull brick-red colour) it might have continued to pass for "green gadolinite," which was the local name given to it. Of these yellow masses, one weighed over ten pounds, and twenty kilos. were found in all. Upon being broken open they are of an olive-green colour tending in places to a drab shade. Peculiar minute ragged lines permeate the mineral in all directions, causing an apparent muddiness or semi-opacity. No crystals have as yet been observed, but a seemingly orthorhombic symmetry was apparent in some of the masses. The mineral breaks easily in two directions, with a shell-like fracture, but separates into small flakes very readily. (Gadolinite is broken only with difficulty). Nothing like a cleavage has been noticed. A thin white crust of a mineral related to tengerite occupies the cracks in the mineral, and this is equally true concerning the gadolinite of the locality, as Genth has already noted. We have named the mineral *yttrialite*, in allusion to the prominent part played by the yttria earths in its composition.

The specific gravity is 4.575; hardness 5—5.5. It is readily soluble in hydrochloric acid. When heated over the Bunsen flame it decrepitates violently, and falls to powder upon being ignited over a blast, becoming snuff-brown, infusible, and insoluble. These characteristics serve to at once distinguish it from gadolinite, which has specific gravity from 4.2 to 4.3 (Texas varieties), and which when heated glows vividly and swells into ragged fragments. The analysis shows several fractions of the yttria earths (A, B, C, D), which were separated by successive precipitations with sodium sulphate. The atomic weight of each fraction was determined, showing successive increase with each separation. The fractionation was discontinued after the fourth separation, as the amount of material was getting very small, but the atomic weight shows that the lanthanum and didymium are still mixed with an earth of higher atomic weight. The results obtained are as follows:—

	Per cent.	Oxygen ratio.
SiO ₂	29.17	97.234 = 4
PbO	0.854	
ThO ₂	12.00	0.383
MnO	0.77	9.108
FeO	2.89	1.084
CaO	0.60	4.014
Al ₂ O ₃	0.55	1.071
Ce ₂ O ₃	1.86	1.617
	Atomic weight.	1.722
(A) Y ₂ O ₃	22.67 = 110.3	72.918 = 3
(B) Y ₂ O ₃	5.30 = 110.53	
(C) Y ₂ O ₃	4.50 = 114.9	
(D) Y ₂ O ₃	14.03 = 120.	
(LaDi) ₂ O ₃ , &c. .. .	2.94 = 162.	
UO ₃	0.83	
Ignition loss	0.79	0.843

99.754

Total yttria earths = 46.50 p.c. Erbium spectrum distinct.

Regarding the loss by ignition as non-essential, the oxygen ratio of all the bases to silica is exactly 3:4, which leads to the formula R₂O₃, 2SiO₂, in which R₂O₃ may be replaced by its equivalent in RO, RO₂, or RO₃.

* Eakins found sp. gr. = 4.239; our own determination, on a very compact mass, gave us 4.306.

† Dr. Genth was misinformed by the party who supplied him with his "Burnet Co. gadolinite," as it has not as yet been discovered in that county, and the error of crediting Burnet Co. with having produced it was probably owing to the fact that it had been shipped from Burnet (Burnet Co.), which was the nearest R.R. point to the true locality some 19 miles distant.

‡ Stated on the authority of Mr. Barringer and many of his neighbours.

Gadolinite, Llano Co., Texas.

	GENTH.	Sp. gr. = 4.254. Oxygen ratio.		EAKINS.	Sp. gr. = 4.239.* Oxygen ratio.	
SiO ₂	22.80		76.00	23.79		79.30
ThO ₂	—			0.58	0.44	
MnO	0.18	0.25	} 56.86 } } 116.11 }	trace	} 63.75 } } 121.13 }	
FeO	12.93	17.96		12.42		17.25
GlO	9.19	36.61		11.33		45.18
CaO	0.71	1.27		0.74		1.32
MgO	0.11	0.27		} traces		}
K ₂ O	0.12	0.13				
Na ₂ O	0.23	3.37				
Al ₂ O ₃	0.31	0.90				
Fe ₂ O ₃	—	—		0.96		1.80
Ce ₂ O ₃	2.66	2.46		2.62		2.43
(DiLa) ₂ O ₃	5.01	4.59	5.22	4.77		
(Y,Er) ₂ O ₃	44.45	51.30	41.55	47.94		
H ₂ O	0.79		1.03	†§		
P ₂ O ₅	—		0.05			
Insoluble	0.93					
	100.42		100.29			

There is no simple ratio between the sesquioxide and other bases. This mineral, therefore, differs from gadolinite in containing twice as much silica. It has other points of difference, viz., it contains no glucina, which has been regarded as a characteristic constituent of gadolinite, and there is a very large preponderance of sesquioxides among the bases. For comparison we append two analyses of gadolinite from this locality by Genth (*American Journal of Science*, September, 1889) and Eakins (private communication from Professor F. W. Clarke).

Regarding the water and phosphoric acid as accidental, and using the molecular weight for the yttria earths determined by Eakins (260) for the calculation of Genth's analysis, we get the oxygen ratio of all the bases to silica of 3.055 : 2 and 3.054 : 2 respectively, giving the general formula R₂O₃, SiO₂, in which R₂O₃ may be replaced by its equivalent in RO and RO₂. Both of these analyses seem to show a tendency towards an equality of the sesquioxides to the monoxides, though there is a preponderance of sesquioxides in the one and of protoxides in the other. They differ also from our analysis of yttriate in the small percentage of thoria, which in the latter amounts to one-eighth of the total bases in equivalency.

(To be continued).

NOTICES OF BOOKS.

The Story of Chemistry. By HAROLD W. PICTON, B.Sc. With a Preface by Sir HENRY ROSCOE, D.C.L., LL.D., F.R.S. London: W. Isbister (Limited).

THIS little book is truly, as Sir Henry Roscoe characterises it, "a short and attractive history of chemistry." It is not a series of biographical notices of the men who have made the principal discoveries in our science, but a view of the development of its leading ideas.

Mr. Picton fully recognises the truth that chemistry did not originate in alchemy, but had a previous independent existence.

He accepts Pliny's somewhat mythological account of the accidental discovery of glass, and, what is much more strange, the story of Cleopatra dissolving pearls in weak vinegar. If we remember rightly, G. H. Lewes showed

that pearls are not, at least in any admissible time, soluble in vinegar.

The remarks on the construction and use of hypotheses are truly philosophical and should be had in remembrance by the student.

Roger Bacon is here admirably appreciated. This old-time thinker, as far back as the thirteenth century, perceived that force is invariably subject to mathematical laws. This is the more significant since, as the author reminds us, "even the great Kepler thought the revolutions of the planets might be accounted for by guiding spirits."

Mr. Picton, it will be perceived, though a chemist, is not solely or exclusively one. Sometimes he raises questions which may make our modern industrialists thoughtful. For instance, we read here:—"Perhaps it may be well, therefore, to remind ourselves that the mere production of sulphuric acid, even to the amount of inland seas, is in itself no special boon. Chemistry has, so far, been applied to manufacture: good, but how far has the manufacture increased the happiness of life."

Rudolf Glauber is quoted as denouncing "this mischievous composition and diabolical abuse of gunpowder." What would he have said could he have witnessed the development and use, or abuse, of the "high explosives"? With reference to the passage just quoted, our author says:—"What a man visibly *does* may not be so important as what he *is*. As Emerson puts it, 'we do not want actions, but men.'" Here he comes in collision with Buckle, who tells us that what a man *is*, is overlooked, or is, at best, soon forgotten, unless his actions are such as to have earned the gratitude of the world.

The beginnings of science, in the present sense of the word, our author places in the seventeenth century. He does not, however, mention that alchemy did not even die with Woulfe in the beginning of the present century. Quite in our own day, a person unknown advertised in the *Athenæum* his readiness to teach the "Hermetic Art" for a fee of 100 guineas.

Passing over the epochs of Boyle, of Mayow, Hales, and Black, we come to Phlogiston and its author, Stahl. The history of this aberration being, perhaps, equivalent in chemistry to that wrought in biology by the school of Cuvier, is ably and impartially given. It may, perhaps, be hinted that the ghost of phlogiston—"caloric"—is even yet not thoroughly exorcised, especially in France.

Priestley receives here something more than justice. We must remember that he was persecuted, not as a chemist and physicist, but as a reputed heretic and revolutionist. Had he followed the wise advice of Edward Gibbon, to stick to physical science and leave controversial theology

* At 17° C.
† Didymium spectrum very strong.
‡ Molecular weight = 260.
§ Erbium spectrum weak.

and politics alone, he would not only have lived and died in honour, but have acquired still stronger claims on our gratitude. In the account of Priestley's life, we find a slight error. Needham Market, his first residence after leaving Daventry, is not in Surrey, but in Suffolk.

The author does not point out Priestley's great defect—his versatility. That a man who dabbled in so many subjects should have done good service in any sphere is something remarkable.

The discoveries of Cavendish in electricity are not here noted; strictly speaking, they do not belong to the subject; but the fact that he could leave such sterling work unpublished throws an interesting cross-light upon his character. We think that Mr. Piñon is scarcely justified in wondering that Cavendish did not do more.

We are, in turn, surprised to find Bergman and Scheele spoken of as "two Swiss chemists of renown."

We learn that Lavoisier's refutation of the phlogiston hypothesis caused so much ill-will that he was burnt, in effigy, at Berlin. But his death, like Priestley's expatriation, was due to his having concerned himself with politics. The Republic certainly declared that she had "no need of savants," but, had Lavoisier been merely a *savant*, he might possibly have been overlooked by the leaders of faction.

It is something strange to find the atomic weight of platinum still given as higher than that of gold. In a table of the elements discovered this century, with the names of their discoverers, we have the names of workers observing and recognising bodies printed in italics, whilst "that of the observer" by whom the element was first isolated is printed in italicised capitals. In this manner, if we turn to thallium, we find "*Crookes*" merely given as recognising the existence of this metal, whilst to "*LAMY*" is awarded the honour of its first isolation.

All who desire a clear, readable, and, in the main, correct account of the rise and progress of chemical science, will find this book well suited to their purpose.

A Text-Book of Assaying: for the Use of Those Connected with Mines. By C. BERINGER, F.C.S., F.I.C., and J. J. BERINGER, F.C.S., F.I.C. London: C. Griffin and Co.

In the authors' preface we find reference to the definition of the term "assaying," as distinct from analysis. They do not agree with those authorities who restrict the term to dry processes for the determination of metals, nor with those who confine it to methods for the estimation of gold and silver. They consider that "the distinction between assayers and analysts will, in time, become difficult to detect." But why use two words for the same thing?

The work before us is, in fact, a general treatise on inorganic quantitative analysis, but with the addition of "dry," or "furnace," processes, which, save in the case of gold and silver, are not generally recognised.

As regards copper, the authors fully admit the unsatisfactory character of the Cornish assay, which, if we remember rightly, is totally proscribed in Chili. In many other instances, the authors admit the inaccuracy of the "dry" methods given.

We do not find any mention of the quantitative blow-pipe processes, which the authors may possibly have found unsatisfactory.

The rarer metals are not omitted, it being very justly remarked that their presence often modifies the behaviour of the common metals.

The separation and determination of the various metals associated with platinum are very briefly dealt with.

As an instance of the extraordinary comprehensiveness of the work, we may mention that there is a short notice of gas analysis, though with the reservation that it is not much used by assayers.

We find also a sketch of the sanitary examination of waters by the Nessler and the permanganate processes.

The instructions concerning "total solids" are drawn up with reference to mineral impurities, though we do not see any notice of the possible presence of phosphoric acid. We note the remark that "distilled water is only used by assayers in certain exceptional cases, so that by many it would be classed among the rarer oxides. Water of ordinary purity will do for most purposes, but the nature and quantity of the impurities must be known." We think this principle, which might be just as well extended to other reagents, is unsound and unsafe.

This work is an excellent manual, as far as the dry assays—where admissible—are concerned. As regards the other methods, the space at the disposal of the authors is, in many cases, insufficient.

Revised and Illustrated Catalogue of Apparatus for Technical Instruction. Part II., Science and Technology. Rigg's Technical Education Appliances, Limited, Bucklersbury.

This catalogue is exceedingly comprehensive, since it includes not merely apparatus required for instruction in the physical and natural sciences, but also lists of the works recommended by the Science and Art Department as text-books.

For the arrangement of the subjects the publishers, we presume, cannot be held responsible; otherwise we might venture to take exception to a classification which includes morphology under physiology, and confounds both with general biology. We find Dr. McAlister's work on the "Zoology of the Invertebrate Animals" (is there any zoology other than that of animals?) recommended under "Animal Physiology," whilst the same author's "Zoology of the Vertebrate Animals" comes in under "General Biology."

Morphology does not seem to be recognised by the Department as a "subject." Further, McAlpine's "Zoological Atlas" figures under Botany! Among the models (?) or diagrams for general biology we find No. 2214 "Butterflies of the silk-worm, male and female." This insect is generally considered, not as a butterfly, but as a moth!

That part of the catalogue which deals with chemistry and physics does not present any such sins against scientific method.

Energy and its Transformations: Mechanical Power, Heat, Light, Chemistry, Electricity, Magnetism. (L'Energie et ses Transformations: Mécanique, Chaleur, Lumière, Chimie, Électricité, Magnétisme). By R. COLSON, Captain of Engineers. Paris: Georges Carré.

This work reminds us of the "Correlation of the Physical Forces," by Sir W. R. Grove. The author, after explaining the primary conceptions of energy, work, and potential, considers the transformation of mechanical energy into heat, and the inverse process; the conversion of mechanical energy into light, with the reversal of this change. He shows that though chemical actions may be provoked by mechanical, thermic, or luminous energy, but without transformation of any of these energies into chemical energy—inversely, chemical energy may be transformed into thermic or luminous energy, but not directly into mechanical energy.

The third chapter is devoted to electricity, after which comes the question of the origin of energy. That this question is not solved, at least in its proper sense, is only what the reader must expect. The sun, we are of course told, maintains motion, activity, and life on the surface of the earth; but whence does it, in turn, derive its energy? Heat, light, chemism, electricity, and magnetism are next considered from the point of molecular mechanics.

In the concluding chapter we have reference to the

conservation of energy and the hypothesis of ether. But we scarcely see that the author has thrown any novel light on the arcana of the universe.

Chronic Bronchitis, and its Treatment: a Clinical Study.
By WILLIAM MURRELL, M.D., F.R.C.P. London:
H. K. Lewis.

THIS little work can be appreciated only by medical practitioners. We do not see that any point is raised upon which we are competent to form an opinion. Much of the treatment recommended turns on inhaling vapours; hence the author makes the practical suggestion that as "winter cough" is the commonest affection in the out-patients' department, a small room in every large hospital might be kept filled with the required vapour, so that a number of patients might be submitted to the treatment at once.

CORRESPONDENCE.

PENDULUM EXPERIMENTS AND GRAVITATION.

To the Editor of the Chemical News.

SIR,—I am obliged to Professor Boys for his criticism. This matter requires discussing, and by competent persons. He says it may interest me to know that the deviations are *many thousand times* as great as any that can be due to gravitation alone. Many thousand times as great would be ten thousand times at least, four or five thousand would be only several thousand. Let us see what this gives us:—We will take the ten-pound cylinder on the pendulum, and the five-pound cylinder fixed. The pendulum moves over an arc of seven thousandths of an inch; now, ten thousand times less than that will be seven ten-millionths of an inch! Can the Professor appreciate that length, or say that he knows that it is so? But we will not take many thousands, but only one thousand times, then the pendulum would pass over seven millionths of an inch; still many times less than can be appreciated.

Professor Boys suggests that the force of approach of bodies is complicated with magnetic force and electrification, besides these, with tilting and convection currents; these latter are effect and cause, and can affect only the Cavendish apparatus, the pendulum apparatus not at all.

The pendulum apparatus is made of brass and lead, which are not affected by magnetism. Why put that down as a source of complication?

As to electrification, it is well known that no piece of metal can be moved, but electricity will be induced if it cross the magnetic meridian at any angle; but the disturbance will be momentary at the beginning of the motion and at the end of it, but will cease instantly after the stoppage. The pendulum, of course, is liable to this; but then the motion is so small, never more than $\frac{1}{40}$ of an inch, and mostly $\frac{1}{80}$, and very slow, taking half a second, that the induction is so infinitesimal that it might be neglected, but it is not; the final measure is never taken till the pendulum is at rest. Thus, there is neither magnetic nor electric complications. The only force in action is the force which causes bodies to approach. With the Cavendish apparatus, electric induction is continual, for the beam is continually on the swing. But this is not the worst fault of that apparatus by a long way: the force of torsion cannot be weighed in the position in which it works, and to take it in any other position would give misleading results; besides, the torsion is not constant, the continued twisting and untwisting disturbs the molecular arrangement of the wire, and the variation of temperature alters the force of torsion; but

the worst fault is that one cannot get the real torsion to nearer than the one-hundredth of an inch. The beam has to be taken on the swing; for though one may have a graduated arc and a pointer passing over it, as I had, the central point of the swing cannot be ascertained to nearer than $\frac{1}{100}$ of an inch, under or over. All these defects make it an uncertain and unreliable apparatus; for these reasons I rejected it and devised the pendulum apparatus.—I am, &c.,

J. BAYNES THOMPSON.

DETECTING METALLIC SILVER IN THE PRESENCE OF LEAD.

To the Editor of the Chemical News.

SIR,—A far simpler and easier method of detecting silver in the presence of lead than that given by Mr. A. Johnstone, consists in adding to the nitric solution of the lead bead a few drops of a saturated solution of lead chloride, prepared by boiling a few grains of the salt with distilled water, allowing to cool, and decanting from the crystals. I called attention to this process and its use for quantitative purposes in the analysis of minium in your columns many years ago—so long that I have mislaid the reference.

The process consisted essentially in adding to a solution of pure nitrate of lead, of about the same gravity as the assay solution and containing lead chloride, a very dilute solution of nitrate of silver of known strength, until, on comparing the beakers on black cloth, the turbidity in the second beaker equalled that which had been produced by the lead chloride in the first.—I am, &c.,

THOS. P. BLUNT.

The Wyle Cop, Shrewsbury,
December 28, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 25, December 16, 1889.

The President announced that it is proposed to erect at the Conservatoire des Art et Metiers a statue in honour of Boussingault. M. Pasteur is President of the Committee.

The Colour and the Spectrum of Fluorine.—Henri Moissan.—If observed in a stratum of $\frac{1}{2}$ metre, fluorine possesses a distinct greenish yellow colour, fainter and more inclining to yellow than that of chlorine. If examined with the spectroscopie in a stratum of 1 metre it does not present any absorption-bands. If a very small quantity of water is added to the fluorine in the tube, the water is decomposed, yielding hydrogen fluoride and ozone. The latter gas is produced in such a degree of concentration that the entire tube takes a deep indigo-blue colour. In a few minutes the ozone is destroyed and the blue colour is destroyed. The spectrum of fluorine, as obtained in a tube traversed by powerful sparks from a coil fitted with two condensers, comprises 13 rays in the red. With hydrogen fluoride we obtain several bands in the yellow and the violet, so indistinct and broad that their position could not be exactly determined.

Temperature of the Solidification of Arsenic Chloride and of Stannic Chloride, and their Power of Absorbing Chlorine at low Temperatures.—M. Besson.—Arsenic trichloride, if perfectly free from excess of chlorine, solidifies at -18° . If saturated with chlorine

at 0° it does not solidify above -30°. If saturated with chlorine at this temperature it congeals only at -60°. Stannic chloride freed from an excess of chlorine forms at -33° small white crystals. It absorbs large quantities of chlorine at low temperatures, whilst its solidifying-point rises.

Action of Ammonia on the Combinations of Mercury with the Chlorides.—Raoul Varet.—This paper does not admit of useful abstraction.

Adulteration of French Oil of Turpentine, and its Recognition.—A. Aignan.—The impurity added is resin oil, in the proportion of about 5 per cent. The fraud is detected by a determination of the rotatory power.

Synthesis of Dioxydiphenylamine and a Red-brown Colouring-matter.—M. Seyenitz.—The author obtains these results by heating resorcin in sealed tubes with 4 parts of ammoniacal calcium chloride.

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Zeitschrift für Physikalische Chemie.
Vol. iii., Part 3.

The Transient Equilibrium of Atoms.—E. Pringsheim.—The endeavour to represent chemistry as the mechanics of atoms has caused it to be like physical mechanics divided into statics and dynamics. When Dalton put forward his atomic hypothesis, and when the chemical statics propounded by Berthollet thus became the doctrine of the equilibrium of atoms and molecules, the view was prevalent that atoms were in general at rest, and merely during the process of chemical transposition executed such movements as were necessary in order to pass from the position of rest, corresponding to the first chemical state, to that which they assume in the new body formed by the chemical transposition. Consequently, according to this view, the statics of atoms must be regarded as tantamount to the doctrine of ready-formed chemical compounds, whilst the dynamics of atoms represented the doctrine of compounds in course of formation or of chemical changes. But after the mechanical theory of heat had proved that the molecules are by no means at rest, but are constantly executing very violent movements, and after it was inferred with equal probability that the atoms also were in special motion within the molecule, chemists were obliged to develop new views as to the conditions of atomic movement in a state of chemical rest, and what changes of this movement correspond to a change in the constitution of the body in question. The simplest and formerly accepted theory is that the state of chemical rest is defined by the permanent continuance of each atom in its molecule, and that a chemical change occurs so soon as the individual atoms leave their molecules or several molecules combine to a single one. Another hypothesis regards chemical compounds as stable only when the mean condition of all molecules is alike, whilst the individual atoms travel constantly from one molecule to another. This theory, at which Williamson and Clausius arrived independently, proceeding from different points of view, is now shared by almost all thermochemists, at least in such a manner that they regard a great number of chemical states of rest as so-called conditions of movable equilibrium, in which simultaneously two (or more) chemical transpositions between the same elements are effected in such a manner that constantly so much of an existing chemical compound is decomposed to form another, as at the same time the second is decomposed for re-conversion into the first. If, therefore, we do not wish to come in collision with one of the best established physical disciplines, *i.e.*, the mechanical doctrine of heat and its consequence, the kinetic theory of gases we must no longer regard the state of chemical rest as a state of perfect atomic rest, but as a (in a wider sense) stationary movement of the atoms. Still it is possible to regard chemical rest as a state of equilibrium of the atoms (just as in mechanics we speak of a dynamic equilibrium), and consequently to retain the old conception

of chemical statics if we are able to indicate or even assume that these energies remain in equilibrium so long as the chemical compound remains unchanged, and that a disturbance of the equilibrium of these energies involves a chemical change. The only energies hitherto introduced into chemistry, those of affinity, by no means possess this property. If still the expressions "chemical statics and dynamics" and "equilibrium of atoms" are frequently used in their old significations, this persistence is harmless only if we remain conscious what meaning must be attributed to these terms according to the kinetic view. But although all chemists, generally speaking, are convinced of the special movement of molecules and atoms, this view is not yet sufficiently elaborated in detail, but with the old words old ideas have been retained. In most departments of chemistry a phenomenon is supposed to have been sufficiently explained by stating the arrangement of the atoms in a molecule, as though the atoms remained in unvarying positions. In many cases words and ideas are in use which cannot be readily accommodated to the new views, and even some which on these views are entirely unmeaning. As such, the author mentions the "transient equilibrium of atoms." He shows that those compounds which it was thought could be explained only by the assumption of a movable (*labe* as opposed to *stable*) equilibrium of their atoms, do not differ qualitatively in the arrangement and the motion of their atoms from other chemical compounds which can be converted into other forms with liberation of energy.

Electro-chemical Thermo-dynamics.—Professor Willard Gibbs.—From the "Third Report of the British Association," p. 5.

On Aluminium Methyl.—Fr. Quincke.—The author's experiments, made by the process of gas-displacement, do not confirm the results of Louise and Roux; they testify decidedly against the existence of gas molecules of the form $Al_2(CH_3)_6$.

On the Magnitudes of the Affinities of Organic Acids and their Relation to their Composition and Constitution.—W. Ostwald.—This voluminous memoir, which is to be continued, does not admit of useful abridgment.

Relations between Osmotic Pressure, Depression of Freezing-point, and Electric Conductivity.—J. H. van't Hoff and L. Th. Reicher.—Between the two series of electric experiments there are only minimal differences which in the least favourable case (LiCl) do not reach 3 per cent. On the other hand, there exists between osmotic pressure and depression of the freezing-point an almost complete agreement, the greatest difference being only 4 per cent ($MgSO_4$). If the osmotic and electric numerical values are compared, an almost perfect agreement cannot be denied in the case of potassium and ammonium chlorides, calcium nitrate, and potassium ferrocyanide. It is somewhat different in magnesium sulphate and the remaining chlorides. The former shows, contrary to expectation, an unexpectedly small isotonic coefficient and a small depression of the freezing point; the latter, on the other hand, one unexpectedly great.

The Determination of the Latent Melting-heat by Depression of Freezing-point.—J. F. Eykman.—This paper consists chiefly of tables.

A Calculation of Atomic Refractions for Sodium Light.—Eugen Conrady.—This paper does not admit of useful abridgment.

The Molecular Volume of Sulphur.—H. Blitz.—A reply to Prof. Ramsay.

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Journal für Praktische Chemie.
New Series, Vol. xl., 1889, Nos. 14 and 15.

Researches from the Laboratory of the University of Freiburg.—These consist of a paper by F. Kehrmann

and O. Weichardt on some derivatives of nitronaphthalic acid, and a memoir by the former author on iodophenol-sulphonic acids and iodoquinones, with a preliminary notice of the second iodthymoquinone.

Reply to a Notice by A. Saytzeff.—K. Hazura.—A controversy of little scientific interest.

Moniteur Scientifique, Quesneville.
November, 1889.

New Application of Alkaline Sulphides in the Purification of Arsenious, Sulphuric, and Hydrochloric Acids.—Louis Ducher.—The author's process consists in the introduction of an alkaline or earthy-alkaline sulphide into the acid. The arsenic is precipitated by the nascent sulphuretted hydrogen produced. He prefers to use calcium or sodium sulphide, the former in the shape of vat-waste.

Nägeli's Amylodextrine and its Relation to Soluble Starch.—H. T. Brown and G. H. Morris.—From the *Journal of the Chemical Society*.

Behaviour of Phenolphthalein with Ammonia.—H. Long.—From the CHEMICAL NEWS.

The Formation of Incrustations in Marine Boilers.—V. Lewes.—From the CHEMICAL NEWS.

Examination of Feed-Water for Steam-Boilers.—Th. Bruce Warren.—From the CHEMICAL NEWS.

On the Compound $C_{21}Cl_{26}$.—E. Smith and H. Keller.—The authors, re-examining a portion of this supposed compound, found it fusible at 101° , and on analysis it yielded 2.2 per cent of hydrogen. They are still engaged with the investigation.

Estimation of Tannin in Tea.—J. Tsawoo White.—From the CHEMICAL NEWS.

Oxidation by Means of the Electric Current.—E. Smith.—From the CHEMICAL NEWS.

Application of the Same Method to the Separation of Mercury and Copper.—E. Smith and Lee Frankel.—From the *Journal of the Franklin Institute*.

On Chemical Affinity.—M. Pattison Muir.—From *Nature*.

Determination of the Molecular Weight of the Carbohydrates.—Horace T. Brown and G. Harris Morris.—From the *Journal of the Chemical Society*.

Report on a Research presented to the Academy of Medicine on the Physiological Action of Absinthe.—MM. Cadéac and Albin Meunier.—The conclusion which the authors draw from their careful experiments is that the genuine essence of absinthe is the most poisonous, and consequently the most dangerous, of all the substances sold under this name. It alone is capable of producing true epileptic attacks.

Dissociation of the Glycerides by Water under Pressure.—The author describes a thermodynamic apparatus invented by M. Hughes, and now in action at the Stearine Works de l'Etoile. It consists of an upright autoclave of copper, in which 1000 kilos. of a mixture of tallow and palm oil is treated at once. Steam at a pressure of 14 to 15 atmospheres is carried to the bottom of the autoclave by a plunging tube. After six to seven hours of treatment there remains only about 5 per cent of neutral matter, the dissociation of which is completed by means of sulphuric acid. The watery glycerin, at 3° Baumé, is concentrated by means of the waste steam up to the standard of 28° B.

The Life-Work of a Chemist (M. Pasteur).—A discourse delivered by Sir H. E. Roscoe at the Birmingham and Mildand Institute.

Recent Improvements in the Manufacture of Chloroform.—S. P. Sadler.—From the *Pharmaceutical Journal*.

Influence of Temperature on the Specific Rotation of Cane-Sugar.—Clement W. Andrews.—From the *Technological Quarterly*.

Industrial Review of Various Patents.—Abstracts of the specifications of a number of German patents.

MISCELLANEOUS.

An Appeal.—Mr. A. McDonald Graham died about two years ago, after a long illness, leaving a widow and several children quite without means of support. Mrs. Graham has had an operation, which restored somewhat her failing eyesight, but since the operation she has suffered from erysipelas, and is completely prostrated and in actual want. Donations may be made to Messrs. MAY AND BAKER, Garden Wharf, Battersea, London.

Donations received:—

May and Baker	£5 0 0
T. Tyrer	£2 10 0

University College, Liverpool.—The Sheridan Muspratt Chemical Scholarship, of the value of £50 for two years, has been awarded to Mr. J. T. Conroy, who has been a student in the chemical laboratories during the past two years. Mr. Conroy has recently taken the degree of B.Sc., with Honours in Chemistry, at the University of London. The Scholarship, which is the gift of Mrs. Sheridan Muspratt, is intended to enable the holder to continue work in the higher branches of chemistry. The Sheridan Muspratt Exhibition of £25 has been awarded to Mr. A. Carey, of Widnes, who has been a student of the College during the last two and a half years, and is now in the final stage of preparation in the Honours School of Chemistry of Victoria University.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Medical, 8 30.
— Society of Chemical Industry, 8. "Peroxide of Hydrogen; its Preservation and Commercial Uses," by C. T. Kingzett, F.C.S. "An Analytical Tintometer," by Mr. Lovibond.

TUESDAY, 7th.—Royal Institution, 3. "Electricity," by Prof. A. W. Rücker, F.R.S.
— Pathological, 8.30. (Anniversary).

WEDNESDAY, 8th.—Geological, 8.
— Microscopical, 8.

THURSDAY, 9th.—Royal, 4 30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "Electricity," by Prof. A. W. Rücker, F.R.S.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.

FRIDAY, 10th.—Quekett Club, 8.
— Astronomical, 8.

ENTRIES CLOSE WEDNESDAY, 15TH INST.

INTERNATIONAL EXHIBITION
OF
ELECTRICAL ENGINEERING,
GENERAL INVENTIONS, AND INDUSTRIES,
EDINBURGH, 1890.

Patron—Her Majesty THE QUEEN.
President—The Marquis of LOTHIAN, K.T., Secretary of State for Scotland.

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** Section XIX., CHEMICAL AND ALLIED INDUSTRIES—
Class 108, including CHEMICAL APPLIANCES AND APPARATUS; and 111, CHEMICAL PRODUCTS.

THE CHEMICAL NEWS.

VOL. LXI. No. 1572.

NOTE ON THE COLORIMETRIC METHODS FOR THE DETERMINATION OF NITRATES IN POTABLE WATERS.

By A. E. JOHNSON, F.I.C., F.C.S.
Associate of the Royal College of Science.

UNDER the above heading Dr. S. Rideal gives, in the CHEMICAL NEWS, vol. lx., p. 261, an account of the "phenol sulphuric acid" method for determining nitrogen as nitrates in water—a method originally introduced, I believe, by Dr. Sprengel. This extremely useful and accurate method I have had in constant use in the laboratory for the past seven years. I have proved that the results obtained by its means agree exactly with those obtained by Crum's well-known method. The solutions I use, however, are somewhat different from those described by Dr. Rideal.

In the first place I make my standard solution of potassic nitrate as follows. 0.7215 grm. KNO_3 crystals is dissolved in a litre of distilled water. 100 c.c. of this solution is then diluted to a litre with distilled water, and this diluted solution is always used as the standard of comparison, 10 c.c. being most frequently measured out. 10 c.c. of this solution contain N equivalent to 1 part of N as nitrates in 100,000. This will, I think, be generally admitted to be a better solution than Dr. Rideal's, of just ten times the strength, as the errors of measuring so small a quantity as 1 c.c. are avoided.

Secondly, as to the phenol sulphuric acid solution. Dr. Rideal's solution differs from mine both in the relative proportions of phenol and sulphuric acid used, and also in no HCl being used by Dr. Rideal, whilst this is an important factor in giving delicacy of action to my solution. On this point I may quote Mr. D. Lindo as epitomised in the *J. Chem. Soc.* for 1888, p. 1338, the original papers having appeared in the CHEMICAL NEWS. The abstractor says "Phenol alone appears to be but a poor test for nitrates, but in the presence of hydrochloric acid it becomes very delicate." Dr. Rideal, moreover, simply mixes his phenol and sulphuric acid, whereas I have found it absolutely essential to digest the mixture for several hours, otherwise the finished solution gives a green instead of a yellow liquid with nitrates. My solution is made as follows:—Two parts by measure of pure crystallised phenol—liquefied by heat—are poured into five parts by measure of pure concentrated H_2SO_4 and the whole digested in a water-bath kept boiling for eight hours. Allow to cool and add $1\frac{1}{2}$ volumes of distilled water and $\frac{1}{2}$ vol. strong HCl to each volume of the above mixture. Convenient quantities are 80 c.c. phenol, 200 c.c. H_2SO_4 , 420 c.c. OH_2 , and 140 c.c. HCl, producing 840 c.c. of a light brown solution, which is ready for immediate use. The water residue does not require treating with water and sulphuric acid separately, but with this solution only.

My method of procedure, which is very simple, is as follows:—10 c.c. of the water under examination and 10 c.c. of the standard potassic nitrate are pipetted into two small beakers and placed near the edge of a hot plate. When nearly evaporated they are removed to the top of the water-oven and left there till they are evaporated to complete dryness. As this operation usually takes about an hour and a half, it is better when time is an object, to evaporate to dryness in a platinum dish over steam. The residue in each case is then treated with 1 c.c. of the phenol-sulphuric acid, and the beakers are placed on the top of the water-oven. If the water under examination

contain a large quantity of nitrates the liquid speedily assumes a red colour, which, in a good water, will not appear for about ten minutes. After standing for fifteen minutes the beakers are removed, the contents of each washed out successively into a 100 c.c. measuring glass, a slight excess (about 20 c.c. of 0.06) of ammonia added, the 100 c.c. made up by the addition of water, and the yellow liquid transferred to a Nessler glass (6 in. \times 1 $\frac{1}{2}$ in.). The more strongly coloured liquid is then partly transferred to the measuring-glass again and the tints compared a second time. In this way the tints are adjusted, and when, as far as possible, matched, the liquid that has been partially removed is made up to the 100 c.c. mark with water, and, after well mixing, finally compared. If not exactly the same, a new liquid can at once be made up, probably of exactly the same tint, as the first experiment gives very nearly the number of c.c. of the one equivalent to the 100 c.c. of the other. In my "Analyst's Laboratory Companion," p. 50, I have given a very useful table for obtaining it in parts per 100,000, and also in grains per gallon, by this method.

In the case of very good waters, 20, 50, or more c.c. should be evaporated to a small bulk, rinsed into a small beaker, and evaporated to dryness and treated as above—only 5 c.c. of the standard potassic nitrate (= 0.5 N in 100,000) being taken. In the case of very bad waters, 10 c.c. should be pipetted into a 100 c.c. measuring flask and made up to the mark with distilled water; then 10 c.c. of the well mixed liquid (= 1 c.c. original water) withdrawn and treated as above.

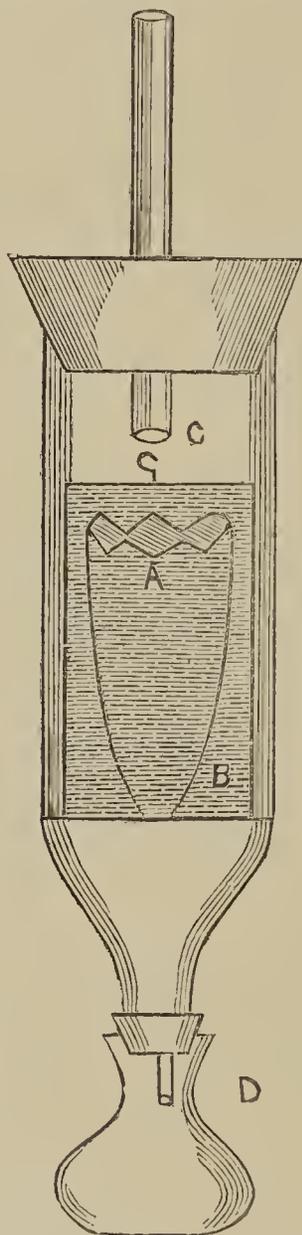
AN ACCURATE AND SPEEDY METHOD OF EXAMINING MEAT EXTRACTS AND OTHER SUBSTANCES OF AN ALLIED NATURE BY MEANS OF THE NEW PLATINUM EXTRACTION APPARATUS

By H. N. WARREN, Research Analyst.

THE various meat extracts of commerce all depend more or less, as far as their dietetic value is concerned, on what is known as the percentage of soluble extract; or, in more technical terms, the relative amount of extract soluble in alcohol of 80 per cent. In order to accomplish this it is requisite to dry the sample until constant, either by the aid of a water-bath or hot air steriliser maintained at the desired temperature. To now extract the dried residue by means of alcohol, and thus obtain a general estimate of its solubility, is void of any difficulty; but to arrive at a true percentage presents an entirely new feature, inasmuch that so obstinate are the gumming or solidifying properties of the remaining portion that any ordinary process, such, for instance, as the employment of a Soxhlet's tube or any form of apparatus where a limited supply of alcohol only is attainable, remains perfectly inadequate.

The following form of apparatus, which is illustrated by the accompanying diagram, and which I am about to briefly describe, invariably results in the formation of a larger percentage of soluble extract than the various ether extractors with which I have compared it, both an account of the large bulk of alcohol that is continuously brought to play upon the enclosed residue, and at the same time retaining a much higher temperature, and, by so doing, performing the operation in less than half the usual time. A brief summary will suffice to explain the construction of the same:—A is a tared paper which has been previously treated with alcohol. Into this is placed the dried extract, to which has been added a small quantity of carefully prepared and weighed sand, and the whole introduced into the platinum cage, B, which is readily contrived by coiling in a spiral manner a piece of platinum gauze, turning inwards the lower ex-

trimities in order to form a bottom, and furnishing the same with a cap surmounted by a small hook, while the whole is maintained in position by surrounding the same by means of the glass tube, c, and in direct connection with the flask, D, and containing the requisite amount of alcohol, the entire apparatus being connected by the usual method to a Liebig's condenser, whence a rapid and effectual distillation is readily accomplished. The platinum cage thus acting twofold, both by retaining any paper that may become mechanically detached by means of the alcohol, and at the same time preventing the paper from becoming attached to the sides of the outer or retaining tube, and, by so doing, retarding the influx of alcohol. In cases where the weight of residue is required it forms a



most effective and simple arrangement, being readily detached from the glass tube when required, and admitting of being readily weighed by suspending it from the beam of a balance by means of the small hook provided at the summit. In certain instances where the inorganic portion is required it may be readily ignited without detaching the residue and the amount estimated.

In the performance of milk analysis a rapid and accurate determination may be made as follows, a sufficiency of the sample having been evaporated in a platinum dish to a convenient bulk. A known quantity of sand which has been thoroughly purified and tared is placed in a paper or fine linen filter and the milk poured into the same, the sand at once retaining without risk of loss the whole of the evaporated sample, which, after drying until

constant, and deducting superfluous substances, gives the total percentage of solids: or it may be divided into two portions, using the residue for extraction of fat only, relying upon a second portion for estimation of solids.

With reference to sand I may also state that I have frequently used with success prepared sponge as an absorbing agent.

The following figures have been actual results obtained when in comparison with other methods, using, in each instance, the same amount of alcohol and an equal duration of time, those marked A, B, C, being results obtained by the platinum apparatus, while those marked D, E, F are results obtained by the usual extractors.

A.	
Extract soluble in alcohol at 80 per cent	54'36
Insoluble	26'18
B.	
Soluble extract	59'98
Insoluble	20'20
C.	
Soluble extract	41'63
Insoluble	19'15
D.	
Extract soluble in alcohol.. .. .	54'01
Insoluble	26'53
E.	
Soluble	59'56
Insoluble	20'62
F.	
Soluble	41'11
Insoluble	19'67

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

THE APPLICATION OF DOUBLE PYROPHOSPHATES FOR THE ELECTROLYTIC SEPARATION AND DETERMINATION OF METALS.

By Dr. ALBANO BRAND.

(Continued from p. 4).

IN acid solutions only the double manganic pyrophosphate is formed without undergoing a decomposition; whilst in a sulphuric solution it remains permanent during the entire duration of the electrolysis; in a strongly nitric solution the reductive action soon preponderates, for the liquid after a time becomes again colourless.

In the electrolysis of the double manganese-ammonium salt in an excess of the precipitant there is formed, with currents of all strengths, merely the double manganic salt, without undergoing a decomposition, and the solution, according to the proportion of manganese, takes a colour ranging from a pale rose to a deep claret.

From these solutions the manganese cannot be separated quantitatively, but its determination succeeds very well if ammonia is added.

From the strongly ammoniacal solution of the double manganese sodium salt, in case of weak currents the manganese separates as peroxide, adhering firmly to the anode; the liquid no longer turns brown, but the formation of the red manganese salt does not entirely cease until about 15 per cent of strong ammonia is added to the solution.

In the preparation of the electrolyte only so much sodium pyrophosphate is used as is fully sufficient for the formation of the double salt, and the precipitate is redissolved in ammonia. The platinum capsule is conveniently used as positive electrode, and if but little man-

ganese is present (0.02 gm. Mn in 100 c.c.), a current is used of 0.1 c.c. detonating gas per minute; if more manganese is present the strength of the current is reduced at the beginning (0.01 c.c. if 0.1 gm. Mn in 100 c.c.). From a solution of 200 c.c. 0.2 gm. manganese can be conveniently deposited as peroxide upon a platinum capsule of 150 c.c. surface. The strength of the current towards the end must not be increased above 0.4 c.c., since with stronger currents gas is liberated and separates the deposit from the capsule.

As the precipitate must be well washed, in order to remove all non-volatile salts, it is well not to try to keep all the deposit adhering to the capsule. All the flakes which become detached are collected upon a small filter free from ash, which is then burnt in the capsule. Only distilled water must be used in washing, since the use of alcohol causes the entire precipitate to become detached.

The conversion of the hydrated manganese peroxide into manganomanganic oxide is effected more rapidly over the blast than over a Bunsen. An oxidising flame gives good results.

5. *Zinc*.—The white gelatinous precipitate of the zinc salts dissolves readily in an excess of the precipitant and behaves normally. In these solutions soda-lye produces a precipitate insoluble in excess.

For the determination of zinc, a solution of the double salt mixed with ammonia (or, better, with ammonium carbonate) is suitable, and the metal is deposited in an adhesive condition and of a zinc-grey colour. If much zinc is present (0.2 gm. or upwards) the bulk is thrown down with a current of 5–10 c.c. detonating gas per minute, but for the completion of the reduction a current of 15–20 c.c. is needed. An anode of wire yields a more uniform deposit than one of sheet metal. As in the case of iron, the deposit must be washed without interrupting the current.

The author has several times—though not invariably—succeeded in dissolving off the deposit of zinc from a platinum capsule (not, of course, from silver or tin) in cold strong aqua regia, so as to leave no residue; the capsule is not attacked.

If the electrolyte contains both zinc and iron, the zinc, as in the case of the double oxalates, is completely deposited only if the iron is in large excess.

6. *Cadmium*.—The white cadmium salt deposited on the addition of sodium pyrophosphate is soluble in a large excess of the precipitant. It is easily dissolved in ammonia, but on the addition of ammonium carbonate there appears a precipitate. The double ammonium salt is more soluble, but is subsequently re-deposited; with ammonia and ammonium carbonate it behaves like the sodium salt.

The sparing solubility of the double sodium salt was an inducement to effect solution by the addition of acids.

From a solution in vitreous phosphoric acid, or sulphuric acid (less than 1 vol. per cent), the metal is deposited by a current of 0.2–0.5 c.c. detonating gas per minute, of a bluish white colour, but it has some tendency to become spongy. The phosphate, dissolved in vitreous phosphoric acid, gives better deposits.

After the addition of a little nitric acid, the metal requires for reduction the current of two to three Bunsen elements.

If the solution contains from 1 to 2 per cent (by volume) of strong sulphuric acid, the metal is deposited by a current of 0.2–1.0 c.c. in a white adhesive and distinctly crystalline condition. If the current, towards the end of the process is increased to 5–10 c.c., the reduction is quantitative. In presence of more than 1 per cent of sulphuric acid, only the sulphate, but not the pyrophosphate, is electrolysed.

The ammoniacal solution of the cadmium pyrophosphate is especially adapted for the quantitative separation of cadmium.

An abundant addition of ammonia is required, otherwise the salt is again separated out on electrolysis. In

order to overcome the strong polarisation, the decomposition is initiated by a current of 2–3 c.c. acting for a few seconds. Then a current of 0.3 to 1 c.c. is allowed to act until the bulk of the metal is deposited, and at the end the decomposition is accelerated by raising the current to about 5 c.c. The metal deposited is dense and of a silvery white colour, and perfectly smooth to the touch. If the initial current is stronger, tufted crystals are readily formed.

Cadmium is precipitated from its double pyrophosphates by sulphuretted hydrogen, but as this reaction is not sufficiently delicate for traces, the end of the reaction is best ascertained by the absence of deposition on fresh parts of the platinum capsule.

7. *Copper*.—The whitish blue precipitate appearing in solutions of copper salts is quite normal in its behaviour. It dissolves readily in an excess of the precipitant. On the addition of ammonia or ammonium carbonate the light blue solution becomes a dark blue.

The solutions of the double pyrophosphate are little suited for the determination of copper. From a solution mixed with ammonia, and still more with ammonium carbonate, the copper is separated out in a dense state only with very feeble currents; with stronger currents it is apt to become pulverulent. The solution of the copper salt in an excess of the precipitant, and without any further addition, is most suitable. A current of 0.1 c.c. detonating gas per minute, increased at the end to 1 c.c., throws down the copper in an adhesive metallic state, though of a dirty red colour.

If the solution of the double salt is mixed with sulphuric or nitric acid, the presence of the pyrophosphoric acid does not disturb the process, and the copper is deposited with its usual metallic properties.

8. *Silver*.—The white silver pyrophosphate is almost insoluble in an excess of sodium pyrophosphate, but readily soluble in ammonia and ammonium carbonate. The silver salt precipitated by ammonium pyrophosphate is soluble in an excess of the precipitant and in ammonium carbonate, but is re-precipitated by ammonia.

From a solution of the silver-sodium pyrophosphate in ammonia, or in ammonium carbonate, the silver is readily separated by a current of 0.01 c.c., but has a disposition to become spongy.

For a quantitative determination, we may use the electrolysis of a solution of the sodium double salt, faintly acidulated with nitric acid, by a current of 0.01 c.c. detonating gas per minute, increasing towards the end to 0.2 c.c.; but this solution offers no advantages as compared with a potassium cyanide solution.

9. *Mercury*.—Mercurous salts yield, with the sodium and ammonium pyrophosphates, a white precipitate readily soluble in an excess of the precipitant. In this solution ammonia, ammonium carbonate, and many other salts produce a black-grey precipitate; a similar decomposition is also produced by boiling or by electrolysis.

Mercuric salts give with sodium pyrophosphate a precipitate insoluble in an excess of the precipitant, but readily soluble in ammonia or ammonium carbonate. The mercuric nitrate, of which H. Rose and A. Schwarzenberg stated that the white precipitate first formed is turned reddish yellow or yellowish red by an excess of sodium pyrophosphate, behaves in a similar manner if the saline solution contains so much nitric acid that it has still an acid reaction after the addition of the sodium pyrophosphate necessary for the formation of the double salt. The salt precipitated by ammonium pyrophosphate is soluble in a large excess of the precipitant, but behaves otherwise like the sodium salt.

For quantitative determinations the most suitable are the solutions of the double mercuric salt in ammonia or ammonium carbonate; mercurous salts must previously be converted into the mercuric state.

The reduction of the double mercuric salt is effected by currents of all strengths. With a current giving 2 c.c. detonating gas per minute, 1 gm. of the metal can be

quantitatively deposited in five to six hours. The reduction is complete when a few c.c. of the electrolyte no longer give a precipitate with ammonia.

After pouring off the liquid the metal is washed with distilled water, alcohol, and ether, and dried for a short time over sulphuric acid in the exsiccator.

(To be continued).

A DESCRIPTION OF SEVERAL YTTRIA AND THORIA MINERALS FROM LLANO COUNTY, TEXAS.*

By W. E. HIDDEN and J. B. MACKINTOSH.

(Concluded from p. 9).

THORO-GUMMITE, a Hydrated Uranium Thoro-Silicate.

THIS mineral, of which we have been able to gather about one kilo., occurs intimately associated with fergusonite and cyrtolite, and masses up to three ounces have been found, though for the most part it is in very small pieces. It is of a dull yellowish brown colour, has hardness above that of gummite, or 4-4.5, and occurs commonly massive, though several well-defined groups of zircon-shaped crystals have been discovered with angles near to those of zircon. It has a characteristic colour, after ignition, becoming of a dull greenish hue, thus it is distinguished from freyalite, eucasite, and thorite, which species it otherwise resembles in some respects. Its specific gravity varies from 4.43 to 4.54. It is easily soluble in nitric acid. The analytical results are:—(See Table I.)

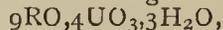
Regarding phosphorus as non-essential and as combined with the slight excess of uranium, above that which is required by the formula which we derive, and with the undetermined and lost constituents, we get the oxygen ratio of $UO_3 : SiO_2 : ThO_2 : H_2O = 1 : 2 : 2 : 2$. The last three terms are in the proportion required by thorite, and we see that the molecule of the mineral may be regarded as made up of three molecules of thorite linked together by one of uranic oxide, forming a compound molecule, which at first sight seemingly complex, is really of great simplicity.

Using graphic notation, the formula of the mineral is $UO_6(ThOSi)_3(OH)_{12}$, or when written in the usual manner $UO_3, 3ThO_2, 3SiO_2, 6H_2O$. The thoria and silica bear the same relation to the uranium, and it seems better to regard the mineral as a hydrated thoro-silicate of uranium, rather than as a urano-silicate of thorium, or as a double silicate of uranium and thorium, if, indeed, we might not go further and consider the whole as a duodeci-atomic molecule of a complex inorganic acid. We name this mineral *thoro-gummite*, because it is a gummite in which the water has been replaced by the thorite molecule.

NIVENITE, a Hydrated Thorium-Yttrium-Lead Uranate.

This mineral we found intimately associated with fergusonite and thoro-gummite. It is as yet a rare mineral at the locality. Its specific gravity is 8.01. $H. = 5.5$. It is velvet-black in colour, and when powdered becomes-brown black. After ignition it turns blue-black. As yet only massive pieces have been found, but some of these suggest that the species may be isometric in crystallisation. It is easily soluble in nitric and sulphuric acids, and some slight effervescence† was noticed upon dissolving the mineral. The analysis gave the following results:—(See Table II.)

The ratios found lead to the general formula—



in which, RO may be replaced by its equivalent in R_2O_3

* From the *American Journal of Science*, Third Series, vol. xxxviii., No. 228, December, 1889.

† Cf. Hillebrand, who has identified nitrogen in uranite, *American Journal of Science*, Oct. 1889, p. 329.

and RO_2 . If the iron be calculated as protoxide, and a corresponding increase be made in the amount of uranic oxide, the ratio for $UO_3 : RO : H_2O$ becomes 12 : 8.74 : 3.40. As it was not possible to determine the state of oxidation of the iron in presence of the two oxides of uranium by any process known to us, we cannot give the exact ratio, as it exists, but would point out that if only 0.33 per cent of ferric oxide is present and the rest of the iron is present as protoxide, then the ratio of UO_3 to bases will be exactly that which is required by the formula.

This mineral is allied to the rare species cleveite* and bröggerite,† and we give below the analysis with the formulæ which we have calculated from them, so that the points of distinction may be made evident. (See Table III.)

In the bröggerite analysis a small amount of silica occurs, which if supposed to exist as admixed silicate will reduce the excess of basic oxygen. Neglecting the water in bröggerite the oxygen ratio for these minerals will be therefore:—

	Bases. $RO_2(R_2O_3RO)$	UO_3	H_2O
Cleveite	$\frac{1}{1}$	2	1
Bröggerite	$\frac{2}{1}$	1	

The comparison of the three formulæ shows the relationship clearly (RO including RO_2 and R_2O_3), as follows:—

Bröggerite	3RO, UO_3 .
Cleveite	6RO, $2UO_3$, $3H_2O$.
Nivenite	9RO, $4UO_3$, $3H_2O$.

We have named this mineral *nivenite*, in recognition of the energy which Mr. Niven has displayed at this locality, and the assistance which he rendered us in obtaining the mineral for investigation.

FERGUSONITE.

This heretofore rare mineral occurs in large quantity at this new locality. Up to this date we have received over seventy kilos., some masses of which weighed over a pound. Broken prisms, rough in form, rarely showing terminal planes, and masses of crystals interlacing each other in the manner of occurrence. The immediately associated minerals are cyrtolite and thermo-gummite and also magnetite. The gadolinite also sometimes encloses it. It also occurs alone in a matrix of orthoclase or of quartz. One large mass of this kind of gangue, upon being broken up, yielded over thirty kilos. of pure mineral in the form of fragments, most of which were basal sections of crystals which had been originally four to eight inches long and about $1\frac{1}{2}$ c.m. thick.

We have found two distinct varieties, of which we here append analyses and description.

Fergusonite, Mono-Hydrated.—Specific gravity = 5.67; hardness 6-6.5; forms tetragonal, with acute octahedral terminations, a zirconoid plane hemihedrally developed, and, rarely, the basal pinacoid. The crystals are rough and dull grey exteriorly, but with a bronzy sub-metallic appearance on the surface of fracture, which is small, conchoidal, and brilliant. Thin splinters show a yellowish brown translucence; colour bronzy hair-brown; streak and powder dull brown. It is infusible, but on ignition the powdered mineral changes to a pale olive-green colour, and a momentary glow creeps over the mass at the point of redness. Fragments decrepitate violently when heated. With a microscope a peculiar light brown muddiness is noticed, and the mineral is filled with minute streaks and spots of a darker shade, all of which may indicate incipient alteration.

Crystals often have a thin coating of, or are otherwise partly altered to, the tri-hydrated variety, next described. It is decomposed when in fine powder by hydrochloric

* Dana's Appendix, III., p. 28.

† *American Journal of Science*, June, 1884, p. 493.

TABLE I.

SiO ₂	13'085		
UO ₃	22'43		Oxygen ratio. 43'62 = 2'000
ThO ₂	41'44		23'37 = 1'071
Al ₂ O ₃	0'965		31'22 } 2'83 } 1'59 } 6'30 } 43'64 = 2'001
Fe ₂ O ₃	0'845		0'97 } 0'73 } 43'78 = 2'008
(CeY) ₂ O ₃ , &c.	6'69	Atomic weight = 135	
PbO	2'16		
CaO	0'41		
H ₂ O	7'88		
P ₂ O ₅	1'19		
Moisture	1'23		
	<hr/>		
	98'325		

TABLE II.

UO ₃	46'75		
UO ₂	19'89		Oxygen ratio. 48'69 = 12'
ThO ₂	7'57		14'62 } 5'74 } 11'34 } 37'33 = 9'20
Y ₂ O ₃ , &c.	11'22	Atomic weight 124'2	1'08 } 4'55 } 14'11 = 3'48
Fe ₂ O ₃	0'58		
PbO	10'16		
(Ignition) loss H ₂ O	2'54		
Insoluble	1'22		
	<hr/>		
	99'93		

TABLE III.

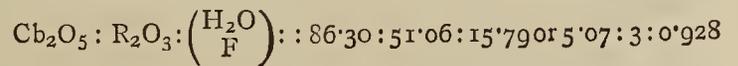
<i>Cleveite.</i>				<i>Bröggerite.</i>			
Specific gravity = 7'49.				Specific gravity = 8'73.			
	Per cent	Oxygen ratio.		Per cent.	Oxygen ratio.		
UO ₃	42'04	43'79		38'82		40'44	
UO ₂	23'89	17'56	} 21'17	41'25	} 30'33	} 34'61	} 44'18
ThO ₂	4'76	3'61		5'64			
Y ₂ O ₃	6'87	9'03	} 42'16	2'42	} 3'18	} 9'57	
Er ₂ O ₃	3'47	2'73		—			
Ce ₂ O ₃	2'33	2'16	} 20'99	0'35	} —		
Fe ₂ O ₃	1'05	2'00		—			
FeO	—	—		0'30	1'75		
CaO	—	—		8'41	0'54		
PbO	11'31	5'07		0'81	3'77		
SiO ₂	—	—		0'83	2'70		
H ₂ O	4'28	23'78		4'61 (neglect)			
	<hr/>						
	100'00			100'09			

acid, with separation of columbic acid. The analytical results are as follows:—

Cb ₂ O ₅	46'27		
UO ₃	1'54		Oxygen ratio. 86'30
ThO ₂	3'38		1'59
Al ₂ O ₂	0'09		2'56 } 0'27 } 1'83 } 26'70 } 52'65
Fe ₂ O ₃	0'98	Atomic weights,	1'83
(A) Y ₂ O ₃ *	23'95	110'55	26'70
(B) Y ₂ O ₃ *	18'38	113'3	20'07
PtO	1'43		0'64
ZnO	0'24		0'30
CaO	0'10		0'18
MgO	0'04		0'10
Ignition H ₂ O	1'98		11'00
110° C. H ₂ O	0'04		—
F	0'91	Atomic ratio	4'79 } 15'79
	<hr/>		
Less O = F	99'33		
	0'38		
	<hr/>		
	98'95		

* Total Y₂O₃, &c., and Ce earths = 42'33

Counting UO₃ as combined with a portion of the bases in the proportion R₂O₃—UO₃, we have for the oxygen ratio of the other constituents, counting fluorine as replacing hydroxyl,—



This leads to the formula Cb₂O₅, R₂O₃, H₂O; or if bases are counted as RO then R₃Cb₂O₇(OH, F)₂.

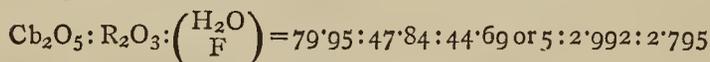
We tested the columbic acid for titanitic acid and tin, but, although we obtained small quantities of precipitates, they proved to be largely, if not altogether, columbic acid, and we did not detect the presence of any other substance; Tantalic acid was not looked for.

Fergusonite, Tri-Hydrated.—Specific gravity = 4'36—4'48; hardness about 5; colour deep brown, almost black, thin edges show a yellowish brown translucence; form and exterior appearance same as the species previously described; streak and powder pale greenish grey; on ignition turns light brown, but does not glow or decrepitate like fergusonite; is decomposed by hydrochloric acid, with separation of columbic acid.

Analysis.

		Oxygen ratio.	
Cb ₂ O ₅	42.79	79.95	
UO ₃	3.12	3.24	
UO ₂	3.93	2.90	}
ThO ₂	0.83	0.62	
Al ₂ O ₃	0.85	2.49	}
Fe ₂ O ₃	3.75	7.03	
Y ₂ O ₃ , &c. ..	31.36	32.28	} 51.08
PbO	1.94	0.87	
CaO	2.74	4.89	}
Ignition H ₂ O ..	7.57	42.05	
110° C. H ₂ O ..	0.62	—	} 44.69
F	0.502	2.64	
	100.002		
Less O = F ..	0.206		
	99.796		

Combining UO₃, as before, with bases to form R₂O₃, UO₃, the oxygen ratio of the remainder will be—



This gives the formula Cb₂O₅, R₂O₃, 3H₂O, or counting bases as RO, then R₃Cb₂O₅(OH, F)₆. On comparing the properties of the two minerals here described with typical fergusonite we notice a graduation from the one extreme to the other.

		Specific gravity.	Hardness.	When heated.
Fergusonite.	R ₃ Cb ₂ O ₈	5.838 (?)		
Mono-hydro-fergusonite	R ₃ Cb ₂ O ₇ (OH) ₂	5.67	6.5	Pale olive-green decrepitates.
Tri-hydro-fergusonite	R ₃ Cb ₂ O ₅ (OH) ₆	4.36-4.48	5.	Light brown, does not decrepitate.

Of other published analyses of fergusonite, that of the Ytterby variety, by Nordenskiöld ("Dana's System Min.," p. 523), corresponds to the di-hydrated mineral. Since we find fluorine in the specimens we have analysed from Texas, we are led to conclude that the water is not present as water of crystallisation, but as hydroxyl which is partially replaced by the fluorine, and this being so, we consider that the name fergusonite should be reserved for the anhydrous mineral, and that the various definite alteration products, with two, four, six, and perhaps more hydroxyls, should be distinguished in some manner, either by prefixing mono-hydro, di-hydro, &c., or by special names. It seems better that the first method of distinguishing them should be followed. We believe that we have observed a still higher alteration product in traces on some of the specimens we have obtained from Texas.

Allanite has not as yet been found very abundantly at this locality, and all of the ten kilos. obtained was massive-nodular in form. Its surface alteration is very slight compared with that of the other allied minerals. Its colour is shining pitchy black. Powder and streak dull greenish brown. Upon ignition it first turns red-brown and then becomes coal-black. It is opaque, except in the very thinnest splinters, when a greenish brown translucence is evident. Specific gravity = 3.488. We have made no complete analysis as yet, but the specimen tested showed the presence of considerable quantities of the cerium-yttrium earths and of thoria, and we learned that it was completely soluble in acids, with separation of gelatinous silica, either before or after igniting the mineral (like the associated gadolinite). The better masses have been found quite isolated from the other occurring minerals.

Molybdenite occurs sparingly in quite large folia, and

in hexagonal tables, with the cyrtolite and fergusonite. Only a few ounces have been collected.

Molybdenite was noticed in the cavities once occupied by molybdenite, and it often yet retained the plate-like form of the mineral from which it was derived by alteration. Its colour was white to greenish white. Specific gravity = 4.004. On two specimens indistinct crystals have been found, having a light apple-green colour and almost perfect transparency. Qualitative tests have shown the absence of any large amounts of anything but molybdic acid.

Cyrtolite has been found abundantly in both massive form and in good crystallisations. One hundred kilos. have thus far been collected while mining the yttria minerals already herein described. This mineral here occurs in thick plates attached to the biotite and also constituting veins in the coarse pegmatite. It is often the matrix of the thoro-gummite and fergusonite. Specific gravity = 3.652. It occurs in tetragonal forms, with all the planes rounded, and polysynthetic groupings of crystals are very common. Its colour ranges from dull grey, through various shades of brown to deep brown and almost black. Hardness about 5. We shall defer further mention of this mineral until we have examined it more thoroughly.

Fluorite occurs in some abundance. Masses of a pale greenish kind were found, weighing fifty pounds, tightly embedded in the pegmatite. Purple and white shades have also been found. A very opaque dark purple kind has been found in small masses. Its property of phosphorescing (green) when gently heated has given rise to a great local interest in this particular mineral.

Gummite occurs sparingly, but we have not as yet been able to find it in a sufficiently pure condition for examination. Several varieties have been seen, and "yttrogummite" is very probably one of them.

Tengerite (?)—In the cracks and fissures of the gadolinite and yttrialite a white mineral, rich in CO₂, is often noticed. We have seen it in globular radiated incrustations and in one instance in distinct transparent isolated crystals. Dr. Genth has already noted its occurrence, and, as he observes, there is not enough now obtainable to show its composition except by qualitative tests.

Fetid Gas.—Upon breaking some of the cyrtolite, while at the mine, a fetid odour, quite different from H₂S, was noticed. Simply rubbing two massive specimens together is sufficient to develop this very disagreeable smell.

In conclusion, we take this opportunity to thank Mr. Barringer for his kind attentions and generous services extended to Mr. Niven and to one of us while visiting this very interesting locality.

VANADIUM IN CAUSTIC POTASH.*

By EDGAR F. SMITH.

THE occurrence of vanadium in commercial caustic soda has been noticed (see Baumgarten, *Zeitschrift für Chemie*, 1865, 605, and Donath, *Zeitschrift für Analyt. Chemie*, xxi., 45). As far as I am aware, it has not been observed in caustic potash, hence the following lines.

While engaged in making certain decompositions, for which I employed the ordinary stick potash, I was rather surprised, after saturating the alkaline solutions with hydrogen sulphide, acidulating with hydrochloric acid, and heating for several hours, to discover that the separated sulphur showed a decidedly chocolate-brown colour. This occurred repeatedly. The quantity of dark material was never very great, yet it was present even in potash from alcohol. Some preliminary experiments were made which pointed to vanadium. I therefore

* Read at the Chemical Section of the Franklin Institute, Nov. 19, 1889.

saturated the warm aqueous solution of three pounds of stick potash with hydrogen sulphide. Heat was applied for several hours longer, and during this period the liquid gradually assumed a yellow to deep red colour. Hydrochloric acid was added to distinct acid reaction. The separated sulphur was quite dark in colour. After filtration and washing, the residue was dried and treated with carbon disulphide to extract the free sulphur. The chocolate-coloured mass remaining after this treatment dissolved, with exception of a slight quantity, in yellow ammonium sulphide, from which it was re-precipitated by dilute acid. Again washed, treated with carbon disulphide, and carefully ignited, there remained a crystalline mass. With a small quantity of this last product I made the phosphorous bead test—yellow, passing through dark to green when cool. Another special test consisted in dissolving a portion of the ignited residue in a drop of concentrated sulphuric acid free from iron. One c.c. of water was next added, and to this colourless solution from one to three drops of a dilute potassium ferrocyanide solution, whereupon the liquid acquired a fine green colouration. This latter test Dr. Walz (*American Chemist*, vol. vi., p. 453) employed in detecting the minute quantities of vanadium in American magnetites. He considers it conclusive evidence of the presence of vanadium. The most important test, and that which I applied to the remainder of the ignited residue, after effecting its solution in nitric acid, was to add a large piece of ammonium chloride to the ammoniacal solution. The morning following, crystals of ammonium vanadate had separated. These gave the true vanadium bead, and when ignited, moistened with pure strong nitric acid, and evaporated, left the deep red-coloured residue characteristic of vanadium compounds.

The vanadium sulphide, as first obtained, was impure, consequently the reactions were at times masked, and it was only after eliminating some silver and iron that the reactions were unquestionable.

The impure sulphide from the three pounds of caustic potash weighed about one-half grm.

THE CHEMICAL PROBLEMS OF TO-DAY.*

By VICTOR MEYER.

WHEN, a short time ago, I was called upon to speak before you, I gladly and zealously approached the work which such an occasion seemed to call forth. It seemed to me that it would be an effort worthy of this assemblage of scientific men to recall the permanent additions that chemistry has made in our day to the treasure of human knowledge, and to enumerate the problems which seem to lie nearest us in the future.

A science which, as such, is hardly older than the great European revolution, the centennial of which we witnessed a few months ago, and which, in this short time, has caused changes in our spiritual and material life hardly less than those of the political revolution, such a science, I have thought, may, without temerity, boast of its achievements.

And yet the chemist approaches such a task with a certain hesitation, from which the astronomer, the physicist, and the mathematician are free. Has it not been in our own day that the most prominent orator amongst German naturalists, one who astonishes us by the comprehensiveness of his knowledge, has adopted as his own Kant's judgment on chemistry, namely, that "chemistry is a science, but not a science in the highest sense of the word, that is, a knowledge of nature reduced to mathematical mechanics." And this dictum is accepted, not as

a blemish upon our science, but with the fullest and most perfect recognition of the immense achievements which modern chemistry has registered as its own.

But all of the marvellous successes of the atomic theory and of the doctrine of structure, the synthesis of the most complicated organic compounds, the blessings of an enlarged pharmacopœia, the potent revolution in technological processes, the new and systematic methods of production, which have been characterised by an eminent technologist as "the gaining of gold from rubbish"—all this seems trifling to the mind that looks down from its standpoint of mathematical mechanics when compared with the work of a promised Newton of chemistry, who some day will represent chemical reactions in the thought and in the language of mathematical physics.

And if he who looks from a height is justified in the expression that to-day chemistry, in the recognition of ultimate causes, stands yet below astronomy of the time of Kepler and Copernicus, must not the chemist lose courage if he attempts, before an illustrious assemblage, to raise a song of praise to his science, to glorify what she has done, and what in the future she seems chosen to do? If, in spite of this, the attempt be made, it must be with that resignation which rests upon the belief that "we should consider everything, but to aim only at that which is possible."

Though we share, with full conviction, the expectations of a Newtonian period in chemistry, we hardly venture to hope that that period is near, and even the most enlightened representatives of the newer physical chemistry seem but precursors of that distant era.

Perhaps the chemist, immersed in the daily work of his science, fails to take the comprehensive view of one who, from a distant height, looks down upon the same. But those who are surrounded by the whirl of hourly renewed work recognise, all the more clearly, the immense amount that remains still to be achieved before those distant aims can be realised. This epoch, so rich in pathfinders in the department of physics, has rarely directed the highest order of research into the territory of our science, and especially have the more complicated chemical phenomena been avoided.

If, in a period that has witnessed the discoveries of Helmholtz, Robert Mayer, Joule, Clausius, and van't Hoff, the revolutionising progress of knowledge has been limited to Physics, and if only modest applications of what was gained have been made in related studies, then the epoch seems not yet to be at hand in which chemical processes can be thought of as we think of the movements which we feel as sound, light, or heat.

A humiliating statement! But, strange to say, the chemist of to-day has hardly time to complain of this resignation imposed upon him, and this for reasons easily understood.

If—without question—it is the aim of all natural science to understand phenomena so fully that they may be described in a mathematical form, and, as far as they are unknown, may be predicted, a science which is so far distant from this aim as to look merely for the *path* that shall some day lead to it must be considered as in its infancy. In the present stage our way of thinking and acting has this peculiarity. In every science phantasy must stand as another power alongside of knowledge and reasoning. But the influence of phantasy upon knowledge is all the greater the further this latter is distant from the mentioned ideal. And thus it happens that in the chemistry of to-day phantasy and intuition have a larger scope than in other sciences, and that occupation with the same, besides the pure scientific satisfaction that it yields, brings an enjoyment which, in a certain sense, reminds one of the activity of an artist. He, however, who only knows chemistry as a tradition of perfectly clear facts, or who thinks to see the real soul of chemical study in measuring the *physical* phenomena which accompany chemical transformations, feels no breath of this enjoyment.

* An Address delivered at Heidelberg at the First General Session of the Sixty-Second Meeting of the Association of German Naturalists and Physicians, Sept. 18, 1889. Translated, by L. H. Friedburg, from the *Deutsche Rundschau*, Nov., 1889.

The feeling is only disclosed to him who ventures into that ocean of the unknown that is spread out before us in the *organic chemistry* of the day; to him who is not appalled by a wilderness populated with thousands of individuals, of which every one shows a peculiar fully unknown originality, and to him who attempts to become better acquainted with some of them, even if he is at a loss for a means of approaching them. To proceed with success in this direction is only granted to the genius—the method that leads onward cannot be learned, and it has only been practised with success by a small number of chosen ones.

Indeed, in the experimental study of organic chemistry the “presentiment” of happenings, the actuality of which is not indicated by any law to be expressed in words, has shown surprising results; here the thought is aided by a something which we may meanwhile term “chemical feeling,” a name which will disappear as soon as the progressive approach of chemistry to the mathematical physical basis shall have disclosed its meaning and shall have tabulated it amongst the methods which lead to the recognition of the new. The effect of this peculiar chemical method of study is not here to be dwelt upon in detail. Let it suffice to say that without it the most brilliant discoveries in organic chemistry would not have been made, just as little as a Kekulé would, without it, have been unable, in contradiction of numerous data in chemical literature never before doubted, to affirm the non-existence of isomeric monochlorbenzol and of such bodies as were said to consist of a benzol ring and but one bivalent atom. Those significant hypotheses by means of which the knowledge of aromatic substances has been revealed to us, could not have been made solely upon the ground of exact observation; they required, at the same time, a pronounced chemical instinct. There was no logical reason in declaring the existence of a phenylene oxide as an impossibility, since the ethylene oxide did exist; he who nevertheless ventured to do so, and at the same time ran directly in the face of experience, was surely led by a feeling which the present status of chemistry forbids us to replace by a process of thought.

But to return from the field of organic to that of general chemistry. Before we can arrive at a mathematico-physical treatment of chemical phenomena in general, two fundamental problems must be solved; an hypothesis which allows a control by experiment (even within the same limits which to this day are imposed upon physics in regard to the law of gravitation) must answer these questions:—*What is Chemical Affinity?* and *What is Valency?*

By means of laborious detail-work chemistry tries to approach the solution of these enigmas, but he who pursues chemical methods, who stands in the midst of chemical work—which aims only, as at a far distant task, at the discovery of a sure *path*—still sees such obstacles to be cleared away that he gives up the hope of living to see the new chemical era. He finds satisfaction in the consciousness of having exerted his best abilities in the elucidation of some minor and precursory principles.

If now we begin to consider—within the appointed limits—the most important achievements of chemistry, we cannot, at this place and at this hour of our meeting, be in doubt as to what is to be mentioned in the first place. The hospitable city that shelters us boasts of an advantage which is envied her by every other *Alma Mater*; here chemistry for more than a human lifetime has been represented by Robert Bunsen, of glorious name, and the very days which find us here assembled follow immediately the moment in which this hero of science has retired from his academical occupation. Who does not think, at such an hour, of the great teacher around whom ardent pupils from all parts of the globe were accustomed to congregate. But who, being called upon to-day to speak of the results of chemistry within the walls of Heidelberg, would not before all direct an eye upon that one discovery which

has lifted chemistry beyond terrestrial research, which has enabled her, like astronomy, to search the universe and to dissect the starry heavens, chemically, by the subtle appliances of analysis. If “old Heidelberg” has become a pearl amongst German cities by its history, by its numerous traditions, by the incomparable beauty of its situation—if its university is the ideal of the German academical youth, we may well regard as an immortal leaf in its wreath of honour, along with these glorious titles, the union of those two great men who first met in this city in the most courageous enterprise of the penetrating mind; who have pursued with astonishing success the investigation which has made spectral analysis the most potent of scientific weapons, and has rendered their names a charm, calling forth the admiration of the older minds and kindling in the minds of mere school-boys the flame of enthusiasm in the study and exploration of nature. The immeasurable results of that discovery—the consequences of which extend every day over new territories—are known in the widest circles, and to mention them to-day in detail would be but carrying owls to Athens. It behoves us in this place to mention reverently the names of Bunsen and Kirchhoff, to think of them with gratitude, and to hope that men, their equals, may not be entirely wanting in the next generation! The younger one of them, whose scientific fertility was only equalled by his greatness of soul and the charming modesty of his heart, has been taken away from us before old age had naturally limited him. Bunsen we still rejoice to call ours, who now, allowing the tools of his work to drop from his hand, looks forth to the evening of his life in quiet, happy leisure. May he be permitted for a long time to look back upon a life filled with greatest scientific achievements; may his calm friendly eye rest for many years upon the incomparable picture of his beloved Heidelberg.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 19th, 1889.

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

MESSRS. W. F. Butcher, C. F. Baker, A. L. MacLeroy, and F. Quincke were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward Whitley Allsom, Palace View, Cork; William Winson Haldane Gee, B.Sc., 124, Raby Street, Moss Lane East, Manchester; Arthur Hutchinson, Christ's College, Cambridge; Arthur Hotham McConnell, 10/2, Russell Chambers, Bury Street, W.C.; William Samuel Newman, Madras, India; Saville Shaw, Durham College of Science, Newcastle; William Charles Sayers, 63, High Street, Lewisham, S.E.

The following papers were read:—

106. “*Frangulin*.” By Professor T. E. THORPE, F.R.S., and H. H. ROBINSON, M.A.

The authors prepared the glucoside frangulin from the bark of the alder buckthorn (*Rhamnus frangula*) by first extracting with low boiling petroleum to remove plant fat, and next with methylated spirit, which removed the frangulin together with resins, &c. To this extract lead acetate was added to precipitate tannins, and after removing the excess of lead in the filtrate by means of sulphuretted hydrogen, the frangulin was obtained from it. 14 lbs. of the bark gave about 5½ grms. of frangulin.

Seven analyses were made of four different portions of frangulin which had been purified by different methods, and the results agreed with one another and corresponded

to the formula $C_{22}H_{22}O_9$: for every analysis the frangulin was dried at 120° until constant.

The frangulin was hydrolysed and the yellow product insoluble in water was analysed, in two cases after crystallising from alcohol and drying at 120° until constant, and in two cases after crystallising from benzene and drying at 180° . The results corresponded to the formula $C_{15}H_{10}O_5$. The product was directly compared with some emodin from rhubarb, and was found to give the same colour reactions, and the authors are satisfied as to its identity with that substance.

A phenylhydrazine derivative of the product soluble in water, and which has the power of reducing Fehling's solution, was prepared and compared with that obtained from glucose, and was found to possess quite different properties: hence it is concluded that the soluble product of the hydrolysis is not glucose.

The investigation of the nature of this soluble product, and of the equation representing the hydrolysis, will be continued by one of the authors.

107. "Arabinon, the Saccharon of Arabinose." By C. O. SULLIVAN, F.R.S.

In a former communication (*Chem. Soc. Trans.*, 1884, p. 55), under the name of α -arabinose, the author has described a substance obtained by hydrolysis of arabic acid, having an optical activity "well above $[\alpha]_D = 140$ "; this is more fully considered in the present communication. The details of its preparation from geddic acid, an acid obtained from Gedda gum—which the author will describe in a future notice—are fully given. As yet it has not been obtained in a crystalline state: when dried over sulphuric acid in vacuo, and then at a temperature gradually increasing to $75-80^\circ$, it is obtained as a glassy mass, which when pulverised forms a white hygroscopic powder. It has a specific rotatory power of $[\alpha]_D = 198.8^\circ$; and 100 parts have the same cupric reducing-power as 58.8 parts of dextrose. It yields arabinose on hydrolysis, and appears to bear a similar relation to this carbohydrate that saccharon (cane-sugar) bears to glucose: the author therefore terms it *arabinon*, preferring the vowel system of nomenclature to that proposed by Scheibler. Combustions were simultaneously made of saccharon and arabinon with the following results:—

	Saccharon.	Arabinon.	Theory for $C_{10}H_{18}O_9$.
Carbon	42.11	42.46	42.58
Hydrogen . . .	6.61	6.55	6.38

The molecular weight found by Raoult's method was 239.2; that of a carbohydrate of the formula $C_{10}H_{18}O_9$ is 282, and although the number obtained is low, bearing in mind the fact that this is the case with the "on" carbohydrates, and that the preparation may not have been free from ash constituents, there can be no doubt that the compound belongs to the "on" and not to the "in" or dextrin class. The amount of arabinose obtained on hydrolysing 100 parts arabinon was 104.9; the theoretical yield, if $C_{10}H_{18}O_9 + H_2O = 2C_5H_{10}O_5$, is 106.3.

108. "On the Identity of Cerebrose and Galactose." By HORACE T. BROWN, F.R.S., and G. HARRIS MORRIS, Ph.D.

The authors give the results of an examination of a sample of *cerebrose* prepared from phrenosin, which was placed in their hands early in 1888 by Dr. Thudichum, who first isolated and crystallised this substance. They show that its specific rotatory power, cupric reducing power, and molecular weight, as determined by Raoult's method, are identical with those of *galactose*, thus confirming the recent work of Thierfelder (*Zeit. Physiol. Chem.*, xiv., 209), who has proved the sugar produced by the action of acid on cerebrin to be galactose.

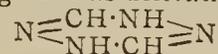
DISCUSSION.

Dr. THUDICHUM said that the specimen of cerebrose which has been examined by the author was prepared by him from *phrenosin*, $C_{41}H_{79}NO_8$. Messrs. Brown and Morris's experiments had been conducted in July, 1888,

and Mr. Brown's communication to him (Dr. Thudichum) on the subject, which he held in his hand, was dated August, 1888. Phrenosin consisted of the sugar now shown to be identical with galactose, $C_6H_{12}O_6$; of *neurostearic acid*, $C_{18}H_{36}O_2$, an isomer of stearic acid, fusing at 84° ; and of *sphingosin*, an alkaloid of the formula $C_{17}H_{35}NO_2$. There were, however, present in the brain a number of glucosides or saccharides, of which phrenosin was the most abundant and most characteristic; amongst the more neutral bodies of this kind was *kerasin*, $C_{42}H_{85}NO_8$, and amongst the more acid ones, which formed insoluble compounds with baryta or lead oxide, were three—cerebrinic acid, spherocerebrinic acid, and the principal (in quantity) cerebrinacide—compounds containing from 54 to 59 atoms of carbon, and from 9 to 21 atoms of oxygen. Of these, cerebrinic acid had also yielded the sugar; the others had not yet been tested in that respect. The compounds of this group present in the human brain were very numerous, and one of them contained as much as 4 per cent of sulphur in organic combination. Some human brains contained as much as 4 per cent of phrenosin, and therefore a human brain of 1500 grms. in weight contained potentially 15 grms. of galactose. In some diseases of a neurotic type he had found "cerebrose" in the urine, and of the cases of glycosuria of nervous origin (so-called) a certain proportion was no doubt due to the decomposition of some phrenosin in the brain and the consequent passage of the "cerebrose" into the circulation and out of it by way of the renal emanatories. It was an important fact that the crystallised sugar from phrenosin was always accompanied by an almost equal weight of uncrystallisable sugar of which the nature was not yet ascertained. Mr. Brown believed that his (Dr. Thudichum's) crystallised galactose, made from pure phrenosin, contained a little dextrose: the question then arose whether the uncrystallised sugar obtained was altered galactose or dextrose, or a sugar *sui generis*; if it was dextrose, or a sugar *sui generis*, the formula of phrenosin would have to be doubled, and it must be assumed to contain an *amylonide radicle*, such as he in his theory of the organoplastic substances had considered as forming the chemical skeleton of the albuminous matters. The special details concerning the substance alluded to were to be found in his "Treatise on the Chemical Constitution of the Brain," London, 1884, and an exhaustive critical consideration of the literature and chemistry of the "cerebrosides" or cerebrin bodies of the brain was contained in his German work on "Anatomical and Clinical Chemistry," Berlin, 1886.

109. "The Action of Chloroform and Alcoholic Potash on Hydrazines." Part III. By S. RUHEMANN, Ph.D., M.A.

The products formed by the interaction of these substances are to be regarded as derivatives of *tetrazine*,—



(*Chem. Soc. Chem.*, 1889, 242). The author describes the di-paratolyl, orthotolyl, and pseudocumyl derivatives, and their behaviour with nitric acid and bromine.

Paraditolyltetrazine is a weaker base than the diphenyl homologue; it forms an unstable monochlorhydride and a monomethiodide.

The ortho-compound appears to be somewhat more basic. It is noteworthy that while the formation of tetrazines from phenyl- and paratolyl-hydrazine is accompanied by that of the formylhydrazine, the formyl-derivative is not produced in the case of orthotolyl-hydrazine, although it is easily obtained by the interaction of the hydrazine and formamide.

Incidentally, the author describes pseudocumylhydrazine and several of its derivatives.

Mr. P. Braham exhibited a spectroscope without a lens, which was described at the meeting of the British Association at Newcastle. It consists of a taper tube, with a slit at one end and a direct vision prism at the other.

NOTICES OF BOOKS.

The British Journal Photographic Almanac and Photographer's Daily Companion, 1850. Edited by J. TRAILL TAYLOR. London: Greenwood and Co.

THE present rage for photography is something altogether exceptional. If we glance into the window of an optician, or a manufacturer of "philosophical" apparatus—as it is still occasionally called—we may be sure to see ten cameras to one microscope, or telescope, or spectroscope.

The volume before us gives the names and addresses of about 125 photographic societies in Britain alone; we can find no estimate of the number of members—amateur and professional—which must certainly amount to several thousands.

But before we pronounce this an encouraging feature we must ask how many of this multitude bestow any portion of their time and their energies on the important applications of photography in astronomy, biology, or geology? We fear that the majority of the host do little more than take portraits. On carefully examining the table of contents we find nothing on microscopic photography. There is, indeed, a paper on "telescopic photography," but it is merely terrestrial telescoping, and gives us nothing which might not be obtained without the telescope, if the operator conveyed his camera nearer to the objects.

Prof. C. Piazzini Smyth contributes, however, a very interesting paper on photography applied to the violet portion of the solar spectrum; when to the sight and to the author's spectroscopes all was darkness, the camera recognised "spectral lines of inconceivable delicacy, and in appalling numbers."

There still seems to be a little soreness between amateurs and professionals. A writer, speaking on behalf of the former class, reminds us of a time when the professional was not, and when the art was elaborated by amateurs, who had to devise their own apparatus, prepare their own chemicals, and elaborate the method of their use.

One writer here projects to form a photographic Trade's Union, with all the machinery for strikes, and for boycotting refractory members, &c. A "trade union organiser" is to be employed at £2 weekly. The union proposes to place men of equal merit on an equal footing. Here it differs from the generality of trades' unions, which seek to place men of unequal merit on an equal footing. This seems to us the first attempt to extend to brain-workers the benefits—real or imaginary—which result from such combinations.

A writer, who was on board H.M.S. *Thames* during the review at Spithead in honour of the German Emperor, reports that he obtained a negative not merely of two vessels which he intended to take, but also of three others at a considerable distance on the opposite side!

A Forecast of the Religion of the Future: being short Essays on some Important Questions in Religious Philosophy. By W. W. CLARK. London: Trübner and Co.

THIS book was published as far back as 1879, and is said to have been written between 1870 and 1876. Its subject-matter is not of a kind which admits of any formal discussion in the CHEMICAL NEWS. The origin of "Evil," one of the questions here raised, is not one with which scientific men are ordinarily occupied. They prefer to study the ætiology not of evil in the abstract, but of particular evils, such as pathogenic germs, malaria, vermin, blights, and the like, with a view to their destruction.

Mr. Clarke's position is fully antagonistic to doctrinal religion—a matter upon which we do not feel authorised to enlarge. But he is, perhaps, no less at issue with the conclusions of modern science, and with the scientific habit of thought. He seems disposed to recognise the obsolete notions of a fundamental abrupt boundary be-

tween the plant and the animal and between the animal and man. He quotes approvingly from a "recent writer"—not named—that "all progress is preceded by calamity, that all improvement is based upon defect." Of course, if there were no imperfection no improvement would be possible. Equally, of course, if we look back far enough from any of the great epoch-making discoveries in the world's history, we may feel certain of finding some calamity; but here the *post hoc* is not necessarily the *propter hoc*. It seems to us that the greatest improvements are made in times of peace and tranquillity. Shakspeare and Bacon were the offsprings of an age of remarkable national prosperity. Buffon, Lamarck, Lavoisier, and, in our own country, Cavendish, Davy, and Dalton, were not the children of the Revolution. The "Origin of Species" saw the light at a time disturbed neither by war nor by "reforms."

But we cannot undertake to examine in detail theories which have certainly no direct bearing upon chemistry or physics.

Catalogue of Standard Second-Hand and New Books, English and Foreign, on Chemistry and the Allied Sciences, Technology, Physical and Electrical Science, Metallurgy, Agriculture, Brewing, Dyeing, &c. By W. F. CLAY, 2, Teviot Place, Edinburgh.

THIS periodical catalogue has now reached its 28th issue, and certainly does not decline in value. In addition to standard works of quite recent date, we find many scarce and curious books which are otherwise difficult to meet with. The managers of scientific institutions, libraries, &c., will be able to procure from Mr. Clay sets of various journals, transactions, &c., which are now rarely in the market. How such works as the new edition of Watts' "Dictionary of Chemistry" can be offered at such relatively low prices is a mystery.

CORRESPONDENCE.

TO DETECT IRON IN ORGANIC TISSUES.

To the Editor of the Chemical News.

SIR,—I observe that Professor Zorner has recently published a simple method for the detection of iron in the tissues and direct products of plants and animals. His method I understand is merely to allow the organic substance to remain immersed for some time in a fresh solution of ammonium sulphide, when the presence of iron (?) is shown by the surfaces of the tissue in contact with the solution becoming black. The following mode, however, of identifying this metal in organic compounds is certainly more rapid, and I think also more correct and delicate than Zorner's. Heat the substance for a very short time with a little moderately strong *pure* nitric acid: then add water and potassium sulphocyanide solution. The red stain which forms on the surface of the body and the red colouration which spreads through the solution are of course excellent indications of the presence of iron. Or the substance after treatment with nitric acid and water may be brought into contact with excess of potassium ferrocyanide, and the presence of the metal proved by the formation of a blue stain on the body.—I am, &c.,

ALEXANDER JOHNSTONE.

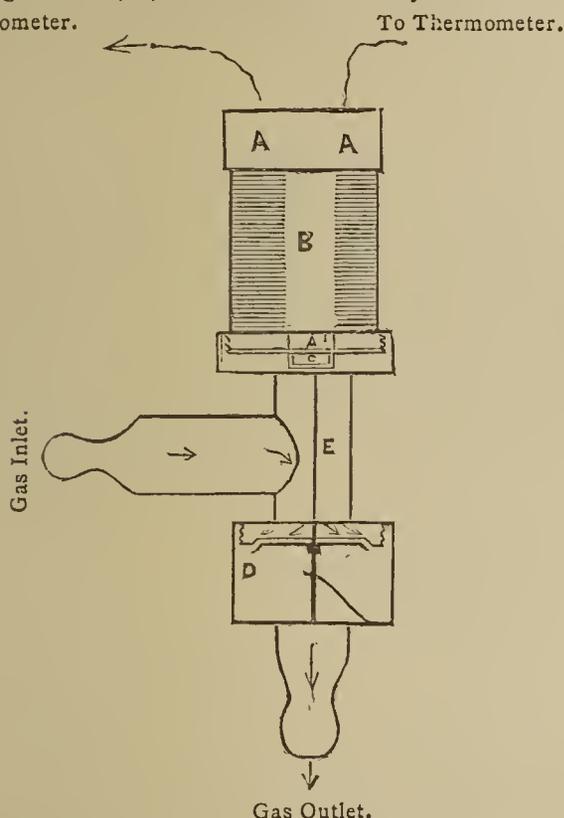
Edinburgh University.

ELECTRICITY IN CHEMICAL MANIPULATIONS.

To the Editor of the Chemical News.

SIR,—We observed in the CHEMICAL NEWS, vol. lxi., p. 4, a description by Mr. Reginald Fessenden of a piece of electro-thermostatic apparatus. We do not wish to discount Mr. Fessenden's claims to originality, but we think

it necessary to state that we devised a similar arrangement during the year 1888, and that for the last six months our thermostat has been on the market. We send a rough drawing of the latest form, which has, we think, this advantage over Mr. Fessenden's—that it cannot be tampered with or get out of order. A, A, A' are the iron poles of the electro-magnet, B, which is connected with an electric thermometer in the usual manner by means of a platinum wire fused into the bulb and another thrust down the stem. This is quite sensitive enough for ordinary work. c is the armature which, when the current passes, is pulled against A', pulling with it the rod E and the cup-edged valve, D, which fits accurately into its seat



and stops all supply of gas which passes round it in all directions when no current is flowing. The necessary quantity of bye flame is, of course easily arranged for. We may say that we lately saw in Paris another form of electro-thermostat, in which a hinged armature was made to act as a clip upon a piece of india-rubber tubing. In our form the valve falls of its own gravity, since we consider that any introduction of springs merely serves to make mechanism more costly, more cumbersome, and more likely to get out of order.

Thanking you in anticipation for the insertion of our letter, we are, &c.,

W. F. TAYLOR AND CO.

Harrow-on-the-Hill.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 26, December 23, 1889.

Formation-heat of Potas- and Sod-ammonium.
—M. Joannis.—For potassammonium, proceeding from solid potassium and liquid ammonia, the result obtained is +1.9 cal.; for sodammonium, with the same conditions, +0.8 cal.

On β -Inosite.—M. Maquenne.—This compound corresponds to the same formula as normal inosite,

$C_6H_{12}O_6$. It also possesses the function of a hexatomic alcohol.

A New Class of Diacetones.—A. Béhal and V. Auger.—This paper is not adapted for useful abridgment.

Analysis of the Meteorite of Migheï (Russia); Presence of a Combination not hitherto met with in Meteorites.—M. Stanislas.—The portion of this meteorite soluble in hydrochloric acid (85.167 per cent of the whole) consists of silica, magnesia, and ferrous oxide. The portion insoluble in acid (14.833 per cent) contains 31.804 per cent of organic matter. The fixed residue is composed of silica, magnesia, ferrous oxide, lime, alumina, with traces of manganic and chromic oxides. The organic matter, which forms 4.72 per cent of the whole, is split up, if heated to redness in a current of hydrogen, into carbon and a volatile compound of a bituminous odour.

Moniteur Scientifique, Quesneville.
November, 1889.

The Origin of Petroleum.—M. Anderson.—A discourse delivered at the last meeting of the British Association.

Detection of Margarine in Butters.—F. Jean.—The oleorefractometer of Amagat and Jean may be used for the detection of margarine. The zero of the graduation of the apparatus is found by means of an oil taken as type, operating at 45°. If the fatty matter of pure cow-butter is then introduced into the interior cell of the apparatus we see a deviation of 35° to the left of the zero of the scale, whilst oleomargarine prepared with the kidney-fat of calves and oxen, examined at the same temperature and under the same conditions, gives a deviation of -19°, or a difference of 16° from pure butter.

Industrial Society of Mulhouse.—Session of September 11, 1889.—M. Prud'homme sent in an extensive memoir on the salts and oxides of chromium. The green gelatinous chromium oxide precipitated from its alkaline solution is not anhydrous. Its composition, when dried at 100°, is $Cr_2O_3 + 5H_2O$. The violet and green salts of chromium oxide do not correspond to two different modifications of this oxide, but their nature depends on the temperature at which the oxide was dissolved. The minimum temperature of the formation of the green salts or of the transformation of the violet salts into green is 65°. Chromic oxide has the curious property of carrying with it, in its alkaline solutions, other metallic oxides, such as ferric and cupric oxides. The alkaline solution of chromic and cupric oxides in blue; if heated to a boil it deposits a red precipitate of cuprous oxide. Chromium chlorate is a very energetic oxidising agent, and may be used with advantage in rendering aniline blacks ungreenable. A solution of double chromium and ammonium sulphite obtained by mixing 45 grms. $K_2Cr_2O_7$, 20 grms. sodium carbonate, 100 c.c. ammonium sulphite at 36° (B.?), 100 c.c. of ammonia, and 1 litre of water keeps well, and may be used for mordanting cloth with chromium oxide, either by a slight steaming or a passage through the Mather and Platt apparatus.

M. Fehr exhibited specimens illustrating his researches on the formation of colouring-matters by the action of light upon a mixture of diazosulphonates and phenols.

M. Bourcart presented a note on the volumetric determination of alcohol and aldehyd by means of chromic acid.

M. Baumann sent a paper on the applications of *negrisine*, a new grey colouring-matter produced by the works of St. Denis (formerly Poirrier).

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. vii., No. 1.

The only chemical matter in this issue is a brief communication by Dr. L. L. de Koninck, referring, with evident scepticism, to the alleged decomposition of cobalt and nickel.

MISCELLANEOUS.

A Curious Invention.—Mr. C. S. S. Webster, F.C.S., sends us an india-rubber stamp which he has devised for stamping the double benzene chain. He is perfectly right in supposing that this little apparatus will be useful to demonstrators, abstractors, and to gentlemen preparing chemical papers for the press, or for reading before any Society. A skilful draughtsman may, indeed, draw such diagrams neatly and easily by hand, but to the majority of chemists we believe that Mr. Webster's little contrivance will be decidedly welcome.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Medical, 8.30.
TUESDAY, 14th.—Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8.
WEDNESDAY, 15th.—Society of Arts, 8. "London Sewage," by Sir Robert Rawlinson, K.C.B. (Adjourned Discussion).
— Meteorological, 7. (Anniversary).
THURSDAY, 16th.—Royal, 4.30.
— Chemical, 8.
FRIDAY, 17th.—Society of Arts, 5. "The India Office Records," by F. C. Danvers.
— Physical, 5. "On a Carbon Deposit in a Blake Telephone Transmitter," by F. B. Hawes. "On Electric Splashes," by Prof. S. P. Thompson. "On Galvanometers," by Prof. W. E. Ayrton, F.R.S., T. Mather, and W. E. Sumpner.

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By Order of the Board of Works for the Wandsworth District.

HENRY GEORGE HILLS,
Clerk to the Board.

East Hill, Wandsworth, S.W.,
January 1, 1890.

BOARD OF WORKS FOR THE ST. SAVIOUR'S DISTRICT.

APPOINTMENT OF GAS EXAMINER.—

The Sanitary Committee of the Board will meet on Monday, the 20th instant, at 3 P.M., to receive applications for the appointment of Gas Examiner for the above district, in accordance with Sect. 27 of the Metropolitan Gas Act, 1860, at a salary of £25 per annum. The person appointed must provide, at his own expense, a place suitable for gas-testing within the district, but all necessary apparatus for so doing will be provided by the Board. Applications should be in writing, and accompanied by a copy of testimonials (not more than three in number), and marked outside "Application for Appointment of Gas-Examiner." Six Candidates will be selected and submitted to the Board, who will meet on a subsequent day to make the appointment. Canvassing is strictly prohibited, and will disqualify Candidates. Particulars of the duties may be had on application.

W. H. ATKINS, Clerk.

Offices:—

Emerson Street, Bankside,
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January 6, 1890.

BOARD OF WORKS FOR THE ST. SAVIOUR'S DISTRICT.

APPOINTMENT OF ANALYST.—The

Sanitary Committee of the Board will meet on Monday, the 20th instant, at 3 P.M., to receive applications for the appointment of Public Analyst for the above district, in accordance with the provisions of The Sale of Food and Drugs Act, 1875, at a salary of £75 per annum. The minimum number of articles analysed to be 150 annually, and all above that number to be paid for at the rate of 10s. 6d. per sample. Applications should be in writing, and accompanied by a copy of testimonials (not more than three in number), and marked outside "Application for Appointment of Analyst." Six Candidates will be selected and submitted to the Board, who will meet on a subsequent day to make the appointment. Canvassing is strictly prohibited, and will disqualify Candidates. Particulars of the duties may be had on application.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1573.

ON ACETO-METANITROBENZOIC ANHYDRIDE.*

By WILLIAM H. GREENE.

In the reaction of acetyl chloride with silver metanitrobenzolate, L. Liebermann† claimed to have obtained metanitrobenzoyl acetic acid, a reaction which would be inexplicable and without analogy. In the course of another investigation, Bischoff and Rach‡ took the opportunity of studying the action of acetyl chloride on the silver salt of *o*-nitrobenzoic acid, and found that the reaction did not take place in the sense indicated by L. Liebermann.

Under the name acetylmethanitrobenzoic anhydride, Beilstein in his "Organische Chemie" (ii., 786) describes the product supposed by Liebermann to be metanitrobenzoyl acetic acid, but the properties mentioned accord as little with those which this anhydride should exhibit as with those which would be expected in the acid Liebermann thought he had obtained.

A preparation of this compound, according to the indications of L., by the addition of dry silver metanitrobenzoate to an excess of cold acetyl chloride, and pouring the product into water, yielded an acid fusing between 126° and 137°. 0.1866 gm. of the silver salt of this acid yielded 0.0731 gm. silver.

Ag found, 39.17 per cent. Ag calculated for nitrobenzoate, 39.42 per cent.

The acid is metanitrobenzoic, regenerated from the silver salt employed.

By the reaction of sodium metanitrobenzoate with acetyl chloride, extraction of the product with absolute ether, and evaporation of the latter, aceto-methanitrobenzoic anhydride may be readily obtained, as also by exposing silver metanitrobenzoate to vapour of acetyl chloride and extraction with absolute ether in the same manner. It crystallises in colourless needles, fusible at 45°, and remaining in superfusion at a much lower temperature. It is insoluble in water by which it is not at once decomposed when crystallised, so that it may be washed with dilute sodium carbonate and water, and quickly dried between filter papers without change. The presence of either alcohol or water in the ether used for extraction results in the complete decomposition of all the anhydride.

SIMULTANEOUS DETERMINATION OF CARBON AND SULPHUR IN ORGANIC SUBSTANCES.

By L. PRUNIER.

HAVING been compelled, in researches on a group of sulphuretted organic compounds, to execute numerous determinations of sulphur and carbon, the author has observed that such analyses are not only laborious (if we obey the classical method of making two separate determinations, one for sulphur and one for carbon), but often give erroneous results, generally in deficiency. The larger the proportion of sulphur the more these errors are to be dreaded.

After many trials, he has adopted a process, very manageable and relatively expeditious, which gives in

one and the same combustion the determination of the sulphur with more ease and accuracy than at present, and the determination of the carbon, though with rather more trouble and less exactitude.

He employs, to this end, pure crystalline permanganate, which is powdered and mixed with the weighed portion of the substance in question, in the proportion of 80 or 100 parts to 1. The whole is introduced into an ordinary combustion-tube, and the combustion is effected as with copper oxide. It takes place in an atmosphere of oxygen derived from the decomposition of the permanganate, which begins to be given off at 240° or upwards. The gases liberated are allowed to bubble through a solution of permanganate, and the apparatus is terminated by a tube containing baryta-water, which should not become turbid if the process is working regularly. The carbon and the sulphur ought to remain entirely either in the combustion-tube or in the solution of permanganate.

The contents of the tube are extracted with water. All the sulphur is found in the aqueous solution, which is filtered over asbestos to remove a deposit of manganese oxides, sometimes retaining a little carbon.

In half the filtrate, which is previously acidified and decolourised with hydrochloric acid, the sulphur is determined as barium sulphate in the ordinary manner.

The second half of the liquid and the totality of the insoluble residue left upon the asbestos serve for the determination of the carbon, which is rather more troublesome than that of the sulphur. In fact, the carbon is only partially converted into carbonic acid. As M. Berthelot has shown in his researches on the attack of organic substances by permanganate in solution, certain acids, such as the acetic, benzoic, and phthalic, obstinately resist complete oxidation. It is therefore necessary to submit this second half of the liquid to a prolonged ebullition in presence of sulphuric acid after having ascertained that there remains sufficient permanganate to complete the oxidation. All the carbon is thus ultimately transformed into carbonic acid, which escapes and is collected in the ordinary manner.

A similar treatment is applied to the insoluble residue. Lastly, to the quantity of carbonic acid obtained from the insoluble residue there is added double that resulting from the liquid, and from the total the proportion of carbon is inferred.

In the cases when the permanganate used contains substances capable of influencing the determination of the carbon (nitrates, chlorates, &c.), a blank experiment will show the corrections to be made.

This method has been found successful in the analysis of a great number of bodies containing, in some cases, more than 65 per cent of sulphur. Hitherto the determinations have been made on ternary compounds (carbon, hydrogen, and sulphur), or quaternary (carbon, hydrogen, sulphur, and oxygen), but not nitrogenous. Experiment will show if the process is equally applicable to all groups of organic compounds.—*Comptes Rendus*.

THE APPLICATION OF DOUBLE PYROPHOSPHATES FOR THE ELECTROLYTIC SEPARATION AND DETERMINATION OF METALS.

By Dr. ALBANO BRAND.

(Continued from p. 18).

10. *Tin*.—The stannous and stannic pyrophosphates are white and readily soluble in an excess of the precipitant, especially the former. In both the solutions of the sodium and ammonium double salt bear the addition of ammonium carbonate; ammonia occasions precipitation.

The double stannous salt is readily reduced either from a pyrophosphoric or an alkaline solution. On account of

* Read at the Chemical Section of the Franklin Institute, May 21, 1888.

† *Berichte*, x., 863.‡ *Berichte*, xvii., 2799.

the application of the salt in electro-metallurgy it is to be expected that the deposited metal must be of good quality. In fact, with feeble currents which give up to 0.1 c.c. detonating gas per minute they are dense, adhesive, and of a silvery whiteness, but they become grey if the current is a little stronger.

The quantitative determination of tin by the electrolysis of the double stannous salt is a failure, since a portion becomes oxidised to a stannic salt at the anode and thus escapes reduction. The sensitive reaction for stannous salts (which in a hydrochloric solution give, on the addition of iron chloride and potassium ferricyanide, a precipitate of prussian-blue) can after a time no longer be produced, whilst sulphuretted hydrogen throws down yellow stannic sulphide.

The double stannic salt requires very powerful currents for its reduction. Five freshly-charged Bunsen elements produce no deposit on a platinum capsule if the solution contains 0.3 gm. tin per 100 c.c. By more powerful currents from a dynamo, the metal is obtained as a beautiful dense white deposit of a silky lustre.

The quantitative determination of tin from the double stannic salt did not succeed. In several experiments there was always found a smaller quantity of tin than that corresponding to the quantity of double stannic chloride employed.

It is an open question whether this deficiency results from spitting (in consequence of the liquid becoming heated by the powerful current) or from imperfect reduction, since the completion of the reaction remained doubtful, as sulphuretted hydrogen does not immediately react in the cold with traces of the tin-salt.

This property of tin of not being reduced from the double pyrophosphates, except by powerful currents, might seem to promise a means for its separation from many other metals; but in this case, if the action is prolonged, traces of tin are generally deposited.

A peculiar phenomenon was observed in the deposition of tin. After the white metal has been dissolved away by hydrochloric acid the platinum capsule appears coated with a thin layer intermediate in colour between gold and pinchbeck, and neither soluble in hydrochloric nor in nitric acid. If heated to whiteness this film loses its colour and becomes dull. The weight of the capsule was increased by 0.001–0.002 gm. On melting with saltpetre the film disappears and the weight of the capsule diminishes by some m.grms. In the solution of the melt nothing but platinum can be detected. It is derived from the anode, for with so strong a current a faint odour of chlorine is perceptible even if the solution is not alkaline.

11. Chromium.—Chromic oxide forms with sodium and ammonium pyrophosphate double salts, which behave normally in the preparation of the electrolyte. The solutions in ammonium carbonate or ammonia are green or violet. Ammonium sulphide produces no precipitate. On the electrolysis of the double salt the chromic oxide passes into chromic acid, both in acid and alkaline solutions.

If nickel and cobalt is present in alkaline solution along with the double chromic salt, they are deposited quantitatively; but if the alkaline solution contains at the beginning chromic acid, neither nickel nor cobalt is separated, even with a strong current. In presence of iron there appears in the latter case (in a solution mixed with ammonium carbonate) a reddish yellow body on the cathode containing iron and pyrophosphoric acid. If iron occurs in the solution along with chromic oxide, metallic iron is first deposited; but if the oxidation extends to chromic acid the reduction of iron ceases and the above-mentioned body is formed.

12. Lead.—The white lead pyrophosphate is soluble in an excess of the precipitant and bears the addition of ammonium carbonate, but it is precipitated by ammonia. The salt precipitated by ammonium pyrophosphate behaves similarly, but it is sparingly soluble in an excess of the precipitant.

From an alkaline solution electrolysis separates simultaneously peroxide on the anode and lead on the cathode; the less of the latter the more alkali is present and the feebler the current. The author has never succeeded in entirely preventing the separation of lead.

From a nitric or a phosphoric solution lead is separated out alone, but the anode is transiently covered with a layer of peroxide. A determination of lead cannot be effected in this manner, as the metal becomes rapidly oxidised in the air.

13. The thallium double salts behave like those of lead and are formed very easily. In a solution of thallium sulphate there appears no precipitate, and dilute acids occasion no precipitation in the solution.

In an alkaline solution the double thallium salt behaves on electrolysis quite like the lead double salt. In a nitric solution metal and sesquioxide are deposited simultaneously, but from a phosphoric, and especially from a sulphuric, solution the thallium is deposited quantitatively (without formation of sesquioxide). There is the same obstacle to the electrolytic determination of thallium as in the case of lead.

14. Bismuth.—The white bismuth salt precipitated by sodium or ammonium pyrophosphate is soluble in an excess, and bears the addition of ammonium carbonate, but is precipitated by ammonia.

The double salt in solution is precipitated by dilute acids. This does not contradict the phenomenon that the double salt thrown down from nitric or hydrochloric solutions of bismuth containing little free acid dissolves completely before the acid is neutralised by the alkaline pyrophosphate (which has a basic reaction). In this case there occurs a subsequent deposition in the liquid as long as a trace of free acid is present.

From solutions of the bismuth double salt in an excess of the precipitant bismuth is deposited upon the cathode in an adherent form; but at the same time, white salts separate out on the anode or in acid solutions in the liquid.

A plentiful addition of an alkaline tartrate obviates this evil, but involves another, since the tartaric acid is decomposed in the course of the electrolysis.

On the addition of ammonium carbonate in slight excess the separation of white salt at the anode continues. With a larger excess peroxide apparently makes its appearance, but this deposit does not dissolve in oxalic acid, and hydrochloric acid must be utilised. At the same time, if the excess of ammonium carbonate is very large the metal is more likely to become pulverulent.

These difficulties are obviated by the addition of ammonium oxalate. There is, indeed, a slight formation of yellowish brown peroxide at the anode, but it frequently disappears spontaneously, or it can be easily dissolved by the addition of a drop of oxalic acid towards the end of the process.

For the determination of bismuth the acid solution, slightly diluted, is mixed with four or five times the quantity of sodium pyrophosphate necessary for forming the double salt, and ammonium carbonate is introduced exactly until an alkaline reaction appears, 3–5 grms. of ammonium oxalate (in solution) being finally added.

If much bismuth is present in the solution the salt must not contain too little free acid, as otherwise, on adding the pyrophosphate, the double salt is separated in a curdy form, adhering firmly to the capsule, and cannot be dissolved without difficulty, since heat cannot be applied. Neutralisation with ammonium carbonate before adding ammonium oxalate is essential, since free oxalic acid occasions a pulverulent deposition of the bismuth.

The electrolysis of the double bismuth salt can be effected with a battery of 4–6 Meidinger elements, applying at the outset—according to the strength of the solution, which is diluted to about 200 c.c.—a current of 0.1–1 c.c. detonating gas per minute, increasing it gradually up to 2–3 c.c. towards the end of the reduction. It is thus possible to dissolve as much as 1 gm. bismuth

as double sodium salt per 200 c. c., and to separate it out. It is frequently advisable, in order to obtain an equable deposition over the entire capsule, to apply for a few seconds, at the outset, a more powerful current (1—2 c. c.) per minute until the decomposition is initiated.

As much as 0.25 gm. bismuth can be separated out within twelve hours, beginning with a current of 0.5 c. c. per minute; but it is recommended to use a current of 5 c. c. and more in order to withdraw the last traces. If the proportion of bismuth in the electrolyte is large feeble currents must be used at the beginning. To separate 0.75 gm. bismuth, forty-eight hours were needed. From a solution containing, in 200 c. c., 0.75 gm. bismuth, 0.42 gm. bismuth were thrown down in twenty-four hours by a current of 0.8 c. c. detonating gas per minute.

Towards the end of the electrolysis traces of peroxide are removed, which appear towards the end of the process by a drop of a strong solution of oxalic acid. This must not be done too early, as otherwise the deposition of peroxide may re-commence.

The completion of the reduction is recognised by means of sulphuretted hydrogen. A considerable time is required—four to six hours after the removal of the peroxide—until the last traces of bismuth are reduced and a few c. c. of the electrolyte, after the addition of the reagent, remain clear and colourless as water.

The separated metal gives too high a weight in consequence of oxidation. Hence it is necessary to convert it into oxide, which may be easily effected without loss by dissolving in nitric acid and finally decomposing the nitrate at a red heat.

The form of the anode has an influence on the separation of the metal. If it is a piece of sheet-metal, the coating at the bottom is less dense than at the sides. With an anode of wire the separation is uniform, and the peroxide is easily dissolved by means of a concentrated solution of oxalic acid.

The deposited bismuth has a white-grey colour and a perfectly metallic aspect if feeble currents. With a more powerful current the colour is pale grey or grey, and the metal adheres so firmly that no loss need be feared on washing.

In the course of the previous investigations the author has examined the method of Thomas Moore (CHEMICAL NEWS, vol. liii., p. 209) for the determination of bismuth. He mixes the solution of the metal with tartaric acid, and in order to prevent the deposition of a basic salt, renders it faintly ammoniacal and adds a large excess of vitreous phosphoric acid. The strength of the current for the electrolysis of this solution is stated at for the beginning 20 to 30 c. c. of detonating gas per hour (0.33—0.5 c. c. per minute), and at the end 450 c. c. per hour (7.5 c. c. per minute).

Several experiments have shown that if the solution contain 0.1 gm. of bismuth per 200 c. c. the solution is pulverulent if, on using two (old) Meidinger elements with a current of 0.14 c. c. per minute, a resistance of 80 to 120 ohms is inserted. Even then the metal deposited is not very compact.

15. *Antimony*.—From a solution of antimony trichloride the addition of sodium or ammonium pyrophosphate precipitates a white salt soluble in excess. The solutions bear an addition of ammonium carbonate, but occasion a precipitate. Antimony is thrown down quantitatively by a current of 0.1 to 0.3 c. c. detonating gas per minute, but if the quantities are large it does not adhere firmly enough for accurate determinations.

(To be continued).

A Morphine Reaction.—O. Hesse (*Pharm. Journal and Chemiker Zeitung*).—This reaction was discovered by Kiefer prior to Armitage. Hesse considers that Armitage has not explained the procedure correctly.

AMMONIA-FREE WATER.

By A. G. BLOXAM.

AN analyst who has a considerable practice and is considered no fool by his *clients*, has persuaded me to put on record the possibility of preparing ammonia-free water in any quantity by simply boiling ordinary distilled water in a wide-necked flask; half a gallon of ammonia-free water may be thus obtained in less than an hour. He hopes that other analysts may, by this publication, be spared the tedious process, which he has till now adopted of obtaining such water by distillation.

THE CHEMICAL PROBLEMS OF TO-DAY.*

By VICTOR MEYER.

(Continued from p. 22).

WE have mentioned spectral analysis, though it has been almost for an age the common property of science. Let us also cast a grateful retrospect upon a deeply furrowing revolution—of which chemistry also, for several decades, has boasted as a substantial possession—upon the development of the *doctrine of structure*, that solid theoretical foundation from which the proud edifice of modern organic chemistry rises. A generation has grown up around us which has received as a matter of fact this doctrine which still seems new to us older ones. But those far-seeing men, whose eyes recognised the immensely simple in the seemingly impenetrable complication of the carbon compounds, are still actively alive amongst us, and it is their happy lot to reap in their own activity what once they sowed in juvenile work. Here the eye is directed upon the master of chemical research—August Wilhelm von Hofmann; before all upon his researches upon the organic nitrogenous bases—researches which do not find their equal in organic chemistry, and which, even more perfectly than Dumas's fundamental discovery of trichloroacetic acid, allowed the fundamental conception of substitution to expand into the living consciousness of chemists, at first, curiously, by supporting the theory of types in organic compounds and then by promoting the transition to the structural or constitutional view, which at present embraces, with unparalleled perfection, the whole territory of organic compounds.

But the suggestion of this doctrine, which finds its crowning success in the recognition of the inner aggregation of the atoms, is associated for all time with the name of a man who, although a master of rare art in experimenting, knew how to surpass what he had achieved at the laboratory table by the convincing power of his speculative work. We cannot here dispute the part which other eminent chemists have taken in the development of the doctrine of structure—there are, Butlerow, Cooper, Erlenmeyer, Franklin, Kolbe, Odling, Williamson—but the glorious guide in this great and victorious movement forward, he, to whose eyes was disclosed not only the tetravalence of carbon, but also the solution of the problem of the constitution of organic compounds, in the recognition of the property of carbon atoms to be linked to *each other* by their valencies; he is the *philosopher* of organic chemistry—August Kekulé. The name of this discoverer, who also started upon his high and soaring flight from Heidelberg, is justly mentioned *alone* when we want to recall in a word the putting forth and the development of the leading chemical theories.

The researches in this direction are so numerous and so toilsome, and yet the result is so surprisingly simple! The carbon atom is endowed with four, the oxygen atom

* An Address delivered at Heidelberg at the First General Session of the Sixty-Second Meeting of the Association of German Naturalists and Physicians, Sept. 18, 1889. Translated, by L. H. Friedburg, from the *Deutsche Rundschau*, Nov., 1889.

with two, the hydrogen atom with one point of attack for the chemical affinity. The cause of the aggregation of the atoms within the molecule lies in the mutual saturation of these units of affinity or valencies. It is the number of valencies which decides the possibility of the existence of a compound. Amongst the legion of imaginable combinations of these three elements only those are capable of existence in which every valency is saturated by that of another atom. Through this knowledge a new method of inquiry was opened, in particular for organic chemistry, the immense territory of which for many years seemed totally to absorb the working power of chemists. But then dawned the first signs of a further development. Hardly a decade had elapsed since the general admission of the doctrine of valency, when a fundamental deepening of the same was announced, which our science owes to two savants, working independently of each other—to Le Bel and Van't Hoff. These chemists, considering those substances which turn the plane of polarisation of light, arrived at views which soon led to a result, until then thought to be out of reach, a conception of the aggregation of the atoms within the molecules in space. Thus a field of study was created which Van't Hoff called "*la chimie dans l'espace*," and which we now call *Stereo-chemistry*.

It was recognised that the carbon atom stretched out its four valencies in definite directions, and this in a symmetrical manner. The combination of a carbon atom with four other atoms, for example, methane, CH_4 , is representable by the picture of a tetrahedron in the stereometric centre of which the carbon atom is situated, while the hydrogen atoms occupy its four corners.

Numerous cases of isomerism, until then not understood, could be explained in this manner, and were regarded as stereo-chemical ones. The cause of optical activity was found to consist in the presence of an asymmetric carbon atom, that is, one which is combined with four different groups.

Also the stereometric forms of a few simple molecules were considered; it was recognised, *e.g.*, that a compound of three carbon atoms linked together by one bond respectively, could not contain those atoms in a straight line, but that they must lie in the angles of a triangle, the sides of which form an angle equal to that in which the directions of valency of the carbon atom intersect each other.

By the application of these considerations to more complicated molecules, which contain a chain of atoms closed within itself, Adolph von Baeyer has enlarged our theory in a manner full of consequence.

Kekulé, in times past, had recognised that carbon shows a particular disposition to form *closed* chains of six atoms. The discoveries of Baeyer and his followers, as well as Fittig's work on lactones, taught that such closed chains or rings formed of fewer atoms also exist. But while rings of six or five atoms easily form, it is more difficult to combine fewer atoms, four or three, to a closed chain. The cause of this fact Baeyer recognised as lying in the stereometric conditions. The angles which the sides of a regular hexagon and pentagon form with each other very nearly coincide with those in which the directions of the valencies of the carbon atom intersect each other, and thus, in linking five or six atoms together, the circle, so to speak, closes itself, while if more or less atoms are present, this can only be arrived at by strong deviation of the directions of affinity.

But still more surprising discoveries were hidden in Van't Hoff's theory. The gifted Dutch thinker had penetrated to the idea that two atoms which are linked together by a single valency rotate freely around an axis, the direction of which coincides with that of the linking valency, but that this rotation is stopped as soon as double linking takes place. This latter is an immediate consequence of the tetrahedric conception. If I stretch out my forefingers and let their points touch each other, then the hands can rotate around them as an axis; but if

I stretch both thumbs and both forefingers and allow their corresponding points to touch each other, then a system results in which rotation is impossible.

These two propositions of Van't Hoff having remained almost unnoticed for a decade, have lately come into great prominence. In a series of important researches Johannes Wislicenus has proved, that, applying these propositions and at the same time considering the specific affinities of the groups or elements present, the stereometric aggregation of the atoms in certain molecules can be determined with probability. In an ingenious manner he has utilised the addition phenomena shown by carbon atoms trebly linked together for an interpretation of a stereometric aggregation of the atoms in the compounds formed.

Wislicenus, applying Van't Hoff's ideas with courage and strictness, has advanced organic chemistry in an important manner, and has opened a field for experimental research, which heretofore had been avoided with a precaution suggestive of timidity.

New discoveries came from other sides. An intimate research into the oxims of benzil lead to the surprising result, that the validity of the second proposition of Van't Hoff is not without exception. Cases were noticed in which the free rotation of carbon atoms united by a *simple* bond, which Van't Hoff disclosed, did not obtain. Further inquiry into this subject led to a renewal of the question, "What does *chemical valency* really mean?" A question to which the mind incessantly demands an answer. It had long since been suggested that valency had some relation to the electric behaviour of the atoms. The chemistry of the day expresses Faraday's fundamental electrolytic law thus: an electric current which flows through several fused electrolytes, severs in each of them the same number of *valencies*—not of *atoms*.

It was found by von Helmholtz that those quantities of electricity which during the electrolytic process move with the ions, are distributed among the valencies. Riecke, in virtue of his pyroelectric researches, was led to the view that the atoms are surrounded by certain systems of positive and negative electric poles.

Uniting these results with those of purely chemical experimentation, we arrive at the idea that the valencies do not appear as *points* of attack proper, but as having *linear* dimensions. The carbon atom represents itself as a sphere, surrounded by an envelope of ether which contains the valencies. The latter seem to be determined by the presence of two opposite electric poles which rest at the ends of a very short straight line. Such a system is called a *dipole*. The attachment of two valencies to each other consists in the attraction of their opposed poles. It is evident that in a radial position of the dipoles, they form an axis around which the atoms are able to rotate, but that this rotation is upset in case of a tangential position. In what has been said so far, and through further considerations in regard to the electrical charge of the atoms and of the dipoles, a reason is found for the repulsion of the four valencies and consequently for the tetrahedric grouping of the same.

The fact that the valencies can deviate from this position now becomes intelligible; we perceive why the valencies of *one* atom cannot unite with one another, while those of different atoms can combine; it is clear that there can exist two kinds of simple linking, one of which admits of rotation, while the other does not; finally, that in cases of manifold linking the free rotation must be annulled. Hence this hypothesis opens to us an understanding of the most important properties of chemical valency.

So much may be said of the problems relating to the theory of valency.

But the doctrine of substitution has likewise experienced a peculiar enlargement. Dumas first showed that the properties of organic compounds are generally little changed when the hydrogen of the same is replaced by univalent elements or groups. Now it has been learned from later experiments that even much more radical changes in the

composition do not materially influence the properties of the substance. If, for example, we replace in the hydrocarbon *benzol* two carbon and two hydrogen atoms by one atom of sulphur, the resulting product, *thiophen*, resembles *benzol*, chemically and physically, so closely as to be mistaken for it. We learn from this that the sulphur atom is able to take upon itself the functions of four atoms of entirely different nature. Similar facts have been found in regard to oxygen and to the imido group, which is equivalent to it.

Turning away from these researches to cast a glance upon general chemical studies which lie some years behind us, we must, above all, consider one of the most far-reaching discoveries of our epoch, the revelation of the natural system of the chemical elements. We owe this to the far-seeing Demetrius Mendeleeff. By the side of the titanic figure of the Russian scholar we see the Englishman, Newlands, and our own countryman, Lothar Meyer, successfully co-operating in the foundation and the structure of this work. What these men created has since become generally known: they showed that the properties of the elements are functions of their atomic weights. Mendeleeff taught us to predict the existence and the properties of chemical elements as yet unknown, with a certainty that reminds us of Le Verrier's prediction of the discovery of the planet Neptune. We can say with accuracy that even to-day numerous elements, the qualities of which, as well as the place which they will occupy in the system, can be minutely foretold, wait merely to be discovered.

The natural system has imposed upon us a problem of the greatest significance in the new determination of the atomic weights, the numerical values of which are now of increased interest. But numerous other problems are presented by the new system of the elements. Above all, we are at a loss to discern the cause of the inner nexus of the elements as the system offers it. Also by diligent work the less studied elements must be properly brought within the system. Fortunate circumstances may allow us to discover the numerous elements indicated by the periodic law. Here let us note a peculiar coincidence. We know to-day about seventy elements, but Mendeleeff's table indicates so far two small periods of seven elements each and five large ones of seventeen elements respectively. To these must be added hydrogen forming a "group" in itself.

By addition of these figures, $2 \times 7 + 5 \times 17 + 1$ we obtain exactly the number 100.

It is true that no one can say whether the missing elements will really be discovered or if further new periods might not be indicated by which this number, 100, would be exceeded. But, as far as positive data are at hand, they indicate exactly the number mentioned and nothing points beyond it. An odd coincidence which seems to ally the number of the existing elements with the number of our fingers.

(To be continued).

THE RELATIVE ABUNDANCE OF THE CHEMICAL ELEMENTS.*

By FRANK WIGGLESWORTH CLARKE.

In the crust of the earth, with its liquid and gaseous envelopes, about seventy chemical elements are at present recognised. Others, as yet unknown, are indicated by gaps in the periodic system, and will probably be discovered in the future. Some of the elements are quite plentiful, some are exceedingly rare, and in any thorough discussion of their nature and relations this comparative abundance or scarcity should be taken into account. Even though the full meaning of the facts may not be dis-

coverable for many years to come, it is worth while to put them into something like systematic order.

In its larger aspects the general problem is at present unsolvable, for the reason that we know nothing of the earth's interior. Its surface only is within our certain reach, and from the composition of that we must draw nearly all our conclusions. For that which lies below the crust we must be content with inferences based upon the scantiest of data. Of the crust itself the average composition is easily computable, and the calculation gives results which are in some respects surprising.

In order to have a definite mass of matter under consideration, we may assume for the earth's known crust a thickness of ten miles below sea-level. The volume of that crust, including the mean elevation of the continents above the sea, is 1,935,000,000 cubic miles. Of this amount 302,000,000 cubic miles are ocean and 1,633,000,000 are solid matter. The mass of the atmosphere is equivalent to that of 1,268,000 cubic miles of water, the unit of density. For these data, which cover all the terrestrial matter accessible to us, I am indebted to Mr. R. S. Woodward, of the U.S. Geological Survey, and from them the relative masses of solid crust, ocean, and atmosphere can be determined within narrow limits of uncertainty. To sea-water we may assign a density of 1.03, which is a trifle too high, and to the solid rocks a specific gravity not lower in average than 2.5, nor much higher than 2.7. With these values we can get the following expression for the percentage composition of the known matter of the globe:—

Per cent.	Density of crust, 2.5.	Density of crust, 2.7.
Atmosphere	0.03	0.03
Ocean	7.08	6.58
Solid crust	92.89	93.39
	100.00	100.00

In short, we may regard the earth's crust, to a depth of ten miles, as composed essentially of 93 per cent solid and 7 per cent liquid matter; treating the atmosphere as a small correction to be applied later. More elaborate estimations are unnecessary. Since the known nitrogen of the earth is mainly in the atmosphere, its relative scarcity as an element is at once curiously manifest. It cannot possibly exceed 25-1000ths of one per cent of the total.

For the composition of the ocean, the data given by Dittmar in the "Reports of the Challenger Expedition" are perhaps the best available. The maximum salinity

Composition of Salts.

NaCl	77.76
MgCl ₂	10.88
MgSO ₄	4.74
CaSO ₄	3.60
K ₂ SO ₄	2.46
MgBr ₂	0.22
CaCO ₃	0.34
	100.00

Composition of Ocean.

O	85.79
H	10.67
Cl	2.07
Na	1.14
Mg	0.14
Ca	0.05
K	0.04
S	0.09
Br	0.008
C	0.002
	100.000

* Read before the Philosophical Society of Washington, October 26, 1889.

he puts at 37·37 grms. of salts in the kilogram. of water, and by taking this figure instead of a lower value we can make an allowance for saline masses enclosed in the solid crust, which would not otherwise appear in the final averages. Combining this datum with Dittmar's statement of the average composition of the ocean salts, we get the second of the subjoined columns. The traces of other elements, not named here, which have been found by various observers in sea-water, are too small to be considered.

Dissolved gases need not be taken into account, and no other constituent of the ocean can reach 0·001 of one per cent.

In the case of the solid crust of the earth the problem of ascertaining its mean composition is far less simple; for the crust is not an homogeneous body, but is made up, so to speak, of shreds and patches; of old crystalline rocks, of volcanic outflows, and of all manner of deposits of sedimentary origin. It is veined and seamed with diverse minerals, it encloses pockets of various materials, and upon its surface are quantities of organic matter and great bodies of fresh water. At first sight it would seem to be impossible to determine the average composition of such a mass, and yet, upon consideration, the question is not seriously complicated. In a crust ten miles thick a section having the superficial area of the United States represents only about 1·5 per cent of the total; so that all veins, pockets, patches, organic substances, &c., become insignificant in comparison with the whole mass, and even the lakes and rivers are neglectable quantities. On any attempt to compute their percentages they vanish into the dim recesses of the remoter decimals. Discarding these trivial constituents the question becomes one of the mean composition of the dominant rock material, and in that form it is comparatively simple.

In the first place we may assume that the volcanic and crystalline rocks represent pretty closely the general composition of the whole crust; for from them the sedimentary rocks have been formed, and the latter differ from the parent formations only in the carbon which they have taken up from the air and in the loss of saline constituents which have been leached out to the ocean. For this gain and loss, respectively, approximate corrections are possible.

In the second place, we must regard the original rock matter, volcanic and crystalline, as being, in a large sense, fairly homogeneous. However greatly these formations may vary locally, they should average pretty much alike all over the world when sufficiently large areas are considered. This assumption can be tested in the light of evidence as follows:—We may average together great numbers of analyses, grouped in various ways, and so determine whether the results are sensibly constant. This has been done in the subjoined table, minor and occasional constituents being temporarily omitted, to be separately considered later.

A. The mean of 82 analyses of organic rocks from the Western Territories of the United States, published in Clarence King's Survey of the Fortieth Parallel.

B. 64 analyses of rocks from the Yellowstone Park, taken from the laboratory records of the U.S. Geological Survey.

C. 54 analyses of volcanic rocks collected in Northern California, also from the Survey records.

D. 39 analyses of eruptive rocks from various localities in the Western United States, taken from the Survey records.

E. 80 crystalline and archæan rocks from all parts of the United States. Of these analyses, 50 were taken from the Survey records, 23 from the 40th Parallel Report, and 7 from the "Report of the New Hampshire Survey," vol. iii.

F. 75 analyses of European volcanic and crystalline rocks, taken at random from five recent volumes of the *Neues Jahrbuch*.

G. 486 miscellaneous plutonic rocks, analysed between

1879 and 1883, and collected by Roth in his "Beiträge zur Petrographie der Plutonischen Gesteine."

H. The mean of the foregoing 880 analyses.

	A.	B.	C.	D.	E.	F.	G.	H.
SiO ₂ ..	61·89	61·89	60·49	60·66	60·50	59·80	56·75	58·59
Al ₂ O ₃ .	15·71	15·73	16·08	15·46	14·30	14·65	14·90	15·04
Fe ₂ O ₃ .	1·81	3·18	2·47	2·74	3·35	4·99	4·58	3·94
FeO ..	3·65	2·40	2·86	2·27	4·31	2·92	3·71	3·48
CaO ..	4·51	4·58	6·15	4·71	3·52	5·19	5·79	5·29
MgO ..	2·40	3·08	4·31	3·35	5·00	3·45	5·22	4·49
K ₂ O ..	3·54	2·70	1·80	3·97	2·52	3·06	2·90	2·90
Na ₂ O ..	3·28	3·70	3·31	3·54	2·49	2·98	3·24	3·20
H ₂ O ..	1·69	1·59	1·12	0·97	2·53	2·09	2·12	1·96

98·48 98·85 98·59 97·67 98·52 99·13 99·21 98·89

That these means are remarkably concordant, especially as regards the columns A to F, is at once evident; but a reduction to elementary form renders the agreement even more striking.

	A.	B.	C.	D.	E.	F.	G.	H.
Si ..	28·88	28·88	28·23	28·31	28·23	27·91	26·50	27·34
Al ..	8·31	8·32	8·51	8·18	7·57	7·75	7·89	7·96
Fe ..	4·11	4·09	3·96	3·68	5·71	5·77	6·09	5·47
Ca ..	3·22	3·27	4·39	3·37	2·51	3·71	4·13	3·78
Mg ..	1·44	1·85	2·58	2·01	3·09	2·07	3·13	2·69
K ..	2·94	2·24	1·49	3·29	2·09	2·54	2·41	2·41
Na ..	2·43	2·74	2·46	2·63	1·85	2·21	2·56	2·37
H ..	0·19	0·18	0·12	0·11	0·28	0·23	0·24	0·22
O ..	46·96	47·28	46·85	46·09	47·28	46·94	46·26	46·65

98·48 98·85 98·59 97·67 98·52 99·13 99·21 98·89

The thesis that the crust of the earth is fairly homogeneous in composition is thus sustained by positive evidence. The variations in the foregoing table are as small as could be reasonably expected.

So far, however, only nine of the rock-forming elements are accounted for. The proportions of the others are less easily computable, although in some cases fair estimates can be made. In certain directions very many of the analyses considered, especially in the columns A and G, were incomplete, constituents like titanium, manganese, phosphorus, &c., having been ignored as not essential to the purpose of the analyst. These substances appear in part, therefore, as impurities in the silica and alumina, rendering the latter a trifle too high.

For several of the less frequently determined elements the laboratory records of the U. S. Geological Survey furnish data. In 211 analyses of volcanic and crystalline rocks there recorded, titanium, manganese, and phosphorus were determined in a great majority of cases, and other elements appear frequently enough to prove something as to their relative abundance. Taking these 211 analyses all together, they show the following mean percentages for the constituents in question:—

TiO ₂ ..	0·55
P ₂ O ₅ ..	0·22
MnO ..	0·10
CO ₂ ..	0·37
S ..	0·034
Cr ₂ O ₃ ..	0·021
BaO . ..	0·033
SrO . ..	0·009
Cl ..	0·012
Li ₂ O ..	0·011

All of these figures, obviously, are *under-estimates*, for the determinations were not made in all cases. Furthermore, the rocks analysed were varied enough in origin, locality, and character to avoid any cumulative error due to the peculiarities of any one formation or area. The value for titanite oxide includes whatever zirconia may have been present in the various rock samples, but,

although the latter base is widely diffused, its proportion cannot be very high. Titanium, therefore, must be regarded as more abundant than phosphorus, manganese, or sulphur—a result hardly to have been expected. This conclusion, however, is borne out by evidence from other sources. Titanium is rarely absent from the older rocks; it is almost universally present in soils and clays, and it is often concentrated in great quantities in beds of iron ore. Having no very striking characteristics and but little commercial importance, it is easily overlooked, and so it has a popular reputation for scarcity which it does not deserve. Among all the elements it probably ranks tenth or eleventh in point of absolute abundance, and is rare only as regards obvious concentrations.

For phosphoric acid and manganese the data given are probably not far out of the way, but in the case of carbon the estimation is more troublesome. The percentage of CO₂ in volcanic and crystalline rocks, 0.37, is doubtless untrustworthy, for the reason that surface rocks are mainly represented, in many of which alteration may have begun. The figure, however, may be used as an offset for the undeterminable carbon existing in coal, shales, petroleum, &c. As regards the limestones, rough estimates of their quantity must suffice, and we may provisionally accept that of T. Mellard Reade, as given in his essay on "Chemical Denudation in Relation to Geological Time." According to Reade, the existing bodies of limestone are equivalent to a layer of the rock 528 feet thick and completely enveloping the globe. This is approximately 1 per cent of the crust under consideration, and represents 0.44 per cent of CO₂. To this we may add the 0.37 per cent given above, making 0.81 per cent in all—an estimate which can hardly be too low.

In the case of sulphur, the figure given, 0.034 per cent, is surely much too low, for sulphur is abundant both in sulphates and in sulphides, and iron pyrites especially is widely diffused. The absolute proportion of this element seems to be hardly determinable. It should be at least 0.05 and probably not over 0.10 per cent. For chlorine, chromium, barium, and strontium, the figures are minima, but cannot be very largely increased. The value for lithia is probably not far out of the way, for that oxide is almost universally present in minute traces in the older crystalline rocks, although it is rarely estimated in ordinary analyses.

Now, taking the mean of 880 analyses as cited in column H of the table, we may insert in it the additional values so far determined, but with certain qualifications. In about half of the analyses TiO₂, P₂O₅, and Cr₂O₃ were not estimated, but their amounts appear in the figures for silica and alumina. The silica, then, may be reduced by

about one-fourth the percentage of the titanite oxide, and the alumina by the other fourth, plus half the values assigned to P₂O₅ and Cr₂O₃. Making these corrections, reducing to elementary form, and re-calculating to 100 per cent, we get a rough approximation to the mean composition of the solid crust of the earth. To this approximation the other unestimated elements may be regarded as future corrections of very small amount. Combining this result with the mean composition of the ocean, and including 0.02 per cent for the nitrogen of the air, we get the final column to illustrate the abundance of the elements so far as at present known. Quantities less than 0.01 per cent are left out of consideration.

Nineteen of the elements are here provided for with very varying degrees of probability, although their order in the last column is presumably correct. The uncertainty may reach one per cent in the cases of silicon and iron, one-half as much with aluminum and oxygen, and is proportionally less for the other elements specified. The remaining elements, more than fifty in number, can hardly aggregate over one per cent altogether, and not one of them could pass 0.05 per cent in relative quantity. Some of them may be briefly considered in detail as follows:—

Fluorine.—Abundant in fluor-spar and apatite and present in many rocks as a constituent of topaz or mica. If the phosphorus in the foregoing estimate, 0.09 per cent, represents mainly apatite, the proportional amount of fluorine would be 0.02 to 0.03, the minimum assignable value.

Glucinum.—Widely distributed as beryl and easily overlooked in small traces. If determined, it would appear as a correction to the alumina.

Boron.—Comparatively abundant in tourmaline and datolite, and conspicuous in certain volcanic waters; difficult to estimate.

The Cerium Group.—According to Cross and Iddings, allanite is a wide-spread constituent of rocks. The same is true of monazite, as shown by Derby. These elements, together with thorium, zirconium, and the yttrium groups, would appear as corrections to alumina.

Nickel.—Frequent in rocks composed of or derived from olivine. Less than 0.01 per cent.

The Metallic Acids—stannic, molybdic, tungstic, columbic, and tantallic.—These, if determined, would form corrections to silica. The same is true, to some extent, of barium when present in rocks as sulphate.

The Heavy Metals.—Widely distributed in rocks, according to Sandberger's researches, but very small in quantity.

In the larger items, say from oxygen down to the alkaline metals, the estimates here given do not differ very widely from others which have been long current in chemical and geological literature. They rest, however, upon fuller evidence, and the discussion is, perhaps, more complete. In the smaller items the new results display the greatest novelty, and future modifications are most likely. The comparative rarity of carbon and sulphur is, to say the least, surprising.

On the theoretical side the results attained are not to interpret. That nine of the chemical elements should constitute, at the lowest estimate, 98 per cent of all known terrestrial matter is somewhat startling and difficult to comprehend. Are the other elements concentrated in the interior of our planet? On this point there is little positive evidence.

The mean density of the earth, 5.5 to 5.6, is more than double that of the rocky crust, and the difference may be accounted for as a result of pressure, or by supposing that, as the globe cooled, the heavier elements accumulated towards the centre. Both suppositions may be true in part, but less weight is to be placed upon the second, for the following reason:—A mixture of the elements in equal proportions, in the free state and as they behave at the earth's surface, would have a specific gravity of about

	Solid crust, 93 per cent.	Ocean, 7 per cent.	Mean, including air.
Oxygen ..	47.29	85.79	49.98
Silicon ..	27.21	—	25.30
Aluminum ..	7.81	—	7.26
Iron ..	5.46	—	5.08
Calcium ..	3.77	0.05	3.51
Magnesium .	2.68	0.14	2.50
Sodium . .	2.36	1.14	2.28
Potassium ..	2.40	0.04	2.23
Hydrogen ..	0.21	10.67	0.94
Titanium ..	0.33	—	0.30
Carbon . .	0.22	0.002	0.21
Chlorine ..	0.01	2.07	} 0.15
Bromine ..	—	0.008	
Phosphorus .	0.10	—	0.09
Manganese..	0.08	—	0.07
Sulphur ..	0.03+	0.09	0.04+
Barium ..	0.03	—	0.03
Nitrogen ..	—	—	0.02
Chromium ..	0.01	—	0.01
	100.00	100.000	100.00

73. In combination the density would be greater because of condensation, and below the surface it would also be increased by pressure. Hence it seems clear, since the density of the earth is only 5.5, that in the planet as a whole the lighter elements must very considerably exceed in quantity the heavier ones. Twenty-nine of the known elements have densities below 5.5, and forty exceed that figure, iron being the only one of the heavier group which is at all abundant. The greater part of the earth's mass is almost certainly to be found among the twenty-nine lighter elements. The others may be more plentiful at the centre of the globe than on its surface, but few beside iron can be dominant constituents. This evidence seems to be clear, even though it is not proof positive.

An attempt was made in the course of this investigation to represent the relative abundance of the elements by a curve, taking their atomic weights for one set of ordinates. It was hoped that some sort of periodicity might be evident, but no such regularity appeared. No definite connection with the periodic law seemed to be traceable. And yet certain other regularities are worth noticing. All of the abundant elements are low in the scale of atomic weights, reaching a maximum at 56 in iron. Above 56 the elements are comparatively rare, and only two of them, barium and strontium, appear in my estimates. Below oxygen, hydrogen alone approaches one per cent, while between oxygen and iron only scandium and vanadium are of neglectable rarity. Furthermore, in several elementary groups abundance diminishes with increase of atomic weight. This is plainly seen in the series potassium, rubidium, and caesium; in sulphur, selenium, and tellurium; in chlorine, bromine, and iodine; in arsenic, antimony, bismuth, &c., &c. The regularity is not certainly invariable, but it occurs often enough to be suggestive.

Perhaps a part of the difficulty in tracing relations of this sort arises from the fact that our field of view is limited to the earth, and does not include the whole solar system. Indeed, several writers, reasoning on the broader basis of the nebular hypothesis and noting the low densities of the outer planets, have argued that the latter may contain the lighter elements mainly, while the heavier substances are concentrated at the original nucleus, the sun. Along this line, however, close reasoning is impossible, partly because evidence is lacking, and partly because the conditions of temperature and pressure differ so widely between the sun and the other heavenly bodies. As thus attacked, the problem becomes one of enormous complexity, and even the solar spectrum gives us no conclusive evidence. That oxygen and silicon are not conspicuous in the sun's atmosphere we may admit, but that non-volatile silica is absent from the solar body is by no means certain. We may assume that compounds can exist nowhere in the sun, but the assumption is unprovable. As to the composition of the outer planets we know practically nothing. How far they may differ from each other, from the earth, and from the sun is, as yet, a matter of pure conjecture.

If, despite Mendeleeff's recent demurrer, we assume that the elements have been evolved from one primordial form of matter, their relative abundance becomes suggestive. Starting from the original "protyle," as Crookes has called it, the process of evolution seems to have gone on slowly until oxygen was reached. At that point the process exhibited its maximum energy, and beyond it the elements forming stable oxides were the most rapidly developed, and in the largest amounts. On this supposition the scarcity of the elements above iron becomes somewhat intelligible; but the theory does not account for everything, and is to be regarded as merely tentative. It is legitimate only so long as its purely speculative character is kept clearly in view. If, however, the evolution of the elements is admitted, it is clear that the later stages of the process must have been seriously conditioned by the chemical affinities developed at first,

NOTICES OF BOOKS.

Applications Industrielles des Residues provenant des Piles aux Bichromates ("Industrial Applications of the Residues derived from Bichromate Batteries.") By GEORGES FOURNIER. Paris: Bernard Tignol.

THE author describes certain electric lighting installations in which the energy employed was obtained by means of bichromate batteries. Both worked satisfactorily, but both came to an end in consequence of the failure of the processes for regenerating or for utilising the residues. In one process, proposed by MM. Grenet and Jarriant, the spent liquids were treated with calcium carbonate, which threw down chromic oxide, but also calcium sulphate, and also a quantity of zinc oxide. The resulting mass was treated like a chrome ore, but, unfortunately, the presence of the calcium sulphate so delayed, or even prevented, the necessary reaction that the process failed.

The other method of treatment tried by the Chrome Company, we believe under the direction of the author, worked successfully, but was stopped by the forced liquidation of the Chrome Company, in consequence of the failure of the bank in which their funds were deposited.

The author's process is first to neutralise every trace of acid by means of zinc turnings, which are placed in boxes of perforated wood suspended in the liquid. If the salt employed in the batteries has been potassium dichromate, chrome-alum crystallises out, and is at once saleable. If the sodium salt has been employed, metallic zinc, suspended in the solution previously heated to 100°, throws down the chrome in the state of hydroxide and takes its place. Zinc oxide may also, if convenient, be used for the precipitation of the chrome. The precipitate if well washed may be put to various uses. By a simple ignition it is convertible into chrome green, used in colouring glass, painting on porcelain, and producing fast colours for printing on paper. If combined with boric or phosphoric acid it yields a beautiful emerald green; chrome picrate is an advantageous substitute for the objectionable arsenical greens; with cobalt it yields a splendid turquoise green, and with alumina a grass green. It may also be converted into a basic sulphate, of value in woollen dyeing.

The liquid from which the chrome has been thrown down contains an alkaline sulphate and zinc sulphate. From this liquid the zinc is precipitated by the gradual addition of dilute milk of lime. The supernatant liquid then contains potassium (or sodium) sulphate, whilst the precipitate is a mixture of zinc hydroxide and calcium sulphate. This deposit is well stirred up in water and treated first with zinc sulphate, until the reaction becomes slightly acid, and then with a solution of potassium dichromate, 1 kilo. to 15 litres of water. The yellow precipitate thus obtained is sold as a yellow colour, and, though containing calcium sulphate, is preferable to chrome-yellow (lead chromate), inasmuch as it does not blacken on exposure to impure air.

In an additional chapter, the author gives instructions for obtaining chromic acid from calcium chromate.

It is possible that the process of M. Fournier may give a considerable impulse to the use of the bichromate battery.

The Cosmic Law of Thermal Repulsion. An Essay suggested by the Projection of a Comet's Tail. New York: J. Wiley and Sons.

THE author of this little work withholds his name, and sums up his doctrine in the words, placed as a motto on his title page, that "Thermal repulsion, like gravitational attraction, is universal between masses as well as between molecules of matter." Starting from this principle he arrives at some strange results. Astronomers and

physicists have concluded that the moon is a dead world, where all the liquid and gaseous matter has been gradually withdrawn into its interior. Our author, on the contrary, holds that the moon's atmosphere and ocean have yet to be formed. He writes:—"The moon must gather meteors as rapidly as the earth, in proportion to size, and the hydrogen and other gaseous matter striking the moon is doubtless at once converted into an atmosphere enveloping the solid body. The moon has not yet gathered enough probably to fill the depressions in its surface, where this atmosphere would first accumulate." He continues:—"The moon appears now to be in the condition that the earth was before the formation of stratified rocks. There is no evidence that the earth during that period had an atmosphere: the indications are that it had none, and it is certainly possible that the earth, in the ages after the igneous period, gathered its atmosphere from meteoric and cometary matter."

Here, then, is the admission that the earth had an igneous period, which has now passed away. Yet the author does not recognise that such secular cooling must convert gaseous matter into liquids and ultimately into solids.

Elsewhere, we find it laid down that "nothing can fall into the sun." If this view is correct, the sun's heat cannot be maintained by the fall of meteorites. Surely a system which leads to conclusions such as those which we have quoted must require a very thorough demonstration before it can claim the acceptance of the scientific world.

We may well also be surprised at finding intelligence placed in the category of "forces," along with gravitation!

A Treatise on the Metallurgy of Iron: Containing Outlines of the History of Iron Manufacture, Methods of Assay and Analysis of Iron Ores, Processes of Manufacture of Iron and Steel, &c. By H. BAUERMAN, F.G.S., Associate of the Royal School of Mines, Associate Member of the Institution of Civil Engineers. Sixth Edition, Revised and Enlarged. London: Crosby Lockwood and Son.

THE author of this work points out some very important differences between the ores of iron and those of the other metals. A mineral containing iron is worth working only if the proportion of actual metal is very considerable, and further, if no injurious ingredients are present. An ore containing 5 to 10 per cent of copper would be very valuable, whilst the same proportion of iron in an ore would be neglected.

Again, the iron ores vary comparatively little in their composition. Substantially speaking, all of them contain their iron in the state of oxide, and all are reduced by the action of carbon or of carbon monoxide. The ores of the other useful metals may be oxides, sulphides (simple or complex), chlorides, or may even be in the free state, and the methods of smelting and refining are, of course, very varied.

Another peculiarity of iron is here mentioned, viz., that when absolutely pure it is of no commercial value. The other metals, on the contrary, rise in value for most purposes exactly in proportion as they approach a state of chemical purity.

On the other hand, minute traces of alien elements, metals or non-metals, singularly modify the properties of iron, for the better or the worse. Here we have a number of problems, the elucidation of which will be of great practical value, and which will still require prolonged and delicate investigation.

We are glad to find that the use of the spectroscope in controlling the conversion of charges, according to the Bessemer process, is here fully recognised. It is admitted at the same time that the exact chemical character of the spectrum of the Bessemer flame is not yet accurately determined.

The supplementary notes appended to the present edition, give an account of the increase of size in the Cleveland blast-furnaces, and of the purple ore, or "blue billy," obtained at Widnes from copper pyrites which have been deprived of their sulphur and copper. We cannot help regretting that the name "blue billy" should be thus applied, since it has long been in use for the spent lime from gas-works.

We find further an account of the composition of the gases of the Bessemer converter, paragraphs on the constitution of iron and steel, on manganese steel, on Gjer's soaking-pit, on Mitis iron, and the new Finland direct reductive processes.

The fact that this work has already reached its sixth edition shows that it is fully appreciated by metallurgists.

Year-Book of Pharmacy: Comprising Abstracts of Papers relating to Pharmacy, Materia Medica, and Chemistry Contributed to British and Foreign Journals from July 1st, 1888, to June 30th, 1889. With the Transactions of the British Pharmaceutical Conference, at the 26th Annual Meeting, held at Newcastle-on-Tyne, September, 1889. London: J. and A. Churchill.

THE Presidential Address, here given, deals with a very important subject, the purity of substances used in medicine. The speaker admitted that the fact of "drugs" being included in the "Sale of Food Act" was an indication that purity was not universal. He noted the fact that few pharmacists have obtained the post of Public Analyst, and enquired whether, notwithstanding their acquaintance with pharmacy, they were deficient in chemical and microscopical skill.

Referring to the decline of chemistry in England, referred to by Prof. Tilden at the Bath Meeting of the British Association, the President raised the question whether our shortcomings—at least as regards the manufacture of pharmaceutical products—may not be in part due to the exceptional stringency of our Excise regulations. He recognises that the Board of Inland Revenue has become in some degree convinced of its error, and it must not look back.

Our opinion is, of course, that our relatively unsatisfactory position in chemistry, as well as in other sciences, is mainly due to our examinational system of education. Hence, we are pleased to see that Mr. Umney is with us to some extent, as he makes the very temperate admission that "examinations are not an unmixed blessing," and that they are "subject to no inconsiderable abuse." He further adds:—"It is to be feared that if the students of to-day were asked why they studied, that by far the larger portion would be bound to acknowledge that they were only occupied in cramming into themselves, in the most rapid and easy fashion, the minimum amount of information that would help them to pass their examinations."

Among the more important papers read at the Conference was one on the action of soft waters upon lead, and one on poisoning effected by means of vermin killers.

CORRESPONDENCE.

PENDULUM EXPERIMENTS AND GRAVITATION.

To the Editor of the Chemical News.

SIR,—The first paragraph in Mr. J. Baynes Thompson's last letter is perfectly correct, and in this only can I entirely agree with him. It would be impossible, with his apparatus, to detect, much less to measure, the excessively small deviation which gravitation acting alone would cause. It is for this reason that no one else uses a pendu-

lum with so rapid a period of oscillation as that now referred to. If the length were made four times as great, the true deflection, whatever it might be, would be four times as great and the period would be twice as great. If the pendulum were 10,000 times as long, the deflection would be 10,000 times as great and the period $\sqrt{10,000}$, or 100 times as great, and so on. Now, it is evident enough that a pendulum 10,000 times as long, that is, a few miles long, is not practicable, but if the same bob that Mr. Thompson used were hung at the end of a torsion arm with another one to balance it, there would be no difficulty in obtaining such a period, or, in fact, one of five or ten minutes. The deflection, then, of each of the attracted weights, if there were a pair of attracting weights, would be the same as they would be if either of them formed the bob of a pendulum swinging in the same period. In other words, the deflection can easily be made 10,000 times as great as what, in Mr. Thompson's instrument, as he himself says, is far too small to be detected. The true effect of gravitation can thus be observed and measured. As to the difficulty of calculation, it does not exist. The other difficulties of experiment, it is true, have given trouble, but they may be, and have been, entirely overcome. The only reason why Mr. Thompson's pendulum seemed an improvement on the Cavendish apparatus, as usually made, is that it is far too stable to respond to the true effect of gravitation, or to any disturbing causes which may be comparable to the gravitational attraction.

These disturbing causes are apt, unless very specially provided against, to produce effects not only comparable to, but far in excess of, the true effect of gravitation; the large forces observed show that one of these, or possibly more than one, is acting with great success. The fact that there is a steel knife-edge shows that possible magnetic disturbances have not been entirely guarded against, but I am inclined to think that the chief disturbing cause is motion of the air due to excess or defect of temperature between the fixed and hanging weights and the air. It might be worth while to warm them a little purposely.

There were two points in Mr. Thompson's original communication which it seemed hardly necessary to correct, namely, that the force required to deflect a pendulum is not proportional to the versed sine, as he supposes, but to the sine of the deflection. As with small angles one varies as the square of the other, calculations based on the versed sine do not apply. Then, again, it is not usual, in finding the effect of distance, to measure the distance between the surfaces, as Mr. Thompson seems to have done, but, in the case of spheres, to measure the distance between the centres of the heavy bodies, and, in the case of bodies of other shapes, between points near the centres, which can only be found by long and troublesome calculation.

Though either of these would be sufficient to entirely vitiate any conclusions at which Mr. Thompson might have arrived, had the deflections observed been due to gravitation, I did not consider that it was worth while to point them out, since, had no spurious action occurred, no deflection of any kind could have been observed.—I am, &c.,

C. V. BOYS.

GRAVITATION.

To the Editor of the Chemical News.

SIR,—A friend has shown me that most astounding article on "Pendulum Experiments," which appeared in the CHEM. NEWS. (vol. lx., p. 295), in which the author gravely applies the Newtonian law of gravitation for two indefinitely small particles to the case of two massive cylinders of lead, and, because he does not find their attraction to be inversely proportional to the square of the *shortest distance between their surfaces*, denies the law! It would be a mere waste of time to point

out the childish error involved in such work as this, but I desire to call the attention of your readers to more subtle fallacy usually exhibited by people who write about the bombarding or "pelting" theory of gravitation. The fallacy is this: two bodies, *a* and *b*, in presence of each other in the ether *screen each other* on their adjacent sides from the pelting of the atom streams, and so experience a pressure towards each other. On the contrary, they do not screen each other at all, for we must remember that by *reflection* from the surface of *b* there will reach *a* a bombardment of atom streams which, in the absence of *b*, would never strike *a* at all.

No such simple off-hand theory of pelting streams will account for any attraction. A most interesting treatise on the subject is the "*Essai sur la Synthèse des Forces Physiques*," by le P. Leray (Gauthier-Villars), which I would recommend to any of your readers who are interested in the matter.—I am, &c.,

GEORGE M. MINCHIN.

R. I. E. College, Cooper's Hill.

A NOTE ON ORTHOGRAPHY AND NOMENCLATURE.

To the Editor of the Chemical News.

SIR,—Perhaps the following memoranda, printed in the columns of your journal, may produce a useful discussion:—

Aluminum or Aluminium.—Although the former name has been much in use, the latter has been adopted by several dictionaries, on the ground that the termination *ium*, for the sake of uniformity, is preferable. But we still have the ending *um* in glucinum, tantalum, molybdenum, &c., and in all the Latin names, such as ferrum, aurum, stannum, and so on. In the present case the oxide is universally alumina, and not alumina, and aluminium seems to be objectionable on the ground that it changes an accent unnecessarily. Aluminum, moreover, to many ears, has the advantage of euphony.

Glucinum or Beryllium.—Here the first name is the original one, and should hold according to all rules of priority. The grounds of change to the latter name are not clear.

Columbium or Niobium.—The original name, given by the discoverer, was columbium. Later, Rose gave the names niobium and pelopium to two supposed new elements. Why the name which has clear priority should give way to one which perpetuates the memory of an error is by no means obvious. "Niobium" is distinctly objectionable.

Gramme or Gram.—Although a simplification of orthography is generally desirable, in this case we seem to have an exception. "Gram" is too easily misprinted and misread *grain*, and even a defect in a sheet of paper may transform the one into the other. The French spelling "gramme" is therefore preferable as conducive to precision. The phonetic form of the word is a source of dangerous error.—I am, &c.,

F. W. CLARKE.

Washington, Dec. 28, 1889.

Wire-Gauze Air-Bath.—F. Muck (*Chemiker Zeitung*).—An arrangement for applying a gentle heat to small quantities of liquid in large vessels, as on re-dissolving small precipitates in the vessels in which they were thrown down. It admits also of the application of a stronger heat. It consists of a rectangular frame of iron resting on four feet, about 22 c.m. in height. A movable sheet-iron box (about 60 by 20 c.m.) with a bottom of wire gauze, about as fine as that used in safety-lamps, four wire-gauze covers working on hinges, and four Bunsen burners. If a gentle heat is required the flames are reduced and the vessel is set upon the highest of the four covers.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 27, December 30, 1889.

This number contains merely the report of the Annual Public Session of the Academy, with announcements of the prizes awarded and of those offered.

Zeitschrift für Analytische Chemie.
Vol. xxviii., Part 5.

Wine Statistics of Germany.—The continuation of a lengthy treatise, which would not present such an interest to our readers as to warrant its insertion.

Application of the Double Pyrophosphates for the Electrolytic Separation and Determination of Metals.—Dr. Albano Brand.—(See p. 2).

Lime in Tan-wares.—M. Petrowitsch.—In the examination of tanwares the only question is generally the determination of tannin. Impurities are scarcely ever sought for, as they are not intentionally added. A tanner in Zambor recently procured a large cargo of valonias from a drysalter in Vienna. A part of the lot was ground and used for tanning sole-leather. When ready the leather was found to be closely spotted over with large bluish white stains, such as have been known to be formed if the tanware is contaminated with lime. A portion of the ground valonias was sent to the author for examination. As mineral impurities might be chiefly expected in the finest portion, the sample was passed through a sieve having meshes of 1 m.m., and the fine matter was taken for examination. In 100 grms. of the ground valonias the total ash was 6.36 grms. and the lime 0.466 gm. In pure valonias the total ash was 2.554 and the lime 0.240 gm. The ash in samples of sumach ranges from 5.74 to 37.24 per cent.

A New Washing- and Absorption-Bottle.—F. A. Kühnlenz.—This paper cannot be reproduced without the accompanying illustration.

Capillary Analysis.—F. Goppelsröder.—The author's original pamphlet has been already noticed.

A New Method of Chemical Analysis with the Aid of Capillarity.—Ch. W. Phillips.—From the CHEMICAL NEWS.

A Systematic Course of Qualitative Analysis.—Edgar Everhart.—From the *Journal of Analytical Chemistry*.

System of Qualitative Analysis.—G. Vortmann.—No particulars are given.

Method of Calorimetric Determination by Means of Combustion in Oxygen under a High Pressure.—F. Stohmann, Cl. Kleber, and H. Langbein (*Journal für Praktische Chemie*).—No details are given.

Sources of Error in the Use of Hydrometers.—A. Fock.—The author proposes to apply a correction for the elevating power of the air. The error thus occasioned is very small, and in the most unfavourable case does not exceed a unit of the fifth decimal. The error occasioned by surface tension is more important. A formula is proposed for its correction, which, however, is in many cases inapplicable. The error occasioned by its neglect is about four units of the third decimal. The errors caused by the temperature of the air is at most five units of the fourth decimal.

A New Absorption-Apparatus in Ultimate Analysis.—J. Tsawoo White.—From the CHEMICAL NEWS.

A Valve Washing-Bottle.—E. Stroschein (*Chemiker Zeitung*).—No particulars are given.

A Sifting-Machine for the Laboratory.—A. Stutzer (*Zeitschrift für Angewandte Chemie*).—The arrangement requires an illustration.

The Presence of Arsenic in Glass and in Alkalies.—J. Marshall and C. Pott.—From the *American Chemical Journal*.

The Decolouration of Litmus in Closed Vessels.—R. Dubois.—The decolouration is produced by a micro-organism which, in the absence of air, has a decolouring action. In sterilised vessels litmus retains its colour.

Determination of Water in Silicates, such as Tourmaline, Vesuvian, Mica, &c.—P. Jannasch (*Ber. der Deutsch. Chem. Gesell.*).—This paper will be inserted in full.

Reduction of Ferric Salts by Means of Zinc-Powder.—Douglas J. Carnegie.—From the *Journal of the Chemical Society*.

Volumetric Determination of Phosphoric Acid by Means of Molybdic Acid.—A. Grete.—(See vol. lx., p. 310).

Quantitative Determination of Hydrosulphocyanic Acid.—P. Klason.—Hydrosulphocyanic acid can be determined like hydrochloric acid with a solution of silver, using neutral potassium chromate as an indicator. In an acid solution (sulphuric) he adds an excess of silver solution, then iron-alum, and titrates back with centinormal solution of ammonium sulphocyanide until the colour appears. Both the above methods are of little practical value, since hydrochloric acid must not be present. A method for the determination of hydrosulphocyanogen can also be founded upon its ready oxidation in an acid solution by means of potassium permanganate, forming hydrocyanic acid and sulphuric acid. The result obtained is too low if the concentration is less than decinormal.

New Method for Determining Nitrites.—T. Cuthbert Day.—From the *Journal of the Chemical Society*.

Determination of Nitric Acid.—H. N. Morse and A. F. Linn.—From the *American Chemical Journal*.

Quantitative Determination of Chloric Acid in Chlorates by Means of a Copper-Zinc Element.—C. H. Bothamley and G. R. Thompson.—From the *Journal of the Chemical Society*.

Preparation and Properties of Fumaric.—R. Reichwald.—Fumaric is readily soluble in chloroform, less readily in benzene, but it is sparingly soluble in water, alcohol, ether, and petroleum ether. With strong sulphuric acid it gives a splendid violet colour. If covered with Friche's reagent it turns violet and then dark green; with vanadic sulphuric acid it becomes a persistent emerald green, turning, after some hours, to a more yellowish shade. By strong sulphuric acid it is turned at first pale yellow and then light brown.

The Ultimate Analysis of Organic Bodies by Means of Electricity.—M. Levoir.—The weighed substance is placed in a platinum tube placed vertically among three spirals of platinum in a vertical glass tube. The wire is $\frac{1}{8}$ m.m. thick and 1 m. long, and is raised to redness by a dynamo. The combustion is effected by means of a current of oxygen. The products of combustion are received in absorption-tubes in the ordinary manner.

Conduction of Elementary Analyses by the Combustion of Organic Substances with Oxygen under High Pressure.—Arnold Eiloart.—From the CHEMICAL NEWS.

The Kjeldahl Determination of Nitrogen.—M. L'Hôte, C. Vidette, E. Aubin, and L. Alla.—From the *Comptes Rendus*. The matter has been already inserted.

Determination of Sugar by Fermentation.—M. Jodlbauer (*Dingler's Journal*).—The author has studied

the conditions under which a definite relation is obtained between the quantity of sugar fermented and the weight of the carbonic acid formed. He concludes that under certain conditions the products of alcoholic fermentation are constant. These conditions are the use of a powerfully developed yeast, which has undergone no loss of its tissues or of the protoplasmic contents of its cells by autofermentation. The preservation of a certain proportion between yeast and sugar; the yeast must not exceed 50 per cent of the sugar. Free oxygen must be excluded and a suitable nutritive substance must be supplied. The best temperature is 34° and the most favourable concentration is 8 per cent. Of the products of fermentation carbonic acid admits of the easiest and most exact determination. Saccharose and anhydrous maltose yield 49.04 of carbonic acid, and dextrose 46.54 per cent. Saccharose requires twice as long a time for fermentation as maltose and dextrose.

Determination of Alkalies in Waters.—Fr. Muck.—For this purpose an indirect method is mostly used which depends on converting the residue of the evaporation of several hundred c.c. into sulphates. From the weight thus obtained is deducted the weight (determined in another portion of the water) of the silica and the potassium and magnesium sulphates present. If no appreciable quantities of alumina and iron are present the remainder is the weight of the alkalies determined as sulphates. In the conversion of the residue into sulphates it is difficult to hit the exact quantity of sulphuric acid to be used. The author overcomes this difficulty as follows:—He moistens the residue with alcohol containing sulphuric acid (3 drops to 1 c.c.) and burns off the alcohol. If the quantity added is insufficient the resulting saline mass is dry; if sufficient it is moist, and vapours of sulphuric acid are given off before the alcohol is entirely consumed. Until this takes place the moistening and burning off are repeated, using, each time smaller and smaller quantities of the sulphuric alcohol. The final ignition and treatment with ammonium carbonate takes place in the ordinary manner.

Detection of Foreign Colouring-Matters in Wine.—A long compilation from the *Comptes Rendus*, the *Journal de Pharmacie*, the *Bulletin de la Soc. Chimique*, and the *Chemiker Zeitung*.

Determination of Free Hydrochloric Acid in the Human Gastric Juices.—Boas mixes 5 to 6 drops of the secretion with two or three drops of a solution of 10 grms. resorcin, 3 grms. sugar, and 3 c.c. alcohol in 100 c.c. water, and evaporates to dryness in a small platinum capsule over a small flame. If hydrochloric acid or some other powerful mineral acid is present there is produced a fine rose or scarlet surface, which gradually loses its colour on cooling. This reaction indicates 1-200th per cent of hydrochloric acid. Organic acids do not produce it. For the quantitative determination Sjögqvist takes 10 c.c. of the filtered fluids of the stomach, mixes them in a silver or platinum capsule with a slight excess of barium carbonate, and evaporates them to dryness on the water-bath, thus converting the free acids into barium salts. By carbonising the residue and igniting for a few minutes the organic barium salts are converted into carbonates. The cold carbon, comminuted as much as possible with a glass rod, is extracted at a boil with 10 c.c. of water, poured on a filter, and washed until the filtrate makes up 50 c.c. In this solution the barium is determined, and shows the proportion of hydrochloric acid originally present. The author has also developed a volumetric method for the same purpose.

Sensitiveness of the Reactions for the Sugar in Urine.—G. Rosenfeld.—The author gives the preference to Böttcher's bismuth test.

Re-determination of the Atomic Weight of Zinc.—H. N. Morse and W. M. Burton.—From the *American Chemical Journal*. The value decided on is 65.3.

Revue Universelle des Mines et de la Metallurgie.

Series 3, Vol. vii., No. 3.

This issue contains no chemical matter which we do not find elsewhere.

MISCELLANEOUS.

Ozone.—According to a letter in the *Electrical Review*, Ernst Fahrig has discovered a method of producing ozone on the large scale, and at a cost which will admit of its general industrial application. He hopes also to condense it, so as to render it portable. We regret to find that the inventor insists on applying to ozone the long and vague name "electrical gas." Chemists cannot sanction the application of a new name to any substance merely because it has been produced in a novel manner.

Lectures on Coal-Tar Products.—The First of a Course of Twelve Lectures on Coal-Tar Products was delivered by Professor R. Meldola, F.R.S., F.I.C., F.C.S., at the City Guilds Technical College, Finsbury, on Thursday evening, January 16th, 1890, to be continued on successive Thursdays. The Lectures will commence at 7.30 p.m. The raw materials used in the manufacture of artificial colouring-matters and other commercial products will be dealt with and their technology described. The lectures will be adapted for those engaged in the industry, as well as for manufacturers of fine chemicals, and for students of technical chemistry.

MEETINGS FOR THE WEEK.

- MONDAY, 20th.—Medical, 8.30.
— Society of Arts, 8. "The Electro-magnet," by Silvanus P. Thompson, D.Sc., M.I.E.E.
- TUESDAY, 21st.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
— Society of Arts, 8. "Tea, Coffee, and Cocoa Industries of Ceylon," by John Loudoun Shand.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
- WEDNESDAY, 22nd.—Society of Arts, 8. "Vision-testing for Practical Purposes," by R. Brudenell Carter, F.R.C.S.
— Geological, 8.
- THURSDAY, 23rd.—Royal, 4.30.
— Royal Society Club, 6.30.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Sculpture in Relation to the Age," by Edwin Roscoe Mullins.
- FRIDAY, 24th.—Quekett Club, 8.
— Royal Institution, 9. "The Scientific Work of Joule," by Prof. Dewar, M.A., F.R.S.
- SATURDAY, 25th.—Royal Institution, 3. "The Natural History of the Horse, and of its Extinct and Existing Allies," by Prof. Flower, F.R.S., &c.

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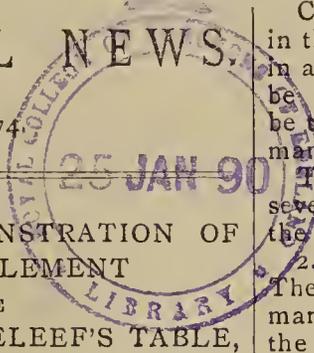
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THE CHEMICAL NEWS.

VOL. LXI. No. 1574



SPECTRO-ANALYTICAL DEMONSTRATION OF
TRACES OF A NEW ELEMENT

BELONGING TO THE
ELEVENTH SERIES OF MENDELEEF'S TABLE,
AND OCCURRING ESPECIALLY IN TELLURIUM AND
ANTIMONY, BUT ALSO IN COPPER.

By Dr. ANTON GRÜNWARD.

THE author concludes that the assumed elements tellurium, antimony, and copper contain traces of a new, hitherto unknown element, X, of Mendeleeff's eleventh series. It is on the one hand related to tellurium, and on the other hand very closely to bismuth. It is very probably identical with the element of group VI., series II, having the approximate atomic weight 212, and also with Dr. B. Brauner's "Austriacum" recently discovered in tellurium. The author gives the wave-lengths of 16 rays of the new substance observed in the ultra violet between 2768.9 and 2159.7.—Reprint from the *Proceedings of the Imperial Academy of Sciences in Vienna*, Vol. xcvi., Part II., October, 1889.

THE APPLICATION OF DOUBLE
PYROPHOSPHATES FOR THE ELECTROLYTIC
SEPARATION AND DETERMINATION OF
METALS.

By Dr. ALBANO BRAND.

(Continued from p. 29).

II. *Separation of Manganese from other Metals.*—The property of manganese of being electrolytically deposited as peroxide from a strongly ammoniacal solution of the double pyrophosphate, but of remaining in solution as a double salt in presence of free acid, points to a twofold way for the separation of manganese from other metals; in the case of those whose double salts bear the addition of ammonia, the manganese is first deposited as peroxide, whilst the metal is first precipitated in those which can be reduced from an acid solution.

1. *Manganese from Nickel, Copper, Cadmium, Zinc, and Mercury.*—If the ammoniacal solution of the double ferrous and ferric salt is submitted to electrolysis, there ensues, besides the reduction of the metal at the cathode, a separation of a brownish red basic iron salt at the anode. This abnormal decomposition does not entirely cease in presence of manganese and with the feeble currents required for the separation of manganese peroxide, and renders the separation of manganese and iron in this manner impossible.

The double cobalt salt behaves in an ammoniacal solution in presence of manganese just like the double iron salt, although on the electrolysis of the cobalt salt alone the metal only is deposited.

The separation of nickel from manganese in a solution of the double salt with 15 per cent of strong ammonia proceeds very evenly. Even with very feeble currents a little nickel is deposited on the cathode. After pouring off the liquid into another capsule, the reduction of the nickel is completed with more powerful currents. On the suspended electrode 0.3 gm. nickel can be conveniently deposited and weighed; an electrode of strong platinum wire is particularly suitable.

Copper and manganese can be conveniently determined in the same solution. In order to separate out the copper in a compact condition, the strength of the current must be very low at the beginning, and the capsule must be taken as cathode. For large quantities of copper or manganese the method of separation given under II., 2.

The separation of cadmium, zinc, and mercury, or of several metals conjointly from manganese, is effected in the same manner as given for nickel.

2. *Manganese from Copper, Cadmium, and Mercury.*—The property of manganese of remaining in solution as manganic pyrophosphate (or double manganic salt) on the electrolysis of an acid solution which at the same time contains pyrophosphoric acid, enables it to be separated from all metals which can be determined by the electrolysis of an acid solution.

The separation of manganese from iron, nickel, and cobalt in a solution containing little free pyrophosphoric acid is possible, according to the author's experiments, but requires currents of disproportionate strengths for the separation of the three metals.

The separation of manganese from copper and cadmium succeeds readily in a sulphuric solution, and that from copper and mercury in a nitric liquid. The solution of the pyrophosphates is acidified with the corresponding acid, and copper is reduced with a current of 3—4 c.c. detonating gas per minute, mercury with 0.2—0.5 c.c., and cadmium as laid down in I., 6.

After evaporating off the larger quantity of liquid which has been obtained on washing without an interruption of the current, the manganic oxide is reduced in heat by oxalic acid, and the manganese is separated as peroxide by a feeble current from the solution mixed when cold with ammonia. The conversion of a little pyrophosphoric acid into orthophosphoric acid in presence of nitric acid does not interfere with the determination.

3. *Manganese from Iron and Cobalt.*—The abnormal decomposition of the double iron and cobalt salt renders the separation of both from manganese impracticable in an ammoniacal solution.

In experiments for the prevention of the separation of a basic iron salt at the anode by the addition of various salts it was observed that if the solution of the pyrophosphates in an excess of the precipitant contains ammonium oxalate, the manganese remains in solution as a double salt, as it takes place in presence of free acid.

This observation agrees with that of Prof. A. Classen, as stated in one of his earlier publications on the application of the double oxalates in electrolysis. He writes:—"The separation of iron and manganese by the electrolysis of the double oxalates is practicable only when the formation of manganese peroxide is prevented until the greater part of the iron has been thrown down. This can be effected by the addition of sodium phosphate, or most readily by means of a large excess of ammonium oxalate."

In the electrolysis of the solution containing ammonium oxalate there is first formed, on the decomposition of this salt, ammonium carbonate; but so readily as it occasions precipitations in the solutions of the double manganese pyrophosphate, such do not occur on the simultaneous presence of both the above salts except the bulk of the oxalate has been decomposed and much manganese is present.

For the separation the solution containing manganese and iron is mixed with such an excess of sodium-pyrophosphate that the precipitate formed at first is completely dissolved. If the solution of the metals contained free acid, it should be neutralised as completely as possible before the addition of the sodium pyrophosphate, as a subsequent addition of ammonia or of ammonium carbonate is excluded. The solution is mixed either at once or partly during the electrolysis with 4—8 grms. ammonium oxalate.

In order to avoid washing without interruption of the current the metal is best deposited upon a suspended

electrode of round platinum wire (not foil), and, after the completion of the reaction, it is quickly plunged into distilled water. The author easily succeeded in determining 0.2 grm. of iron by means of an annular electrode of wire 1.5 m.m. in thickness, weighing 14.5 grms., and having a surface of 7.8 square c.m. A spiral of four turns of wire 2 m.m. in thickness, with a surface of 24 square c.m., and weighing 27 grms., would suffice for more than $\frac{1}{2}$ grm.

When much iron is present we begin with a current of 5 c.c. detonating gas per minute: towards the end a current of 15—20 c.c. is requisite.

After removal of the iron the solution in the capsule is faintly acidified with sulphuric acid, and the red double manganic salt is reduced by oxalic acid (with the aid of heat) to a manganous salt (I., 4). After adding 15 per cent of strong ammonia the manganese could be at once determined in the same capsule as manganomanganic oxide.

Attempts to ascertain the proportion of manganese by titration (addition to the red solution of potassium iodide and hydrochloric acid and determination of the iodine liberated) did not succeed, but they rendered it very probable that the red double salt contains the manganese in the manganic stage, as the proportion of oxygen is regularly found a little lower than corresponds to this stage.

In a solution which contains the double ammonium salt of manganese there is formed, without any addition on electrolysis, a double oxide salt which undergoes no further decomposition. This solution is not suitable for the separation of manganese and iron, as, in presence of iron, after its deposition, a white manganic salt is found firmly deposited.

The separation of iron requires much attention, and some practice is needed to obtain regularly good results. But the method admits of use if the conditions above laid down are carefully observed, and this the more readily the less iron is present.

4. *Cadmium from Zinc, Iron, Nickel, and Cobalt.*—The readiness with which cadmium can be separated electrolytically from a sulphuric solution facilitates its separation from all metals which are not reduced in a sulphuric solution.

By means of the double pyrophosphatic salts, zinc, iron, nickel, and cobalt may be distinctly separated from the liquid after removal of the cadmium, the solution of the double salts having been first supersaturated with ammonium carbonate. It is indifferent whether the sodium pyrophosphate is added before or after the separation of the cadmium.

5. *Cadmium from Zinc, Nickel, and Manganese.*—The process is the same as the separation from zinc or nickel alone, but in this case sodium pyrophosphate is added before the separation of the cadmium to keep the manganese in solution. The liquid obtained on washing (without interrupting the current) is mixed with oxalic acid and heated for the reduction of the manganic salt; then, when cold, supersaturated with ammonia and treated as in I., 4.

6. *Iron, Nickel, Cobalt, and Zinc from Aluminium, Magnesium, and Uranium.*—Among the metals of the alkaline earths only magnesium forms a pyrophosphate readily soluble in an excess of the precipitant, which bears an addition of ammonium carbonate but is precipitated by ammonia. The uranium double salt behaves similarly. Aluminium pyrophosphate is also soluble in ammonia.

If a solution mixed with ammonium carbonate and containing, along with the double pyrophosphates of iron, nickel, cobalt, or zinc, the corresponding salts of aluminium, magnesium, and uranium is submitted to electrolysis, the former are reduced whilst the latter remain in solution. A separation is thus readily effected, but the presence of the pyrophosphoric acid occasions difficulties in the subsequent determination of the metals which remain in solution.—*Zeitschrift für Analytische Chemie.*

A SENSITIVE TEST FOR CERTAIN IMPURITIES IN MERCURY.

By Dr. G. GORE, F.R.S.

VARIOUS investigators, including Wheatstone, Jules Regnault, Gauguain, Crova, Robb, Lindeck, and Hockin and Taylor (*Journal Telegraph Engineers*, 1879), have examined the electro-motive forces of metallic amalgams in acid and saline liquids, and the latter investigators have shown that 1 part by weight of zinc in 23.6 million parts of mercury is electro-positive to pure mercury in a solution of zinc sulphate.

My object in the present research was different from those of previous investigators, and was briefly to ascertain and illustrate the degree of delicacy of the voltaic energy method when employed as a means of detecting the presence of certain metals in mercury.

Two portions of very pure mercury in an electrolyte were connected by insulated platinum wires with an ordinary astatic torsion galvanometer of 100 ohms resistance, and a sufficiently minute proportion of a very dilute amalgam, of known strength, of one of the particular metals with some of the same mercury was added to one of the portions of mercury, to cause the needles of the instrument to be just visibly deflected whilst being viewed with the aid of a magnifying glass. The volume of water employed in each electrolyte was 120 c.c. The following Table shows the results:—

One part of—	1.0 grain of HCl or H ₂ SO ₄ in 120 c.c. of water. Parts of mercury.	10 grains of KCl in 120 c.c. of water. Parts of mercury.
Mg	110,274,000,000	13,430,858,806
Zn	104,950,000,000	18,034,482,758
Cd	184,828,432	10,404,225
Sn	38,900,000	8,831,632
Cu	15,484,375	1,640,160
Bi	9,762,300	1,621,000
Pb	5,651,149	1,050,341
Ag	905	79

The minimum degree of electro-motive force required to visibly move the needles was found by heating one end of a single thermo-electric couple of iron and pure copper 9.6 centigrade degrees higher than the other end, or of one of platinum and copper 49.5° C. higher than the other, the opposite ends of the couples being immersed in vessels of oil, and was in each case equal to about 0.00013258 volt. This, therefore, was approximately the degree of electro-motive force of amalgam of 1 part of zinc dissolved in about 105,000 million parts of mercury, or of 1 part of magnesium with about 110,000 million parts of mercury, when opposed to pure mercury in solutions at atmospheric temperature of sulphuric or hydrochloric acid of the degrees of strength given. With the aid of a much more sensitive galvanometer, the influence of very much smaller proportions of impurity upon the amounts of voltaic energy and electro-motive force might be detected.

In the above Table the order of voltaic energy of the metals is substantially the same as that of the metals alone and unamalgamated. With each amalgam the amount of energy gradually declined, but recovered on stirring the mixture; the decline was quickest with the most dilute ones. An amalgam of magnesium with 1605 times its weight of mercury rapidly became covered with a thin film of black suboxide of magnesium on exposure to the air.

As the influence of the above minute proportions of all the metals, except silver, may be thus readily detected, I have employed this method to test the purity of mercury. I took about 2000 grains of mercury, containing, dissolved in it, 6 grains of a mixture of the above eight metals, distilled off the mercury, and then used the product in place of the amalgam in the potassium chloride solution

in the above manner; the galvanometer needles were very slightly affected, but after a second distillation of the mercury the needles were not visibly moved.

THE CHEMICAL PROBLEMS OF TO-DAY.*

By VICTOR MEYER.

(Concluded from p. 31).

THE discovery of the system of the elements leads us back to the question whether the chemical elements are separate worlds in themselves or whether they represent different forms or conditions under which *one* ultimate substance exists; a question that has occupied the philosophical mind since very early times. The same question was raised anew by the discovery of spectral analysis. Whosoever regards the numerous lines of the spectrum of a metal will hardly be convinced that the metal from which they emanate should be an eternally indecomposable element. In a similar manner the compound nature of the elements is indicated by comparison of the regularities in numbers of the atomic weights with the homologous series of organic chemistry.

In the pursuit of this question, which, since Prout's hypothesis and the surprises offered by Stas's determinations of atomic weights, has not been allowed to rest, positive results are not to be found. The decomposition of substances called elements into simpler ones has not been accomplished.

Nevertheless, something has been achieved, since an increased interest has been drawn towards pyro-chemical research.

To-day, new methods of experiment permit of a comparatively easy determination of the vapour density, and consequently of the molecular state of the substances at the highest temperatures.

Numerous inorganic compounds, above all the very elements, have been studied in regard to their vapour density at a white heat.

While many of them, as oxygen, nitrogen, sulphur, and mercury, remain unchanged under such conditions, the molecules of chlorine, bromine, and iodine respectively, were split into two atoms, in conformity with Avogadro's surmise of the compound nature of elementary molecules.

In the same manner, the vapour density and the molecular condition of the less volatile substances, zinc, thallium, antimony, and bismuth, was successfully determined at a white heat.

Careful research resulted in the exposure of the old fallacy of the existence of a sulphur molecule containing six atoms.

But how many of the problems which crowd around us at this point are for the time being entirely beyond the reach of the experimenter!

To-day, pyro-chemical work is limited to a temperature of 1700° C., because vessels of porcelain and platinum, to the use of which we are limited, fuse above that temperature. The possibility of performing quantitative experiments at these temperatures seemed to us some years ago to be an unexpected progress, but to-day we complain that the trivial cause of a want of proper vessels forbids us to increase the temperature up to 2000° or 3000° C. There is no doubt that we should arrive at new unthought of facts, that the splitting of still other elementary molecules would be possible, that a new chemistry would be revealed to us if, being provided with vessels of infusible material, we could work at temperatures at which water could not exist, and at which detonating gas would be a non-inflammable mixture!

Let us now enter other fields of physical chemistry. Golden fruit, daily increasing, has been harvested upon this field during these latter days. Again we see Van't Hoff take the lead. His keen eye has enabled us to penetrate the nature of *solution*, which forms the beginning of a new epoch in molecular physics. The quintessence of his discoveries may be thus expressed:—

“Solutions of different substances in the same liquid, which contain in the same volume *an equal number of molecules* of the dissolved substance, show the same *osmotic pressure, the same vapour pressure, and the same freezing-point.*”

This surprising generalisation offers the possibility of determining *the true molecular weight of substances* by experimenting upon them in *solution*, while heretofore this has only been possible by transforming them into the gaseous state, hence only for volatile substances, since *dilute solutions* behave in regard to the molecular state of the dissolved substance like *gases*.

In this manner, new methods are given for the determination of molecular weights, which we are now able to determine by means of measurements relating to the *freezing-point, the vapour pressure, or the osmotic pressure* of a solution of the substance to be tested.

These results are of the highest possible practical importance for chemistry, since they widen in an unexpected manner the possibility of the determination of molecular weights, and in a still higher degree we are surprised by the elucidation which they offer in regard to *the nature of solution*. Clausius had already admitted within narrower limits, that in solutions of electrolytes some of the dissolved molecules were decomposed into their ions, but now this has been proved in a larger measure, particularly by Arrhenius. What a change our conceptions will have to undergo if we have to accustom ourselves to regard a dilute solution of sodium chloride as one containing not undecomposed molecules of this salt, but separated atoms of sodium and chlorine!

We owe these revolutionising innovations to the investigations of Van't Hoff, Arrhenius, Ostwald, Planck, and de Vrie, but, in regard to experimental research, especially to the splendid work of Raoult, which during recent years has effected this mighty theoretical progress.

Thus we see Physical Chemistry moving on in weighty development. Special laboratories are opened for her, and a special journal also has been started, which is open alike to the records of experiment and to theoretical discussion. Through the foundation of this organ, physical chemistry has been furthered in a most active manner. All the questions of the time, and all those in dispute belonging to this department of science, receive in this paper a thorough discussion. Dynamical-chemical questions are successfully studied, a significant impetus is given to the study of structure and affinity (widened as our knowledge of the nature of solutions has made necessary), by means of the study of the relations between chemical nature and electric conduction.

The inquiry into the intimate relations that exist between physical and chemical properties, which was inaugurated half a century ago by Hermann Kopp, is now being deepened and widened.

It is true that the great hopes which sprang from the study of thermo-chemical questions have so far been only partly fulfilled, but consecutive measurements offer more clearness also in this case.

There is no field of our science in which we may expect greater revolutions in the time near at hand than in that of physical chemistry! The value of these for general chemistry will be greater in proportion as the representatives of the same will recognise their task in this: above all to remain upon the *chemical* standpoint, and to improve *chemistry* by the application of *physical* modes of thought and experiment. Those who tried to further the progress of chemistry by the use of physical methods, but with insufficient considerations for chemical relations, have been led into serious errors. The respect

* An Address delivered at Heidelberg at the First General Session of the Sixty-Second Meeting of the Association of German Naturalists and Physicians, Sept. 18, 1889. Translated, by L. H. Friedburg, from the *Deutsche Rundschau*, Nov., 1889.

due to work of the highest merit, continued for years, has thus been lessened. Apparently, this has even been overdone, and it is much to be deplored if the interest of chemists for physical chemistry should be diminished because some of its representatives are inclined to overrate the value of their results. He who swims in the midst of high waves is unable at times to see over the crests.

Innumerable, also, are the problems which meet us in the domain of organic chemistry.

After the astonishing harvest of synthetical results which has been reaped here, hardly any problem of synthesis seems unapproachable. Since the artificial preparation of alizarin by Graebe and Liebermann, of indigo by von Baeyer, of conine by Ladenburg, of uric acid by Horbaczewski, and particularly by Behrend, since Emil Fischer and Kiliani have elucidated the chemistry of the sugar group, and Wallach that of the terpenes, we may well look hopefully for a clearer knowledge of the bodies comprised under the name albumen, and to its synthesis.

But even such success tends only to render us more modest, since they show us at the same time how narrow are the limits within which chemical synthesis moves. Assuming even that the preparation of albumen had been achieved—how infinitely far we should still be from a conception of the nature of *organised* bodies! Perhaps science is separated by an impassable chasm from the artificial preparation of a simple cell. Such an achievement lies at least beyond the sphere of chemistry.

But shall we really never succeed in sounding the process of *assimilation*, which in spite of its simplicity presents itself to us so enigmatically? Will it be found impossible to prepare artificially in our laboratories from carbon dioxide and water, sugar and starch, a process which nature performs unceasingly in the green parts of plants?

The chemist, however, should not step prematurely upon the field of biology, while so many great problems remain untouched in his own peculiar sphere of investigation.

The *method* of research in organic chemistry, in spite of the brilliant successes already recorded, forces us even to-day to confess that only a very minute proportion of known substances is within its reach. In order to isolate an organic substance we are generally confined to the purely accidental properties of *crystallisation* or *volatilisation*. Have not those thousands of amorphous substances, which cannot be characterised by any chemical property, and which the chemist is forced to lay aside because he is unable either to purify them or to transform them into volatile or crystallisable bodies; have they not the same claim upon our interest as their more beautiful and more manageable comrades?

The most significant progress of organic chemistry does not consist in single discoveries, nor in further expansion of synthetical success. What we want are:—*New methods for recognising the individuality of substances*. The black substances of earthy nature, the innumerable formless and resinous products in the bodies of plants and animals, the colouring matter which gives beauty to flowers, all of these to-day mock our efforts to know them; they will form a new and inexhaustible field for the prosecution of chemical research, when *methods* shall have been found with which to begin this research.

And, as in organic chemistry, so in *mineral chemistry*, every step leads to questions, which we have, as yet, no means of answering. The synthesis of minerals and of rocks has made important progress, it is true, and this, as well as the application of the doctrine of structure to the study of mineral species, gradually leads to the understanding of their constitution. But we are, as yet, unable to use, in the study of minerals, the method of *analytical decomposition* which has been so successfully used to study the constitution of organic substances, and, above all, we lack the least knowledge in regard to the *true molecular weight* of minerals.

Quite recently we have been presented with no less than three new and fruitful methods for the determination of the molecular weight, but not *one* of them gives us an indication of the true molecular weight of the most simple oxides, such as silicic anhydride or calcium oxide.

We know to-day very well that silicic anhydride cannot have the formula SiO_2 , that this must be multiplied by a very large factor; but of the numerical value of this latter we have no indication. And thus also in mineral chemistry we must aim, not exclusively at finding new *facts*, but *new methods of research* in the first place, if a period of new discoveries is to be attained in this branch of our science.

But how can we conclude this brief review without mentioning also the *applications of chemistry to the industrial arts*, the progress of which have mainly contributed to spread the splendor of our science most widely? The infinite variety of the tar colours, surpassing the colours of flowers in number and brightness, is daily increased by new discoveries. The industry of these forms the most brilliant triumph of purely scientific laboratory work applied to manufactures. This industry, in the simplest manner, and on the largest scale, performs the synthesis of compounds the complex nature of which is indicated by the names they bear. The unscientific man is frightened when a beautiful and brilliant dye is referred to as *Hexamethylmethoxytriamidotriphenyl-carbinol*; for the initiated there lies in this unpleasant name a full account of the synthesis and the constitution of the dye.

Industry has learned to derive not only colours but healing medicines also from coal-tar. Antipyrin, discovered by Knorr, upon the basis of Emil Fischer's fundamental research upon the hydrazins, brings to thousands suffering from fever, relief at least, if not cure. Let us hope that the time is not far distant when *real* fever curatives, which, like the natural alkaloids of the cinchona bark, not only temporarily *suppress* the disease but really *cure* it, may be prepared by synthesis. Until then be patient and do not chide chemistry if, for the time being, she offers only silver instead of gold.

Events in this field of the great chemical industries are significant. We are the witness of a great combat taking place between the older process of Leblanc for the preparation of soda and the new one of Solvay, called the Ammonia-Soda process. The intelligence and inventive genius of manufacturers have added, under the pressure of this competition, a large number of improvements to the manufacture of sulphuric acid and of soda, and new and valuable methods for the preparation of chlorine. Here, more than in any other branch of chemical industry, the struggle for existence is fierce.

The manufacture of iron, that most important chemical industry, is transformed by innovations. The imposing changes wrought by the older process of Bessemer, by the new one of Thomas, are they not based purely upon chemical reactions? The grandest application of a complicated chemical reaction to a great manufacture is, perhaps, the dephosphorising of pig-iron by lining the Bessemer converter with basic material, an invention which we owe to Thomas and Gilchrist. From this, again, agriculture derives an advantage in the use of the Thomas slag containing the phosphorus which heretofore rendered iron-ore less valuable. This, then, is truly a transformation of stone into bread, similar to the older manufacture of soluble fertilisers from mineral phosphates. Nevertheless, the era of bliss which was prophesied three years ago at the Berlin meeting of naturalists by our illustrious colleague, Ferdinand Cohn, has not yet dawned. He held that all struggles for existence amongst men, arising from want of food, the bread question, will be done away with when chemistry shall have learned to prepare starch from carbon dioxide and water. But since time immemorial the farmer has been occupied in this very chemical industry, and it would hardly be great progress if the farm were merely replaced by a

chemical factory. But we may reasonably hope that chemistry will teach us to make the fibre of wood a source of human food.

Indeed, if we consider how small is the quantity of starch which the grain furnishes us, and further that the wood fibre has exactly the same chemical composition as starch, we see the possibility of increasing the production of food infinitely by solving this problem: to transform cellulose into starch.

If this problem were solved we should find an inexhaustible source of human food in the wood of our forests, in grass, and even in straw and chaff. The beautiful researches of Hellreigel have recently disclosed the fact, which in former times was disputed, that certain plants transform atmospheric nitrogen into albumen and that this process can be improved by suitable treatment.

The increase of albumen in plants, according to a plan, together with the production of starch out of cellulose—this would in reality signify the abolition of the bread question.

May it some day be granted to chemistry, through such a discovery, to inaugurate a golden age for humanity.

I have tried to give a review of the most important problems which are set before chemical science. I have mentioned a goodly number, but the short time of one hour permits me to touch but slightly upon the greater ones. There are so many problems before us which await an immediate solution as to justify what I said in the beginning, that to-day the chemist has no time so complain because the epoch of a mathematical treatment of his science has not yet arrived.

Nevertheless, the brilliant successes which have been gained, the wonderful results which are immediately within our reach, have not the power to turn our eyes from this final problem.

The Newton prophesied to chemistry by Emil du Bois Reymond, may he appear at a later period; until he comes, may many a generation honourably plough on in the sweat of its brow! We must remember that nature is not understood by us until we are able to reduce its phenomena to simple movements, mathematically traceable.

The time will come, even for chemistry, when this highest kind of treatment will prevail. The epoch in which the foremost impulse of its research was a serenely creative phantasy will then have passed; the joys, but also the pangs and struggles, peculiar to youth, will have been overcome.

Re-united to Physics, her sister science, from whom her ways at present are separated, Chemistry will run her course with firm and unfaltering steps.—*Journal of American Chemical Society*, vol. xi., No. 7.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1889.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,

Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act*, 1871.

London, January 4th, 1890.

SIR,—We submit herewith the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of

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

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

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

The whole of the 168 samples examined were found to be clear, bright, and well filtered.

The condition of the water supply to the Metropolis during the past month has been wholly satisfactory. What little difference of character has been observable between the supply of the past month and that of the two preceding months, is in the direction of a greater degree of freedom from colour-tint and from excess of organic matter, as determined alike by estimation of the quantity of oxygen absorbed and of organic carbon present. As regards the Thames-derived supply more particularly, though falling off slightly in November and more than retrieving itself in December, it has not presented any difference of composition that can be regarded as at all noteworthy during the past three months. Just now, indeed, it is for the period of the year of exceptionally high quality, the maximum proportion of organic carbon present in any one sample examined being only 0.155 part, and the mean proportion 0.143 part, in 100,000 parts of the water.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

THE ESTIMATION OF MINUTE QUANTITIES OF GOLD.*

By Dr. GEORGE TATE, F.I.C., F.C.S.,
Principal at the College of Chemistry, Liverpool.

AT a recent criminal trial, wherein experts referred frequently to thousandths of a grain, Mr. Justice Stephens ventured the opinion that the mind untrained in the observation of minute quantities could not comprehend so minute a fraction of what many conceive as being the least ponderable quantity.

As a person that is accustomed to weigh or handle fractions of an ounce, or possibly only of a pound, cannot place before you the most approximate estimate of a grain, so in like manner a chemist, accustomed to weigh only to the hundredth of a grain, would generally fail to form an approximate estimate of a thousandth of a grain. I say this since, although the wonderfully fine workmanship of a good assay balance permits of the estimation of a thousandth of a grain, still such minute portions of chemical substances are commonly estimated by the observation of an eye trained to observe colour, opacity, or other comparative physical effects brought about by the action of reagents, chosen according to the nature of the substance brought under analytical tests. It is virtually only by comparison, by having some bulk, colour, or appearance as a standard of quantity, that the eye can estimate weights either large or small. I purpose endeavouring to show you how minute a quantity of certain substances is capable of recognition; and to show how, by suitable means, such minute quantities as the one ten-thousandth, or even the one hundredth-thousandth

* A Paper read before the Liverpool Polytechnic Society, November 1889.

of a grain, may be estimated with such accuracy and certainty as I think will satisfy the most captious mind.

For the recognition of these minute quantities, what are termed colour reactions are certainly the most sensitive, and therefore most extensively employed by chemists.

I have formed an estimate of the sensitiveness of certain of these reactions, so that their capabilities might be demonstrated to you. I have here portions of brucine, strychnine, iron, and copper in the form of salts, obtained by sub-division of dilute solutions of known strength; these portions contain therefore known quantities of matter. Each of these quantities give with specific reagents distinct colour reactions, indicating, with more or less conclusiveness, the presence of the respective substances.

These powers of such colour reactions, for the recognition of minute quantities of certain chemical bodies when isolated in a fair state of purity, are unsurpassed, saving by the powers of the microscope and spectroscope. When applied, however, to quantities extracted from an ounce or more of organic or inorganic matter, these colour methods would fail to form more than the most approximate estimate of the ten-thousandth of a grain, and could enable me to only state (not in every case with scientific precision) that some minute trace of the substance was present in the ounce weight of matter.

The microscope, however, now an instrument with which a scientific or analytical chemist cannot dispense, can, in many cases, recognise and identify with conclusiveness far less than the millionth of a grain of chemical matter, and estimate its weight with a fair degree of accuracy. I have, during the past year, had frequent occasion to estimate minute quantities of gold, imponderable upon the best assay balances, and have lately proved, to my satisfaction, the general accuracy of my method of working. I purpose demonstrating to you this method of estimating gold, and to lay before you facts and figures that I trust will convince you of the accuracy of my work. It may appear to some a "fancy" method of no practical utility, but when we consider the needs of the gold prospector, and how any method for enhancing the accuracy of estimation lessens the labour involved in an assay or chemical test, any such process is at least worthy of trial.

The method I have elaborated is virtually the system of measurement of gold, after fusion and when in an approximately spherical form, described in Plattner's work on the blowpipe and in other works on assaying. As there described, the weight of a bead of gold is estimated from its diameter, obtained by placing the bead above a divided scale of two divergent lines. The method is no doubt familiar to all assayers, and I think all that have tried it will agree with me that with small beads of gold two independent observations may differ often by 100 per cent. I have found that by employing a compound microscope to largely increase the apparent size of the prills or beads, and an eyepiece micrometer as a scale, that the measurement method becomes one possessed of scientific accuracy and of powers far beyond that of the very finest balance ever constructed. To convince you of this, I have here beads of gold, each respectively the 1-100th, 1-1000th, 1-10,000th, 1-100,000th, and 1-1,000,000th of a grain, which I may guarantee to be accurate to those weights within 10 per cent, even in the case of the smallest weight.

The magnitude of the smallest of these weights may be better conceived when I state that it is quite invisible to the unaided eye, and that one thousand of them would be required to distinctly turn a delicate assay balance, and that the error in estimating the weight of these thousand beads could, only by the most elaborate system of weighing, be made to fall within 20 per cent.

These beads or prills are, what I may term, standard weights, and have been accurately measured with the

microscope; so that by comparison with these, the weights of gold prills such as may be obtained as the result of an assay, may be accurately estimated.

Preparing the Standards.—To obtain these standard beads I take a weight of pure gold (*e.g.*, 0.1 grm. or 1 grain) that can be accurately weighed within 1 per cent on an ordinary analytical balance, or within an error of 0.1 per cent on an assay balance, and alloy it with about 100 times its own weight of pure lead, either by fusion upon a scorifier or in a small crucible. After weighing the alloy obtained I calculate what weight of it contains the quantity of gold I require for the standard bead or prill (*e.g.*, 0.1 m.grm. or 0.001 grain, according to the system of weights adopted).

For the lead, ordinary assay lead or the lead obtained from litharge by reduction, may be employed for gold-lead alloys of one per cent, without introducing an error of more than one per cent in the weight of the bead obtained from them.

This slight error arises from the presence of a trace of silver in so-called pure lead or in litharge lead; this error becomes appreciable when one-tenth per cent alloys of gold are prepared, *e.g.*, for the purpose of obtaining the standards, the one-tenthousandth, and the one-hundred-thousandth grain—in such cases special lead must be used.

Having weighed off several, say ten, portions of the necessary weight of alloy to give the desired gold prill, they are separately cupellated on small bone-ash cupels, either before the mouth blowpipe or in the muffle.

By thus heating the alloy in an oxidising atmosphere, the lead is eliminated, passing away from the gold as fused litharge, which is absorbed by the porous bone-ash of the cupel. If the blowpipe is employed a strong heat should be brought to bear upon the residual gold, so that when the flame is withdrawn, the prill remains fluid for some few seconds and has time to acquire an approximately spherical form before it solidifies. Ten such beads, if each of the thousandth of a grain or of the tenth of a m.grm., together form an appreciable weight, and can hence be together weighed to ascertain if the average weight is correct. The following is an example:—

Five portions of gold lead alloy, each calculated to contain one-hundredth of a grain (0.65 m.grm.) were cupellated; the five gold prills were detached and together weighed on an assay balance.

5 prills weighed	0.050 grain
Average weight of each prill	0.010 "

These beads measured (with a magnifying power that I will refer to as No. 1, and by the method later described), respectively,

21.3, 22, 21.5, 21.5, 21.5,

giving an average diameter for a bead 0.01 grain in weight of 21.5 divisions of the scale.

In a similar way were obtained the empirical measurements of prills.

0.1 and 0.05 m.grm. (0.00154 grain and 0.00077 grain); the diameters of these averaged 11.1 and 8.7 divisions.

The above standard prills are those that have been chiefly employed for the estimation of the weights of gold obtained in the experiments to be later described.

For the preparation of the standards of smaller weight, *e.g.*, the one-tenthousandth of a grain, a gold-lead alloy containing about 0.05 per cent of gold was used, the lead being exceptionally free from silver, and obtained from litharge in the following way:—

A pound of litharge was mixed with about 5 grms. or 75 grains cream of tartar, and fused in a capacious crucible in two or three portions at a time. By this about an ounce of lead was reduced from the oxide, the residual oxide being thus partially freed from the trace of silver invariably found in the commercial litharge.

The residual litharge was pounded, again fused with the above weight of tartar, thus again separating a part

of the lead and of the trace of silver. With the remaining oxide, the partial reduction was again repeated, and, finally, after these three purifications, the rest of the oxide was mixed with excess of cream of tartar and some fine charcoal powder, and fused so as to reduce out all the lead.

To test this lead 50 grms. or 770 grains were heated on a scorifier in an oxidising atmosphere, so as to reduce the weight of metal to 10 grms. (150 grains); this, on cupellation, gave a distinct trace of silver. I therefore decided to oxidise, by scorification, two or three ounces of this fairly pure lead, collected about half an ounce of oxide (still leaving a large excess of lead in the metallic state), purified it by partial reduction, and finally fused with excess of tartar. The lead produced by this final operation was of such purity that I was enabled, by alloying it with 0.05 per cent of gold, to obtain standard prills of gold 0.0001 grain (0.0065 m.grm.), 0.00001 grain (0.00065 m.grm.), and 0.000001 (0.000065 m.grm.), perfectly free from silver, and estimated by comparison with the higher standards to be exact within an error of less than 10 per cent. In other words, the prill of gold that is now under a high power of the microscope is the millionth of a grain, and exact to the one ten-millionth of a grain. It has the colour of pure gold, is apparently perfectly spherical in form, and has a diameter, in actual measurement, according to the mean of a large number of observations, of 0.00075 inch. Assuming this minute bead of gold to be a sphere, its volume would correspond to a weight of gold equal to 0.00000107 grain.

This close agreement between the weight of the gold prill and the weight of the gold in the lead alloy taken for cupellation, proves how minute must be the loss of gold when cupellated with lead.

The average absolute diameters of the standard prills or beads have been calculated, and are given in the following Table. In the column D are given the amounts by which spheres of gold, of the specified diameters, would exceed the weights of the prills. The specific gravity of the gold has been taken as 19.2.

Weight of standard in grains.	Diameter in thousandths inch.	Relative cubes.	D. Per cent.
Hundredth	15.81	9.17	+ 0.4
Thousandth	7.55	1	+ 9
Ten-thousandth	3.63	0.110	+ 22
Hundred-thousandth	1.61	0.0097	+ 6
Millionth	0.75	0.00098	+ 7

The Measurement.—For the measurement of beads ranging in weight from the hundredth to the ten-thousandth of a grain (or from 0.05 to 0.005 m.grm.), the most convenient magnifying power is that afforded by a microscope fitted with a ½-inch objective and B eye-piece; although most of the results here recorded have been obtained with a one inch objective, and the microscope tube drawn out so as to give a total length of 12 inches. Some of the smaller beads (e.g., 1/100000 grain) have been measured with ¼ and also ⅓ inch objectives, by which the accuracy of the measurements have been greatly enhanced.

A convenient stage is one enabling a steady motion to be given to the glass slide upon which the bead is placed, so that the latter may be quickly adjusted to the scale in the eyepiece. A stage moving by rackwork is a great luxury, and enables measurements to be rapidly made.

The micrometer that I have employed is photographed down to ½ inch from a scale ten inches long (an old thermometer scale upon white porcelain) and has about 80 divisions in the half-inch. The glass upon which the positive is taken is cut into circular form and then dropped into the eyepiece upon the diaphragm, where it is in the focus of the upper lens.* This form of micrometer is

superior to any engraved scale, being distinctly visible when the stage is illuminated, and both it and the object upon the stage can be, at the same time, brought into the focus of the eye. It is a convenience if the eyepiece fits loosely in the tube of the microscope, since then a slight turn or movement of the former can bring the apparent edge of the bead or prill, as viewed through the instrument, accurately to a unit division of the scale.

Having a gold prill (say upon the cupel), have ready a dry glass slide, plain, or having a small cell, moisten the point of a knife, gently touch the bead with it until it is loosened; the bead generally adheres to the point, and can be transferred to the glass slide. When the prills are required to be kept for reference, they may be mounted in a cell formed on the glass by gumming one or more thicknesses of paper, in which small holes have been cut, covering with a circle of glass, and fixing the latter in position by gummed paper.

The bead is lighted from below and brought into the focus of the microscope; it then appears as a black circle with well-defined edge. To measure the diameter the stage is moved until the head apparently coincides with the micrometer scale; the units, and approximately the 1-10ths that the bead measures is then read upon the scale. It is well to take the measure in two directions at least, by turning the eyepiece, and with it the micrometer, through 90°; an average of the measurements is then taken.

The beads are slightly flattened at the point where they have rested upon the cupel, and, when resting upon this flattened surface appear spherical in form. Since the flattened surfaces are not always in view in taking the measurements of diameters, they are, when visible, best left out of consideration.

Knowing the measurement of a bead of standard weight, that of the prill can be calculated upon the assumption that both are approximately spherical, and therefore that the weights of the two masses are proportionate to the cubes of the diameters.

Example:—A prill of gold obtained as the result of an assay, measured under the power before recorded, 12.5 divisions.

The average diameter for 0.01 grain is 21.5 divisions, hence the weight of the prill is 21.5³ : 12.5³ :: 0.010 : X

$$X = \frac{0.01 \times 12.5 \times 12.5 \times 12.5}{21.5 \times 21.5 \times 21.5} = 0.00197 \text{ grain,}$$

or approximately 0.002 grain.

If the comparison is made against the average diameter of the 0.1 m.g. beads, the weight would be estimated as 0.143 m.g., or 0.0022 grain, showing a difference in estimate of 10 per cent. I would prefer to accept the estimate made against the lower standard, since it more closely approaches in size, and therefore in form, to the assay prill. Considering, however, that this difference is in weight only 0.0002 grain, and that a balance would differ at least to 0.0005 grain in two observations, the above example will show that with the thousandth of a grain the method of measurement is superior in accuracy to that of weighing. With the aid of a table of cubes the calculations can be quickly performed.

Where the ten-thousandth of a grain of gold is to be measured, before attempting to detach the prill it is advisable (for fear of loss) to measure it while still upon the cupel. For this purpose place the cupel itself on the stage, illuminate the surface from above, focus, and measure as accurately as possible. Measurement in reflected light commonly gives a lower estimate than by illumination from below, owing to the difficulty of seeing the edges of the strongly reflecting bead. After a little practice even the 1-100,000th of a grain can be detached from the cupel and mounted in a cell. The risk of losing the prill is chiefly in detachment.

Outline on the Method of Assaying.—Taking the case of quartzeous gold ores for the sake of illustration, the ore, after careful sampling and pounding into a fine state,

* Mr. Knott, of Elliott Street, Liverpool, photographed these micrometers, and can fit them to any eyepiece.

is sifted. Any metallic particles that remain on the sieve are collected and weighed. The finer ore being also weighed, proportionate parts of the two are weighed off for assay. Convenient quantities for assay are from 100 to 1000 grains, or from 10 to 100 grms., according to the richness of the ore and the degree of accuracy required in the results. By adopting the measurement system, accurate assays may be performed upon much smaller quantities than when the gold is weighed. In fact, fairly accurate and concordant assays of rich gold ores, sufficiently accurate for the purposes of a prospector, have been obtained from one grain only of material. As in all analytical tests, two or more portions should be submitted to assay. Where the method of fusion with litharge in a crucible is adopted, the weighed portions are mixed with flux, litharge, and some reducing substance, and heated to complete fusion in a good clay crucible. Convenient proportions are, in the case of quartz ore (fairly free from pyrites):—Ore, 100 parts by weight; litharge, 200 parts; soda-ash, 200 parts; and cream of tartar, 4 to 5 parts. On fusion about one-tenth or eighth of the litharge is reduced, the remaining portion serving, with the soda, as a flux for the siliceous matter of the ore. With ores containing pyrites or other sulphides, the tartar may require to be reduced in amount, or even altogether omitted, since the sulphur of the pyrites acts as a reducing agent towards the litharge. A good rule to observe is to obtain a large excess of litharge in the slag, and at most 50 parts of lead from 200 of litharge. During the fusion, the lead that forms picks out or alloys with the gold, collects at the bottom of the crucible, and there, when the ore is completely fused, receives such particles of gold that have escaped the action of the globules of lead, and that tend to fall through the fused mass of slag. To further promote the separation of the gold, a little tartar mixed with litharge may be thrown or sprinkled upon the surface of the fused mass in the crucible, so as to form minute particles of lead, which, in falling to the bottom, no doubt serve to perfect the collection of the gold. The contents of the crucible are poured into a mould, the slag again fused with a small quantity of tartar, and again poured.

The lead produced by these two operations contains, according to test experiments described later, practically all the gold of the ore,* together with the silver natural to it and to the litharge, also traces of other reducible metals, such as copper, if the ore contains such.

This alloy is heated upon bone-ash supports or cupels in an oxidising atmosphere, until all oxidisable metals are removed and absorbed as oxides by the porous bone-ash: an alloy of silver and gold is then left as a bead or globule.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

January 17th, 1890.

Prof. W. G. ADAMS, Vice-President, in the Chair.

OWING to the unavoidable absence of Mr. F. B. Hawes, his paper on "A Carbon Deposit in a Blake Telephone Transmitter" was postponed.

Dr. S. P. THOMPSON made a communication "On Electric Splashes," and illustrated his subject by beautiful experiments on the production of Lichtenberg's figures. The author has recently investigated these phenomena as modified by varying the conditions under which the figures are obtained, and has arrived at the following conclusions:—1st. The nature of the dielectric plate does

* Platinum also if present in the ore.

not change the character of the figures produced; and, 2nd, the nature of the powders used seems to have no material effect on their shape.

In the course of his experiments he has found a mixture of sublimed sulphur and lycopodium to give better figures than the red lead and sulphur usually employed, and also that a large and highly polished knob is advantageous, particularly when the Leyden jar is charged negatively. Sometimes when obtaining negative figures, nebulous patches occur, and these were attributed to the so-called electric winds sent off from roughness on the knob when not sufficiently well polished. If, instead of bringing the knob in contact with the plate, it is only brought near to it, then a peculiar figure closely resembling a "splash" results. A positive splash consists of short lines radiating from the point of approach, whilst a negative splash is made up of more or less rounded spots, which become elongated in a radial direction as the distance from the centre of the splash increases. Negative splashes are, however, much more difficult to produce than positive ones.

When viewed in the dark, the discharge producing the splash is seen to consist of a bundle of small sparks which branch outwards on approaching the plate.

In conclusion, the author remarked that roughness on a conductor produced more "electric wind" when the conductor is charged negatively than when positively charged, and invited the opinion of members as to the cause of the differences observed between positive and negative electricity.

Prof. RÜCKER said he had recently obtained figures produced by discharges on photographic plates. Generally, he observed that negative discharges produced roundish patches, whilst positive ones give more filamentary figures. On passing a spark across a glass plate covered with lamp-black, its trace was found to have a black core at one end whilst the other was quite clear. He also made remarks on the distinctive character of the positive and negative discharges in partial *vacuo*, and considered investigations as to the cause of such differences to be of great importance.

Prof. ADAMS thought any attempt to discover the cause of such differences as those noted in the paper was to be commended, for the well-known fact that it is more difficult to insulate a negative charge than a positive one has long needed an explanation.

"A Paper on Galvanometers." By Prof. W. E. AYRTON, F.R.S., T. MATHER, and W. E. SUMPNER, D.Sc.; read by Prof. AYRTON.

In fitting up the physical laboratories of the Central Institution of the City and Guilds of London Institute, the authors have had occasion to obtain galvanometers of various types and patterns, some of which have been made to special designs, and specimens of instruments embodying recent improvements were exhibited at the meeting.

The question as to whether fairly sensitive galvanometers should be astatic or non-astatic was answered in favour of the former system, from the fact of its being less affected by external magnetic disturbances, and the greater ease with which great sensibility may be obtained.

The usual method of placing the mirror inside the coil was shown to be undesirable, and in the newer forms of instruments Mudford's improvement of placing the mirror outside the coils has been adopted, the space near the axis of the coil being nearly filled with wire. It was also shown that if wire be wound in a certain approximately spheroidal space near the magnets, then these convolutions will tend to oppose the more distant portions of the coil; however, by winding the two parts in opposite directions, they conspire to deflect the magnet.

Details as to methods of supporting the coils were then discussed, and the importance of fitting them in boxes mounted on hinges or otherwise so as to be readily removable was pointed out.

A galvanometer devised for teaching-purposes and provided with variable damping arrangement was described, in which the damping is effected by enclosing the mirror in a glass cell whose sides can be caused to approach or recede by turning a milled head outside the instrument. This arrangement enables the damping to be varied between wide limits, and its effect on the swing produced by a given discharge can be determined. The instrument is also serviceable both as an ordinary damped galvanometer or as a fairly ballistic one.

In measuring quantities of electricity by the first swing of a galvanometer needle, a correction has usually to be introduced for damping; this correcting factor is simple enough when the damping is small, but becomes more complex as the damping increases, and to facilitate the calculations a table of values of the factor for various values of λ (the logarithmic decrement) has been calculated. From this it appears that for values of λ less than 0.5 the value of the factor is very nearly $(1 + \frac{1}{2}\lambda)$, the correction usually employed.

Improvements in methods of insulating the coils and terminals of galvanometers required for insulation tests were next described, the principle of which may be gathered from Figs. 107 and 108 in Prof. Ayrton's "Practical Electricity." A special form of instrument for high insulation work was exhibited, in which the copper resistance of the coils is nearly 400,000 ohms, and the shortest path along which surface leakage can take place from the coils to the base of the instrument is between 30 and 40 inches of ebonite artificially dried by sulphuric acid. This is attained by supporting the coils from two corrugated ebonite rods which depend from a brass ring carried on the top of three corrugated pillars fixed to the base plate. The instrument was constructed to drawing and specification by Messrs. Nalden Bros., but the method of supporting the coils was suggested by Messrs. Eidsforth and Mudford.

With reference to the proportionality of deflection to current in reflecting galvanometers, it was pointed out that ordinary instruments may differ as much as 2 per cent within the limits of the scale, hence showing the necessity for calibration when any approach to accuracy is desired. Galvanometers, of the D'Arsonval type sometimes differ from proportionality quite as much as the one above referred to, but by fitting such instruments with curved pole-pieces, and allowing the coil to hang freely from the top suspension, a proportionality true to less than 0.15 per cent has been attained over a scale about 30 inches long.

Coming to the question of sensitiveness, the importance of keeping the wire as close as possible to the magnets was brought prominently forward, as well as the necessity of reducing the "figures of merit" of various instruments to the same standard in comparing their sensibilities. The standard adopted as most convenient, and closely approximating to practical usage, is arrived at by supposing the distance of the mirror from the scale to be equal to 2000 scale divisions, and the sensibilities for current and quantity are given as *scale divisions per micro-ampère*, and *scale divisions per micro-coulomb* respectively. The period of oscillation is also taken into account.

A table showing the resistances, sensibilities, coefficients of self-induction, and volumes of the coils of various instruments, together with the relations existing between them, accompanies the paper, and from this it appears that in the best astatic coil instruments of from 10,000 to 30,000 ohms resistance, the number of scale divisions per micro-ampère may reach 400 times the resistance to the $\frac{3}{2}$ th power ($400 R^{\frac{3}{2}}$) when the period is ten seconds.

In obtaining data of various instruments the authors have consulted, amongst others, Prof. Threlfall's paper on the "Measurement of High Specific Resistances," in the *Phil. Mag.* for Dec., 1889, and noticed two serious errors. The first of these makes an instrument constructed according to Messrs. Gray's pattern nine times less

sensitive than it actually was, whilst the sensibility of a form recommended in the paper is given seventeen times too great.

On account of the lateness of the hour the discussion was adjourned till Feb. 6, before which time it is hoped that a fairly full abstract will appear in the technical papers.

NOTICES OF BOOKS.

A Practical Treatise on the Manufacture of Vinegar and Acetates; Cider and Fruit Wines; Preservation of Fruits and Vegetables by Canning and Evaporation; Preparation of Fruit-Butters, Jellies, Marmalades, Catchups, Pickles, Mustards, &c. Edited from various sources by WILLIAM T. BRANNT. Illustrated by Seventy-nine Engravings. Philadelphia: H. C. Baird and Co. London: Sampson Low, Marston, Searle, and Rivingtons, Limited.

WE have here a work which may be pronounced more comprehensive and more trustworthy than any other on the subject in the English language. The author does not give a mere collection of recipes; he endeavours, and successfully, to place the manufacture of vinegar upon a rational basis. The work commences with a history of vinegar, in which we are sorry to find the myth of Hannibal dissolving rocks by means of vinegar. The manufacture of vinegar from alcohol will, he considers, become increasingly difficult, on account of the price of raw material and of the growing competition of wood-vinegars, which are now obtained free from the trace of tar products. Still, absolutely pure acetic acid has never the aroma of alcohol- and fruit-vinegars, due of course to ethereal compounds. We have never met with a specimen of malt vinegar—so much admired in England—which possessed anything approaching the bouquet of wine-, sugar-, and cider-vinegars. This, of course, is not a point which can be decided analytically.

As regards the theory of the formation of vinegar, the successive results of Dobereiner, Liebig, Pasteur, and Nägeli are duly noticed. A curious fact here mentioned is the occurrence of acetic acid in the mineral waters of Bruckenau and in a river of Brazil. In summing up the principles of the manufacture he shows that all saccharine plant juices are suitable for the production of vinegar, and that specially prepared mixtures of water and alcohol must contain small proportions of organic substances and of salts.

The optimum temperature for the manufacture of vinegar is 86° F. *within* the generator, though the air outside must be kept cool. That the best modern processes are still defective is shown by the fact that the average loss due to evaporation, excessive oxidation, &c., is from 15 to 20 per cent, and that in some cases it reaches 30 per cent.

The best method of operation requires to be modified to suit the nature of the materials employed. Potato spirit, it is remarked, being contaminated with fusel, yields a vinegar of unpleasant smell. Beer vinegars are, of course, spoiled by the presence of the hop, the bitter principle of which is not eliminated. It is even questionable whether the comparatively dull flat taste of malt-vinegars is not mainly due to the presence of dextrin and other extractive matters opposing etherification.

In the vinegar manufacture the author states that irregularities and disturbed actions are more frequent than in any other industry based upon fermentation. Among the chief kinds of mischief are the "sliming" of the generators, especially frequent if too much carbohydrate is present. Vinegar-eels, vinegar-mites, and vinegar-flies are also at times very troublesome, and the most scrupulous cleanliness is required to prevent their

multiplication. Sulphurous acid kills the eels, but if used in large quantities it is also fatal to the ferment, in which case the generators have to be carefully washed out and charged again.

Fruit vinegars, *e.g.*, the American cider vinegar, possess a delicious flavour, but they frequently do not keep well. We believe such vinegars are not made in England upon a commercial scale, though they might probably furnish a remunerative means of utilising apples and small fruits when the markets are glutted.

The vinegar from sugar-beets is quite unfit for use on account of its bad odour and flavour.

Instructions are given for preparing vinegars and vinous fluids from a variety of fruits.

A succeeding chapter enters into the manufacture of "vinegar specialities," *i.e.*, toilet vinegars, table vinegars, such as those of aniseed, anchovies, tarragon (simple and compound), herb, pineapple, celery, and lovage vinegars, &c.

The ravages of the phylloxera have greatly interfered with the production of wine vinegars. It appears that fine wine vinegars can be obtained only by the slow process, the quick process yielding a product lacking bouquet.

The preparation of wine vinegar from lees is an important branch which might be profitably extended.

Next follow a variety of analytical procedures useful to vinegar manufacturers, such as the determination of sugar in the mashes or extracts, the estimation of the alcohol by various methods, and that of acetic acid. An important matter is the detection of extraneous acids and of metals in vinegars.

There are also instructions for ascertaining the derivation of a vinegar. Grain (beer and malt) vinegars are recognised by the presence of phosphoric acid, and by the residue of carbonised dextrin which they leave on evaporation. Wine vinegars are characterised by the presence of potassium bitartrate, which, however, is sometimes fraudulently added to spurious vinegars.

Passing over the manufacture of wood-vinegar, the preparation of commercial acetic acid, and of the acetates, we come to the manufacture of ciders and fruit wines. Very useful tables are here given of the proportions of sugar, of free acid, and of the proportion between acid, sugar, pectine, gum, &c., contained in various fruits and their juices. We may here suggest the propriety of confining the name grape-sugar to that naturally present in fruits, whilst glucose should denote the artificial product.

Various compound ciders are here mentioned, some of which might be usefully made in England.

The author speaks, curiously enough, of "pear cider," a liquor which in this country is always called "perry."

In speaking of "rhubarb wine" Mr. Brannt does not mention that it can scarcely be free from oxalic acid.

The preservation of fruit with a variety of accessory processes is next considered. Here we find it stated that both plums and cherries are comparatively dear in the United States, in part, perhaps, from the climate and in part from the ravages of insect enemies. As regards the solder used in making up tins of fruit, it should be mentioned that zinc chloride, a most formidable poison, is used by the plumbers in place of resin, as being cheaper and easier of application.

This work deserves to be warmly recommended, not merely to vinegar manufacturers, but also to farmers, fruit-growers, pickle-makers, and all persons concerned in the utilisation of vegetable products.

A Handbook of Quantitative Analysis. By JOHN MILLS (of the Normal School of Science) and BARKER NORTH (Associate of the Normal School of Science). London: Chapman and Hall, Limited.

WITH two reservations, this work merits general approval. The first of these excepted points is that it is openly and avowedly examinational in its aims, being written "to

meet the requirements of students entering for" certain examinations duly specified. The second point is that there already exist works conveying instructions for the performance of all the operations here given. There are directions for organic analysis, the nitrogen being determined by the processes of Dumas and of Will and Varentrap. The Kjeldahl process is not mentioned. Gas analysis very properly forms the subject-matter of a chapter. The instructions for water analysis are substantially based upon the Wanklyn and Chapman manual. No reference is made to the estimation of organic nitrogen by the Frankland process, which has been generally supposed to be an article of the faith at South Kensington. Nor is there any notice of the permanganate process, which in its present improved state is not without value. There is a brief account of the determination of the precious metals by cupellation.

The chapter allotted to the analysis of commercial products makes mention only of bleaching-powder, porcelain, gunpowder, white-lead, sugar, soap, and iron in its different forms. We scarcely think that gunpowder or porcelain often come under the hands of the analyst.

Quinine as a Prophylactic or Preventative against Malaria Fever.

THIS pamphlet, which is compiled by Messrs. C. F. Boehringer and Sons, of Waldhof, near Mannheim, does not bear the name of any publisher or printer. The eminent medical authorities recommend that quinine, in combatting malarial fever, should be used in large doses—1 grm. or upwards—and preferably not as sulphate, but as the more soluble hydrochlorate dissolved in dilute alcohol. Sailors arriving at the very unhealthy port of Tandjong Priok in Java received the first dose each 1 grm. of quinine dissolved in gin, repeating the dose on the 8th, 12th, and 16th days, and on the 10th and 14th days $\frac{1}{2}$ grm. Other authorities shorten the interval between the first and the second dose, but all agree that ordinary doses are useless for combatting the malaria of tropical climates. Schweinfuit whilst botanising in the African swamps took $\frac{1}{2}$ grm. three times daily. Stanley took doses of 3 and 3 $\frac{1}{2}$ grms.

CORRESPONDENCE.

THE POSITION OF THE CHEMIST.

To the Editor of the Chemical News.

SIR,—THE CHEMICAL NEWS (vol. lxi., p. 26) contained an advertisement for a "Gas Examiner," to be appointed "in accordance with Sect. 27 of the Metropolitan Gas Act, 1860, at a salary of £25 per annum. The person appointed must provide, at his own expense, a place suitable for gas-testing within the district, but all necessary apparatus for so doing will be provided by the Board."

These terms throw an interesting light on the estimation in which our municipal authorities hold a professional chemist. For the magnificent sum of £25 the grateful recipient is to "provide at his own expense a place suitable for gas-testing," and do the work.

If the latter is aught but a sham it means, say, two hours per day on three hundred days per annum; or six hundred hours' work. If the "suitable place" is obtained for a rent of £5 per annum, then 8d. per hour is the munificent wage of the tester.

Why, sir, even that long-suffering down-trodden creature, the gas-stoker, would have enough of the worm in him to turn at such an offer as this. Did not the docker triumphantly assert his claim to a minimum wage of 2s. for casual employment not exceeding four hours per day? The casual chemist is only to have two hours, however, and be paid only 1s. 4d.

Sir Henry Roscoe, in a recent speech, is reported by *Nature* to have admitted that we "have yet to create a demand for technically instructed persons." True, O King! And yet this has been forgotten, and all our energies are devoted to creating not a demand, but a supply.

What a happy time is in store for the pupils, and still more for the staffs of our various technical schools, now so anxiously pushing their wares on the world's market.—I am, &c.,

R. J. FRISWELL.

Atlas Works, N.E., Jan. 15, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 1, January 6, 1890.

Certain New Fluorescences.—Lecoq de Boisboudran.—The author has obtained certain fluorescences by taking as active matters samaria and the earths $Z\alpha$ and $Z\beta$, and as solid solvents calcined silica and zirconia. He indicates here merely the chief spectral positions.

The Refracting Powers of Simple Salts in Solution.—E. Doumer.—The author's results lead to the following conclusions:—(1) All the salts formed by one and the same acid have the same molecular refractive power when they are formed on one and the same type. (2) The refractive powers of salts belonging to different types are sensibly multiples of a common number. (3) The molecular refringent powers of salts are functions of the number of valencies of the metallic element which enters into their composition. These observations lead to the novel notion of *masses optically equivalent*.

Composition of the Rocks employed in the Manufacture of Porcelain in China.—Georges Vogt.—The Chinese minerals are very different in composition from those used for the same purpose in Europe. Their kaolins differ little from those of Europe, but the yeou-ko and the petun-tse differ decidedly from pegmatite by containing white mica (muscovite). This mineral is met with in Chinese porcelain slip to an extent often bordering on 20 per cent.

On Matezite and Matezo-Dambose.—Charles Combes.—A. Girard has extracted from the juice of the caoutchouc of Madagascar a sugar which he called matezite, which, on treatment with hydriodic acid was split up into methyl iodide, and a sugar, matero-dambose, an isomer of the glucoses. The author now finds matezite identical with β -pinite and matezo-dambose identical with β -inosite.

The Carballylates.—E. Guinochet.—The carballylates much resemble the aconitates, but they are distinguished by the following point:—The solutions of the tribasic carballylates are neutral to litmus and phenolphthalein, whilst the corresponding aconitates are alkaline.

Moniteur Scientifique, Quesneville.
December, 1889.

Notice of the late Dr. Gustave Augustin Quesneville.—The late Dr. G. A. Quesneville was born at Paris, January 1, 1810. His father, J. B. J. Quesneville, had succeeded Vauquelin in the manufactory of chemical products founded by that eminent *savant*. In 1823 Liebig executed here his first great research, the investigation of the fulminates. Shortly before the revolution of 1830 Quesneville had been appointed a professor at the courses instituted at the Tuileries. He was also for some time

assistant to Chevreul. In 1834 he graduated as Doctor of Medicine, and practised for two years as a physician. He then returned to chemistry and occupied himself with the manufacture of chemical products. As far back as 1826, at the age of sixteen years, Quesneville published his first discovery, a method for the separation of iron from manganese by precipitation with potassium arseniate. Among his subsequent results were the preparation of barium dioxide, a method for obtaining cobalt oxide in a state of approximate purity, a process for the production of volatile chlorides, and a method for obtaining uranium oxide without the use of ammonium carbonate. In investigating the composition of urinary calculi he discovered that factitious specimens had been made up of calcium carbonate and phosphate cemented together with bread paste! His studies on hydrogen peroxide seem to have been generally forgotten and re-discovered. His pharmaceutical improvements and discoveries were both numerous and important. Dr. Quesneville had, above all things, an independent spirit; not anxious to please the scientific powers of the day, whose occasional acts of injustice he was always ready to expose. On the other hand, he loved to encourage discoverers who combatted on behalf of some novel truth. Thus, he participated in that revolution in organic chemistry of which Gerhardt and Laurent were the promoters. We have the pleasure of announcing that the *Moniteur Scientifique* will be continued by M. Georges Quesneville, the son of the late editor.

Notes on Colouring-Matters at the Exhibition of 1889.—It is remarked that this industry has made less progress since 1878 than it has done in the eleven years previous. The results comprise the application of more scientific methods to the older manufactures, and the addition of a great number of representatives to series already known. The display in this department would have been more extensive had it not been for the entire abstention of Germany and—save for a single firm—that of Switzerland.

Study on Morphine.—L. Knorr.—The author concludes that morphia is a tertiary base containing a methyl united to nitrogen. In methocodeine there are two methyls combined with nitrogen. In consequence we may explain the transformation of codeine into methocodeine by the rupture of a closed chain, in which the nitrogen of the morphine is included. This hypothesis agrees with the fact that under the same circumstances we may add to methocodeine two atoms of bromine more than to codeine. Morphine contains a phenanthrenic nucleus which, in reason of the high proportion of carbon in morphine, may be reduced in part. Metho-codeine treated with acetic anhydride is decomposed into β -oxyethyl dimethylamine and into a phenanthrenic derivative. Morphine contains a phenolic hydroxyl, an alcoholic hydroxyl, and a third indifferent oxygen, which probably serves as connecting link. The alcoholic hydroxyl of morphia retains its character in metho-codeine, and only appears as phenolic hydroxyl after the decomposition of the methocodeine into acetyl-methyl dioxphenanthrene.

Syntheses in the Series of the Oxazines.—L. Knorr.—The author describes the synthesis of methylmorpholine, of phenylmorpholine, of phenomorpholine, and of *u*-methylphenomorpholine.

Purification of Arseniferous Sulphuric Acid.—Professor Kupferschläger.—The author dilutes the acid with an equal weight of distilled water, passes through it a current of washed sulphurous acid, and then, in two repetitions, a current of washed sulphuretted hydrogen. The purified acid is then rectified.

New Theory of the Double Elliptical Refraction of Quartz.—Dr. G. Quesneville.—A crystallographical paper, incapable of useful abstraction.

Industrial Society of Mulhouse.—Session of Oct. 9, 1889.—M. Matthieu Plessy sends in a note on a new re-

agent for cane-sugar, grape-sugar, and pyrogallic acid. It is a solution of lead paranitrate, NO_4PbH , in an excess of melted ammonium nitrate.

Session of Nov. 13, 1889.—M. Cordillot describes a process of continuous steaming practised since 1874. The apparatus is composed of a large iron chamber in which there are six wagons in which the pieces are successively heaped up.

M. Bœringer is sent in a paper on improvements in printing by hand. The use of gum tragacanth enables the deepest colours to be printed over the lightest.

Aniline Black and the Grawitz Processes.—Opinions on the validity of Grawitz patents.

Patents concerning Colouring-Matters.—A series of specifications of chemical patents.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. iv., No. 47.

Extraction of Glycerin in Soap Works.—This paper is taken from English sources, and gives an account of a process used by Matison and Co., of Widnes.

MISCELLANEOUS.

Central Institution, Exhibition Road.—Mr. Holland Crompton will deliver a special Course of Ten Lectures (commencing Jan. 24, at 4.30 p.m.) on the Theory of Electrolysis and the Nature of Chemical Change in Solution, in which the recent development of the Clausius dissociation hypothesis of electrolysis will be fully discussed. Prof. Armstrong will deliver a special Course of Ten Lectures (commencing Jan. 27, at 4.30 p.m.) on Methods of Analysis as Applied to the Determination of the Constitution of Carbon Compounds, dealing with the more important and typical compounds, including alkaloids, carbohydrates, oils, and fats.

MEETINGS FOR THE WEEK.

- MONDAY, 27th.—Medical, 8.30.
Society of Arts, 8. "The Electro-magnet," by Silvanus P. Thompson, D.Sc., M.I.E.E.
- TUESDAY, 28th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
Institute of Civil Engineers, 8.
Royal Medical and Chirurgical, 8.30.
Society of Arts, 8. "The Relation of the Fine Arts to the Applied Arts," by Edward C. Robins, F.S.A.
- WEDNESDAY, 29th.—Society of Arts, 8. "The Utilisation of Blast-furnace Slag," by Gilbert Redgrave.
- THURSDAY, 30th.—Royal, 4.30.
Royal Institution, 3. "Sculpture in Relation to the Age," by Edwin Roscoe Mullins.
- FRIDAY, 31st.—Royal Institution, 9. "Smokeless Explosives," by Sir Frederick Abel, C.B., D.C.L., D.Sc., F.R.S.
- SATURDAY, Feb. 1st.—Royal Institution, 3. "The Natural History of the Horse, and of its Extinct and Existing Allies," by Prof. Flower, F.R.S., &c.

CITY AND GUILDS OF LONDON INSTITUTE
FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.
CENTRAL INSTITUTION, EXHIBITION ROAD, S.W.

A Course of Ten Lectures on Methods of Analysis as Applied to the Constitution of Carbon Compounds will be delivered by Prof. H. E. ARMSTRONG, F.R.S., on Mondays, at 4.30 p.m., commencing January 27.

Mr. HOLLAND CROMPTON will deliver a Course of Ten Lectures on The Theory of Electrolysis and the Nature of Chemical Change in Solution on Fridays at 4.30 p.m., commencing January 24. Fee for each Course, 10s.

Particulars of and tickets for the Courses may be obtained on application to the Dean, Central Institution, Exhibition Road, S.W.

JOHN WATNEY,
WALTER S. PRIDEAUX. } Hon. Secs.

A. I.C., 22, speaking fluently French, German, and Danish, Assistant in Mineral and Agricultural Laboratory of Prof. Hof. R. Fresenius, Wiesbaden, desires situation in Manure or other Works; home or abroad.—Address E Woodward, 57, Rheinstrasse, Wiesbaden.

A Gentleman (age 40) holding Advanced Science and Art Certificates in the following subjects wishes for appointment:—Mathematics (Second Stage); Sound, Light, and Heat; Electricity and Magnetism; Inorganic Chemistry; Organic Chemistry (Hon.); Geology; Human Physiology; Botany; Biology; Metallurgy; Steam and Applied Mechanics; National Medallist in Physiology; Trained in Chemistry, Physics, and Biology at Normal School of Science, London. Good Demonstrator and Lecturer.—Address, "Science," CHEMICAL NEWS Office, Boy Court, Ludgate Hill London, E.C.

A large Soda Manufactory in Germany, working after the Ammonia Process, seeks a thoroughly experienced and self-dependent Manager who is well acquainted with the process, having worked already in a self-dependent position in similar manufactories, and must be able to give sufficient guarantees for a lucrative working.—Apply, stating salary expected and enclosing testimonials or references, to H 5384, care of Haasenstein and Vogler, A. G., Frankfort-on-the-Main.

TO MANUFACTURING CHEMISTS AND OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 2000 tons of MANGANATE OF SODA, to be delivered at the rate of not less than 100 nor more than 200 tons per week from April 1, 1890.

Persons tendering will be required to declare in their Tender that they pay such rates of wages and observe such hours of labour as are generally accepted as fair in the trade.

The Specification, Form of Tender, and other particulars may be obtained on application to the Chemist of the Council, at the Office, Spring Gardens, until Monday, February 17, 1890. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., must be endorsed "Tender for Manganate," and be sent in not later than 10 o'clock on Tuesday morning, the 18th of February next.

The Council does not bind itself to accept the lowest or any Tender.

Spring Gardens, S.W.,
January 21, 1890.

H. DE LA HOOKE,
Clerk of the Council.

The Valuable and Complete CHEMICAL MANURE WORKS, known as The Silvertown Chemical Works, Silvertown, for SALE.—The premises have been constructed at considerable cost for the purpose of a very large trade, and the machinery is complete in every respect for the immediate carrying on of the business; there is a wharf with a frontage of about 100 feet to the River Thames, so that all goods can be loaded and unloaded direct from the wharf, also a railway siding connecting the works with the various railway systems of the United Kingdom; the premises comprise spacious manufacturing, storage, and packing works, pyrites burners, acid chambers capable of producing 5000 tons chamber acid per annum, office, laboratory, and caretaker's house; the plant is capable of producing 20,000 tons of manure per annum, which could, at a small outlay, be greatly increased; all parts of works are connected by tram lines.—For particulars apply to Walter W. Feast, Esq., Chartered Accountant, St. George's House, Eastcheap, London, E.C.; or to Messrs. Hatchett, Jones, and Co., Solicitors, 47, Mark Lane, London, E.C.

ALKALI MAKERS' PLANT AND MACHINERY.

FOR SALE, by Private Treaty, at the Jarrow Chemical Company's Tyne Dock Works, South Shields, a large quantity of ACID, ALKALI, and CAUSTIC SODA PLANT, in good condition, which may be viewed at any time.—Apply to the Jarrow Chemical Co., Limited, Tyne Dock, South Shields.

Magnesit, Raw, 2s. 6d. per 2 cwt.; in powder, 4s.; also burnt and slightly burnt Magnesia, Silver-polish, Mineral Pumice-stone of every kind, Magnesia Powder, Tripoli of every kind, Polishing Chalk, Emery Powder, Polishing Powder, Spath of every kind, Slate Powder of every kind, Asbestos Slate Powder, Magnesia Marl, cheap from BRÜCK'S GRUBEN COMPTOIR, Berlin, S.O.

Water-Glass, or Soluble Silicates of Soda and Potash, in large or small quantities, and either solid or in solution, at ROBERT RUMNEY'S, Ardwick Chemical Works, Manchester

FOR SALE.—THE CHEMICAL GAZETTE. Complete Set (unbound and uncut), 17 volumes; from November, 1842, to December, 1859.—Address, "Publisher," CHEMICAL NEWS Office, Boy Court, Ludgate Hill London, E.C.

THE CHEMICAL NEWS.

VOL. LXI. No. 1575

ON THE GENESIS OF ELEMENTS.

By H. M. VERNON.

SINCE the time when Prout first formulated his hypothesis of the genesis of the elements from the primordial atom, there has always been a feeling in the minds of chemists that this hypothesis may possibly in some future time be verified experimentally, at least to a certain degree. This feeling has been strengthened during the last few years by the discoveries of Crookes and other chemists, of what have been termed the meta-elements. Crookes, starting from a specimen of mineral supposed to contain only one or two rare earths, has succeeded by a laborious process of fractionation in resolving one of these earths, supposed to be the oxide of a single element, into several other earths, all of which have properties almost exactly similar, and only capable of being distinguished in some cases by the difference in their colours or by the difference of a single line in their spectra. These earths are the oxides of elements of scarcely perceptibly different atomic weights, for all of which it would not seem possible to provide a place in the table of elements arranged according to Mendeleeff's Periodic Law.

Arguing from these discoveries, Crookes asks whether it may not be possible by suitable methods of fractionation to separate many, if not all, of the rest of the so-called elements into a number of other elements almost exactly similar in properties and in atomic weights, and thus to obtain an almost infinite series of elements, the properties of which gradually change in regular order as they pass through the cycles of the series of elements arranged according to the periodic law.

Many almost insurmountable difficulties, which it will be unnecessary to enumerate, have been brought against this chain of reasoning by various chemists. This hypothesis, being for the present, at least, therefore considered unacceptable, we come to the question as to whether there is no other hypothesis that has the same end in view which is capable of being formulated, such that may appeal more readily to the minds of chemists. It is with this object in view that these few ideas have been brought forward.

At the beginning of the universe we may consider it very probable that there existed only the primordial atom, which, as in the course of ages, became gradually cooled down, united amongst itself to form the complete cycle of elements as known to us at the present day. Those elements most stable as regards heat would first be formed as this process of cooling went on, while those least stable with regard to heat would be formed last, all elements but the first being formed by the addition of other primordial atoms to the elements already formed.

If this be the case we may conversely regard it possible to disintegrate some at least of the so-called elements into bodies more simple than themselves, that is, into bodies more stable as regards heat, by heating them to a sufficiently high temperature. If, indeed, a high enough temperature could be obtained, it would be possible to disintegrate all the elements known to us into not only simpler bodies than themselves, but into the primordial atom from which all the elements were originally formed.

The question now comes whether it will be possible to obtain the extremely high temperature necessary for this purpose. The reply is that, as far as can be seen, there is no possibility of ever reaching a temperature high enough to decompose an element into its primordial atoms; but that it may be possible to reach a temperature high

enough at least to decompose some of the elements least stable as regards heat into bodies more stable with regard to heat than themselves.

The reason for this reply is that the only practicable means we have for obtaining high degrees of temperature are (1) utilising the heat evolved by the combination of bodies with each other and (2) by means of electricity.

It is obvious that only a certain degree of temperature can be obtained by the first method, as the compounds formed by the combination would be incapable of existing above this temperature, and therefore no combination would take place, as there would be no affinity between the bodies.

In the case of electricity also, as far as may be judged, it is only possible to obtain a certain degree of temperature. We may therefore ask whether it is not possible by any other means than direct experiment to ascertain whether so-called elements cannot be decomposed into bodies simpler than themselves by the action of heat.

By means of the spectroscope it has been found possible to ascertain the presence of many of the elements in the sun, and to a certain extent those present in the fixed stars.

The temperature of the sun is admittedly very high. Is it not possible that it is high enough to have caused some of our least stable elements to have been disintegrated into more simple bodies?

Of the elements known to us, about half have up to the present been shown by Thalén, Lockyer, and others to exist with more or less probability in the sun. The proofs of the presence of some of these elements depend upon the coincidence of only a very few lines of the sun's spectrum with those of their spectra as known to us; their presence may, however, be provisionally accepted.

If these elements be arranged in order of their atomic weights according to Mendeleeff's Periodic Law, the places of the elements whose presence in the sun has not been proved being left as blanks, we obtain the following table:—

Groups.	1.	2.	3.	4.	5.	6.	7.	8.
1.	H							
2.	Li	Be						
3.	Na	Mg	Al					
4.	K	Ca	—	Ti	V	Cr	Mn	Fe Co Ni
5.	Cu	Zn	—	—	—	—	—	—
6.	Rb	Sr	Y	—	—	Mo	—	Ru Pd
7.	Ag	Cd	In	Sn	—	—	—	—
8.	Cs	Ba	Ce	La	—	—	—	—
9.	—	—	Er	—	—	—	—	Ir Pt
10.	—	—	—	Pb	Bi	—	—	—
11.	—	—	—	—	—	U	—	—

From this table we see that almost all the most positive elements are present, but that as the elements become more and more negative, fewer and fewer appear capable of existing in the sun's photosphere. Thus no less than eight of the elements occurring in the first group and seven of those in the second group have been shown to be present. When, however, we come to the third group, in which the elements are of a more negative character, their instability with regard to heat becomes more marked, only five of them being found to be present. Only four of the elements of the fourth group are found to be present, and of the fifth group only two; of the sixth group three elements apparently are present, while of the seventh group manganese is the solitary representative. The eighth or extra group of the table is very well represented, probably seven, if not more, of the elements occurring in this group being present. Of these elements, too, iron and nickel occur in the sun in quantities as great as almost any other element. The behaviour of this group is therefore abnormal in very much the same way as it is in the arrangement of elements according to the periodic law.

We therefore find with striking regularity that as we

proceed from the left hand group of positive elements to the right hand group of negative elements in Mendeleeff's table, the number of elements of each group found to exist in the sun's photosphere decreases proportionately to the increase of negative properties of the elements of each group taken as a whole.

If, now, it be granted that the majority, at any rate, of the other known elements are not present because they are decomposed by the high temperature of the sun into bodies simpler (that is, more stable with regard to heat) than themselves, we find, as a rule of general applicability, "that as we pass from positive to negative elements the stability of the elements with regard to heat decreases proportionately as their negativity increases."

We see from the above table that it is not merely that non-metallic elements taken as a whole are less stable with regard to heat than metals, but that elements, whether metals or non-metals, are stable with regard to heat or the reverse according to their positivity.

The fact that no non-metallic elements appear in the table, unless we except hydrogen, would show that these bodies taken as a whole are much less stable with regard to heat than the metals. This is quite borne out by what is otherwise known of their behaviour when subjected to moderately high temperatures. Thus almost all the non-metallic elements which have been volatilised have been found to possess simpler molecules at higher than at lower temperatures. The molecule of sulphur at 450° C. contains six atoms, while at 800° C. it contains only two. At a still higher temperature it would probably contain only one.

Phosphorus and arsenic at a red heat contain four atoms in their molecules, while at a white heat they contain only two. Up to moderately high temperatures the molecules of bromine and iodine contain two atoms, but at 1800° the molecule of bromine and at 1500° the molecule of iodine contain only one atom. At a still higher temperature chlorine would probably act in a similar manner. Even in the case of the non-metals carbon, boron, and silicon, which have not been volatilised, it has been shown by Weber with a considerable amount of certainty that the constitution of these elements is much more complex at lower than at higher temperatures. This follows from the fact of their specific heats being very much greater at higher than at lower temperatures; thus the specific heat of the diamond at 985° C. is about seven times greater than it is at -50°, so probably the molecule of diamond at a temperature slightly below this contains eight times as many atoms as the molecule at 985° C. Very much the same thing will hold in the case of boron and silicon. If, then, as is shown by these facts, the molecules of the non-metallic elements are more simple at higher than at lower temperatures, it would seem very probable that at higher temperatures still their constitution would become still more simple, that is, they would be split up into other bodies, which bodies might very possibly be some of the more stable elements at present known to us.

When we examine the constitution of the gaseous molecules of some of the metals we find their behaviour to be totally different from that of the non-metals. The molecules of all the metallic elements at present examined are found to contain one atom and one atom only, whatever be the temperature to which they are subjected. The metals which have been examined so far are sodium, potassium, zinc, cadmium, and mercury. All these elements, except mercury, have been found to exist in the sun, and it has not been conclusively proved that this element is not present.

If the vapour densities of other metals were taken it would very probably be found that at all temperatures the molecules of the more positive metals contained only one atom, but that as they began to develop negative properties their molecules would be more complex at lower than at higher temperatures, thus indicating that at higher temperatures still, such as that of the sun, they

would probably dissociate into still more simple bodies, that is, that they would cease to exist in the form of the original elements, but would be changed to some other bodies more stable with regard to heat.

At a temperature still higher than that of the sun, it would be reasonable to suppose that a still smaller number of elements would be capable of existing as such. As a proof of this supposition, it has been shown by Huggins and others that the constitution of the white, and therefore presumably hottest, stars is exceedingly simple, their spectra containing only a few lines, and therefore showing the presence of only a very few different kinds of matter.

From the above result may we not conclude that there is a possibility, if not a likelihood, of our arriving at some knowledge of the genesis of elements by endeavouring more exactly to ascertain the temperature of the sun and the elements forming it, and also by endeavouring to split up some of the least stable of the elements, as known to us, by the action of heat. If it were possible to ascertain the variations in the temperature of the sun at different points of its photosphere and chromosphere (and it is very probable that it varies enormously), and also the composition of the vapours at these points, it might be possible to arrive at a rough conclusion as to the elements which were capable of existing as such at various temperatures and those which were not.

ESTIMATION OF FATTY ACIDS IN ALIZARIN OIL.

By FRED. GUTHRIE.

ABOUT 5 grms. of the oil are weighed out in a small beaker and washed with a little water into a 6 oz. flask, 10 c.c. of normal caustic soda added, and the contents boiled slowly for half an hour. 20 c.c. of normal sulphuric acid are now added, and the flask heated on a water-bath for half an hour or more; the contents of the flask are then transferred to a tared Swedish filter, the flask shaken vigorously several times with boiling water, and the contents each time being added to the filter. The fatty acids are washed with boiling water till free from acid, the filter and fat transferred to a tared platinum capsule and dried at 212° for eight hours or till constant. The advantages of this process are threefold:—

1. The sulpho-fatty acids are decomposed, the sulphuric acid washed away; therefore the fatty acids do not blacken and decompose on drying at 212° F.

2. The fatty acids are practically insoluble in boiling water, and can be washed well from the acid used to liberate them.

3. Any free oil which the alizarin oil may contain will be saponified and weighed as fatty acid.

NOTE.—In exact estimations it is well to dry the small flask in which the fatty acids were liberated, and to wash it out with a little ether into a small beaker, the ether boiled off, and any fat left weighed.

Birchvale Print Works,
Via Stockport, Jan. 21, 1890.

ON COOLED FLAMES.

By Dr. L. C. LEVOIR, Delft, Holland.

WHEN a small semi-globular iron spoon is held with the plane of the orifice nearly vertical to the flame of a Bunsen burner, and a very small quantity of arsenic is in it, then the flame directly appears bluish; even very small quantities of arsenic show that colour.

When Fletcher's compound blowpipe (List No. 160 May, 1889, p. 76), or what is also called a Maugham-

Burner, is used, and air is not admitted, then arsenic gives no colour, and at three feet above the burner no smell is perceived. But as soon as blowing begins a peculiar smell is perceived at three feet above the flame, which shows that unburned hydrocarbons escape from it. Evidently the temperature of the flame is lowered by the excess of cold air. These flames are very sensitive for elements of different volatility.

Arsenic shows its colour before potash or soda.

This experiment and its explanation show that it is not good in coal-gas stoves to cool the flames by pumice or asbestos bundles, as hydrocarbons which might have given heat escape unburned by their cooling influence.

When splinters of wood boiled in water with arsenious acid are held against the tube of a Bunsen burner it is possible to cool their flames to such a degree that neither luminous hydrocarbon flames nor flames coloured by the potash and soda from the ash can be perceived.

In that way I believe that cooled flames may become a fruitful field in qualitative analysis.

SEPARATION OF BARIUM AND STRONTIUM.

By R. FRESENIUS.

FOR the separation of barium and strontium, independently of indirect methods the following processes have been proposed and tried:—

1. Separation depending on the different behaviour of the sulphates in alkaline carbonates.
2. Separation by hydrofluosilicic acid.
3. Separation by chromic acid.

The two former methods have, for a long time, been neglected, or only very imperfectly elaborated; for, although P. Schweitzer ("Catalogue of the University of the State of Michigan," 1876, Part 1) undertook very thorough studies on the determination of barium as sulphate, carbonate, chromate, and oxalate, as also its conversion into silicofluoride, as well as on the determination of strontium as sulphate, the research does not seem to have extended to the separation of the bases.

The separation of the bases by means of chromic acid has certainly been discussed in a series of memoirs, but the results of experiments vary greatly, so that the method is recommended by many as good, but rejected by others as worthless. Hence it seems advisable to submit the question to a new critical scrutiny.

1. Separation founded on the Different Behaviour of Barium and Strontium Sulphates with Alkaline Carbonates.

H. Rose founded a process for the separation of both bases upon the fact (ascertained by himself) that strontium sulphate, even at common temperatures, is gradually but completely converted into strontium carbonate by a solution of ammonium carbonate, whilst barium sulphate, on similar treatment, remains unaltered. If the conversion of strontium sulphate is to be effected rapidly, Rose recommends that the sulphates should be boiled with a solution of potassium carbonate to which a third, or rather more, of potassium sulphate has been added, boiling for about ten minutes.

Rose gives the preference to this method of separation.

To this process P. Schweitzer objects, saying that barium sulphate, though when existing alone it is not affected by ammonium carbonate, is converted into barium carbonate if it co-exists with strontium sulphate in large quantity. On the other hand, strontium sulphate, if existing alone, is readily converted by ammonium carbonate, but undergoes no change if it is mixed with much barium sulphate.

These communications by Schweitzer are in direct contradiction with the statements of H. Rose.

A number of experiments showed that neither an excess

of solution of ammonium carbonate, nor a prolongation of the time of action, nor an alteration of the degree of concentration, led to satisfactory results. All the experiments confirmed the view of Schweitzer that barium and strontium sulphates, when mixed, behave quite differently from what would be assumed from the behaviour of the separate sulphates with ammonium carbonate. If barium sulphate predominates strontium sulphate escapes decomposition, and if strontium sulphate exists in excess barium sulphate is converted into carbonate. Both reactions occur more or less simultaneously, and sometimes the errors arising may happen to compensate each other.

Experiments were also made on the application of a mixture of potassium carbonate and sulphate. Here also satisfactory results could not be obtained by any modification of the process. Thus a trustworthy separation of barium and strontium cannot be effected in this manner.

—*Zeitschrift für Analytische Chemie.*

NOTE ON THE PURIFICATION OF ALCOHOL FOR LABORATORY USES.

By E. WALLER, Ph.D.

COMPARATIVELY recently several papers have appeared on the subject of the reactions of potassium permanganate with alcohols, and the impurities which they may contain.*

In preparing alcoholic solutions of caustic alkalies, and also of silver nitrate (for fat tests, &c.), I have been annoyed, as have other chemists, by the unsatisfactory character of the solutions obtained in consequence of the presence of impurities in the alcohol bought for laboratory use. I find also that most alcohol of 93 per cent, when kept in tin cans, slowly reacts on the tin, giving, after a while, a cloud of SnO_2 , which is too fine to filter out, and renders purification by distillation necessary. In the light of the results obtained by the writers above alluded to, I have adopted the following method for the purification of my alcohol, on which I ask the criticism of the members of the Society:—

A convenient amount of the alcohol to be purified is shaken with pulverised potassium permanganate until it assumes a decided colour. It is then allowed to stand for some hours, until the permanganate has been decomposed and brown manganese oxide is deposited. A pinch of pulverised calcium carbonate is then added, and the alcohol distilled at the rate of about 50 c.c. in twenty minutes from a flask provided with a Wurz tube or one of the Lebel-Heninger pattern. The distillate is tested frequently until about 10 c.c. thereof, when boiled with 1 c.c. of strong (syrupy) solution of caustic soda or potash, gives no perceptible yellow colouration on standing for twenty minutes or half an hour. What distils over after that time is preserved for use.

The first distillates may be added to the small amount remaining in the distilling flask (which should not be driven down to complete dryness), and a fresh portion of purified alcohol recovered.

The rationale of the proceeding appears to be that the permanganate oxidises and destroys chiefly the fusel oil, furfurol, and other compounds of that nature, the acids resulting from the reaction are neutralised by the calcium carbonate added before distillation, and by distilling slowly the aldehyd, at least, is concentrated in the first portions of the distillate. Distillation of alcohol containing caustic potash or soda seemed to cause a constant formation of aldehyd. The alcohol thus purified is perfectly neutral, and gives most satisfactory results when

* Habermann, *Fres. Ztschr. Anal. Chem.*, xxvii., 663. Roese, *Ib.*, xxviii., 355. Cazeneuve, *Bull. Soc. Chim. (Paris)*, [3] i., 700. See also *Dingl. Polyt. Jour.*, cclxxiii., 374.

used as a solvent for caustic alkalis or silver nitrate, the solutions remaining as colourless as distilled water, even after boiling and standing indefinitely, if properly protected from dust and other external influences.—*Fourn. Am. Chem. Soc.*

THE TECHNICAL ANALYSIS OF WOLFRAMITE.

By B. SETLIK.

THE author pulverises the mineral finely and dries it at 110°. For the analysis from 3 to 5 grms. of the sample are melted for about two hours in a platinum crucible with from three to four times the weight of sodium carbonate. The melted mass along with the crucible is then boiled in water until nothing remains adhering to the sides. The crucible is then rinsed with water, the solution is filtered, and the residue is washed until the waters are no longer rendered turbid by hydrochloric acid. The alkaline solution, while hot, is poured into an excess of hydrochloric acid, and the whole is then boiled for half an hour in order that the precipitate may be the more readily decanted. This deposit, consisting chiefly of tungstic acid (along with which there may occur stannic, silicic, and molybdic acids), is washed, dried, ignited, and weighed. When igniting the precipitate must first be removed and incinerated with ammonium nitrate.

The ignited residue is treated with 4 c.c. hydrofluoric acid in an air-bath, evaporated to dryness, and again ignited. This removes the silica, which is almost always present. If the wolframite contains no tin, the weight of the precipitate, when freed from silica, shows the proportion of WO_3 . If tin is present it is best determined as follows, calculated as SnO_2 , and deducted from the weight of the mixture $WO_3 + SnO_2$.

The mixture of the two acids is fused for half an hour with potassium cyanide, the melt is dissolved in water, the residue of metallic tin is filtered off, dissolved in ferric sulphate, and titrated with permanganate. If the manganese and iron are to be determined, the residue of the soda melt is dissolved in hydrochloric acid and the solution is divided into two equal parts; the one is reduced with zinc and titrated with permanganate to give the quantity of iron, and the other part is precipitated with sodium carbonate and oxidised with chloride of lime. The precipitate is decanted, filtered, washed, and, together with the filtrate, dissolved in ferrous sulphate of known strength, when the excess of ferrous sulphate is titrated back.

The tungstic acid in wolframite generally ranges between 60 and 80 per cent, and that of manganese between 10 and 20. The tungstic acid in scheelite may be determined in the same manner.—*Chemiker Zeitung*.

THE ESTIMATION OF MINUTE QUANTITIES OF GOLD.*

By Dr. GEORGE TATE, F.I.C., F.C.S.,
Principal at the College of Chemistry, Liverpool.

(Continued from p. 46).

The Parting and Fusion of the Gold into a Bead.—In the estimation of minute quantities of gold, with which this paper only deals, remove the silver-gold alloy from the cupel and place it in a small clean porcelain crucible; add one, two, or more drops of pure nitric acid (diluted with half its bulk of distilled water), according to the amount of alloy, and gently heat upon wire gauze by means of a small flame until all action appears to have

ceased. The Bunsen burner or spirit lamp should be held in the hand, so that when violent ebullition commences the heat may be quickly withdrawn.

When the silver is in appreciable excess of the gold ($2\frac{1}{2}$ to 1) the former metal dissolves, leaving the gold as one black spongy mass, or as a number of particles. In the latter case the particles may be made to cohere by slightly turning the crucible between the fingers and causing them to touch. About half fill the crucible with distilled water, allow the gold particles to settle, and then decant off the fluid by pouring against the finger used as a decanting rod. The contents of the crucible should be carefully watched during this decantation, so that no gold particles are allowed to escape. Fresh water is then added, and the liquid again decanted. If the silver has been appreciable in amount, the washing may be repeated a second or third time.

The crucible, and with it the gold, is dried on an iron plate or wire gauze, kept warm by a small flame. If a strong heat is applied the metal diminishes in bulk, acquiring the yellow colour of gold, and cannot then be so readily removed. Cut a small piece of lead (as free as possible from silver, and weighing about half a grain) with a smooth flat surface. Hold the lead upon the point of a penknife, and press the bright surface upon the particles of gold; the latter generally firmly adheres to the lead. Transfer the lead, and with it the gold, carefully to a small bone-ash cupel. The gold will then be on the under surface of the metal and protected from loss during the next operation of cupellation.

This cupellation is performed in the manner described for the preparation of standard prills, or by placing the cupel containing the metal in the muffle of an ordinary muffle furnace, or in a miniature furnace that may be constructed for the purpose. The prill of gold left after cupellation should have a bright golden colour and rounded form. If not round it can be again picked up on a piece of lead, and again cupellated. The measurement and estimation of the weight of the prill is performed in the way previously described.

The cupels that are employed by myself are made from very fine prepared bone-ash, and are about $\frac{1}{2}$ in. in height and $\frac{3}{8}$ in. wide. The mould was fashioned from an old file handle from which the brass ring or ferrule of the above dimensions was removed; on to the round end of the wooden handle was fixed a round-headed brass nail such as are used for ornamental purposes; the end of the handle from which the ring had been removed was slightly lessened in size so that it readily slipped into the ring. To prepare a cupel, stiffen the bone-ash with water, press some into the ring-mould, fashion a cup-shaped depression with the rounded end of the handle, and then force out the moulded ash with the other end. Keep the cupels for some time in a warm place, and then heat them for a few minutes in the muffle-furnace. If the bone-ash has been originally fine, such cupels are fairly strong, freely absorb fused litharge, and are even, when viewed under the microscope, smooth in texture and much superior (for cupellations in miniature) to the ordinary cupels employed for assaying, since among the irregularities of these latter, minute gold prills are very often lost. Moulds of various sizes can be made in the above way; the moulds also serve for making miniature clay scorifiers, and by a little alteration of the moulding rod, for clay crucibles suitable for miniature assays.

A miniature muffle-furnace may be constructed out of two plumbago crucibles, 4 to 5 inches high, to serve as the furnace body, and a short length of porcelain or fire-clay tube of 1 to $1\frac{1}{2}$ inch bore to serve as a muffle. By means of a penknife, cut the bottoms from the two crucibles. One crucible is supported mouth upwards in the ring of a retort stand, and upon the mouth (in semi-circular depressions that have been cut with a knife) is placed the porcelain or clay tube; the tube is then covered with the other crucible, cut in the lip in the same manner as the under one. The furnace as thus constructed

* A Paper read before the Liverpool Polytechnic Society, November 1889.

is open at the top and bottom, and tapers down and up from the muffle. The muffle is heated by a Fletcher or other convenient blowpipe from the lower orifice, and with a good blast can be brought to the temperature necessary for cupellation in two or three minutes. Doors for the two ends of the tube may be constructed out of the crucible bottoms. In place of the tube, a small sized triangular crucible, in the bottom of which a hole is drilled, will serve as a muffle.

When the gold obtained by parting appears to be less than the thousandth of a grain, it is generally advisable to cupellate with lead (so as to obtain the prill) in a muffle, rather than by the blowpipe, since the cupel is then less liable to crack and no risk is incurred of loss of the gold by its being mechanically carried away by the force of the blast from the blowpipe.

Utility and Accuracy of the Measurement Method.—The following considerations will point out the utility of the application of the microscope to the assaying of gold ores and auriferous metal.

An ore yielding an assay 6 dwts. 12 grains of gold per ton (or 0.001 per cent) is generally an ore that pays for working, yielding a slight margin of profit. Where the assay balance is employed for weighing the gold obtained by assay, at least 500 grains (or 32 grms.) would be required to be assayed so as to estimate the proportion of metal per ton within an error of 1 dwt. Such an ore in this quantity would yield on assay 5 one-thousandths of a grain. The gold from the same, or even one-half of the above quantity of ore, could be estimated with one half of the above possible error by means of the microscope. Upon 10 grains, if they could be trusted as being a representative sample of the rock, yielding an unweighable quantity of gold, a prospector could quickly estimate the proportion of gold within an error of 1 dwt. per ton. In other words, a skilful manipulator of the blowpipe, with the aid of a microscope, could, with comparatively few and simple apparatus, quickly perform rough assays of rock or trace the yield of gold in different parts of a bearing lode, or, by comparative tests, obtain valuable indications of the genuineness, or, otherwise, of auriferous rock when taken from the mine.

By working upon 1000 grains of rock or metal (65 grms.), gold in the proportion of only 2 grains per ton has been obtained and estimated by this method of measurement—the estimate erring presumably only to the extent of 20 per cent; since, the author has found that the one ten-thousandth of a grain (0.00065 m.grm.) can be parted even from many thousand times its own weight of silver with a loss of gold less than the percentage above mentioned, and that even the millionth of a grain of the metal still leaves some proportion after parting from silver and collection by lead.

Needless to say, the litharge employed for the assay by fusion should itself be free from any such proportion of gold as might entirely nullify the accuracy of the assay conducted with its aid. A method for the purification of litharge has been previously described.

The commercial litharge employed for my experiments yielded (by assay of 2 lbs.) gold in the proportion of only one-hundredth of a grain per ton.

No doubt the most scientific worker is apt at times to overrate the powers of any method of analysis or estimation that has been found by him to give accurate results.

It is impossible to free the mind from some trace at least of prejudice. I am glad, therefore, to be able to give more or less independent evidence of the extreme degree of accuracy to which gold estimations may be carried by means of the microscope. This opportunity has been afforded me by a sceptical friend—Mr. A. H. Knight—who has had considerable experience in gold assaying, but who, I think, will in future, in necessary cases, weigh his gold with the microscope.

Mr. Knight introduced, by means of an alloy of lead, gold, and silver, known quantities of gold into assay lead,

and supplied me with six portions of alloy, in each of which he required me to estimate the total gold.

In each case I cupelled and parted the gold from the silver, collected and weighed by measurement in the manner described. The following are my returns, side by side with the calculated quantities of gold assumed to be present, on the assumption that Mr. Knight's alloy of gold was uniform throughout* :—

Sample No.	Estimated weight of gold (G.T.). Grain.	Actual quantity of gold (A.H.K.). Grain.	Error in weight.	Error in per cent.
1	0.0052	0.00499	+0.00021	+4
2	0.0100	0.00991	+0.00009	+1
3	0.0026	0.00242	+0.00018	+7
4	0.0012	0.00132	-0.00012	-8
5	0.00066	0.000678	-0.000018	-3
6	0.00028	0.000244	+0.000036	+14

In actual weight, the greatest error is approximately two one-ten-thousandths of a grain of gold (or 0.013 m.g.), the smallest error is approximately two one-hundred-thousandths of a grain (0.0013 m.g.).

(To be continued).

NOTE ON THE MOLECULAR VOLUMES OF AROMATIC COMPOUNDS.

By JŌJI SAKURAI, F.C.S.
Professor of Chemistry, Imperial University.

It is well known that the observed molecular volumes of benzene and its derivatives are less than those calculated with the use of Kopp's constants, which, when applied to saturated fatty compounds, give results fairly agreeing with the observed values.

Other values for carbon and hydrogen to be applied to benzene (and its derivatives?) have therefore been calculated. Lothar Meyer regards the hydrogen of benzene as having the value 5,† instead of 5.5, while the carbon is regarded as having the value 11, as in saturated fatty compounds. Löschmidt assumes that half the carbon atoms in benzene have the value 11, and the remainder the value 14, and that hydrogen has the constant value 3.5.

Each of these sets of values, I consider, has been arbitrarily deduced from the observed specific volume of benzene, and therefore, when calculated back, they naturally give results agreeing with the latter.

Meyer's calculation.	Löschmidt's calculation.	Observed.
$C_6 = 6 \times 11 = 66$	$C_3 = 3 \times 14 = 42$	
$H_6 = 6 \times 5 = 30$	$C_3 = 3 \times 11 = 33$	
	$H_6 = 6 \times 3.5 = 21$	
96	96	95.9

Now, Meyer's and Löschmidt's constants are only applicable to benzene, and cannot be regarded as giving results agreeing with the observed values when applied to the homologues of benzene. For,—

1. If we regard these constants to be applied to the side chains as well, then the calculated values of the homologues of benzene would be less than the observed values; for, while benzene possesses abnormally low molecular volume, its homologues show the constant increase of 22 in the volume for an increment of CH_2 . The hydrogen in the side-chain cannot, therefore, possess the value 5, and still less the value 3.5.

* I have convinced myself that gold-lead alloys containing minute quantities of gold are practically uniform in composition.

† I have not been able to refer to Meyer's original paper. Thorpe (*Journ. Chem. Soc. Trans.*, 1880, 381) states:—"Lothar Meyer makes $H=3$," . . . but this I regard as a misprint for $H=5$. This misprint is reproduced in "Watts's Dict.," III. Suppl., p. 2126, and again in Mr. Kuhara's paper to be referred to later on.

	Observed.		Calculated. C=14 and H, H=3.5.
	Kopp.	Schiff.	
Benzene, C ₆ H ₆	95.8	95.94	96
Toluene, C ₆ H ₅ .CH ₃	—	117.97	114
Xylene, C ₆ H ₄ .(CH ₃) ₂	—	139.74	132
Ethyl benzene, C ₆ H ₅ .C ₂ H ₅	—	138.93	132
N. propyl benzene, C ₆ H ₅ .C ₃ H ₇ ^a	—	161.82	150
P. Ethyl toluene, C ₆ H ₄ .CH ₃ .C ₂ H ₅	—	161.94	150
Mesitylene, C ₆ H ₃ .(CH ₃) ₃	—	162.41	150
Cymene, C ₆ H ₄ .CH ₃ .C ₃ H ₇ ^a	183.5	184.46	168
Naphthalene, C ₁₀ H ₈	149.2	—	147 or 153†

2. If we regard the above constants as applicable to the benzene nucleus only, and the carbon and hydrogen in the side-chain as possessing their normal values, then the use of Meyer's constants means an advantage of 2.5 units over Kopp's values for one atom of hydrogen replaced by CH₃, C₂H₅, &c.; for C₆H₅=91 instead of 93.5. For di-substitution products the advantage is 2.0, for tri-substitution products 1.5, and so on, until we shall find in hexamethyl-benzene, for example, a body possessing normal molecular volume. This, however, does not seem to be the case. The use of Löschmidt's constants for only the benzene nucleus leads to a singular result. For mono-substitution products the advantage over Kopp's constants is 1 unit, as C₆H₅=92.5 instead of 93.5; but for di-substitution products the *disadvantage* is 1 unit, for tri-substitution products the *disadvantage* is 2 units, and so on.

Meyer's and Löschmidt's constants are, therefore, only applicable to benzene, and not to its homologues with any strictness.

I have calculated another value for carbon which, I admit, is as arbitrary as Meyer's or Löschmidt's, but which has the merit of being applicable to aromatic hydrocarbons in general. I regard each of the six atoms of carbon in benzene nucleus as having the value 10.5, while the hydrogen of the nucleus, as well as the carbon and hydrogen of the side-chains, possess their normal values, viz., C=11 and H=5.5.

This consideration is, of course, derived from the observation that the replacement of hydrogen in benzene by CH₃, C₂H₅, &c., causes the same increase in volume as in saturated fatty compounds.

The following comparison will make the above statement clear, the numbers under "observed" being those obtained by R. Schiff.* Kopp's determinations of benzene, cymene, and naphthalene are also added. The ten atoms of carbon, in the last hydrocarbon, constituting the two benzene nuclei are each of them regarded as having the value 10.5.

	Observed.		Calculated. C=10.5 & H. H=5.5.
	Kopp.	Schiff.	
Benzene, C ₆ H ₆	95.8	95.94	96
Toluene, C ₆ H ₅ .CH ₃	—	117.97	118
Xylene, C ₆ H ₄ .(CH ₃) ₂	—	139.74	140
Ethyl benzene, C ₆ H ₅ .C ₂ H ₅	—	138.93	140
N. propyl benzene, C ₆ H ₅ .C ₃ H ₇ ^a	—	161.82	162
P. ethyl toluene, C ₆ H ₄ .CH ₃ .C ₂ H ₅	—	161.94	162
Mesitylene, C ₆ H ₃ .(CH ₃) ₃	—	162.41	162
Cymene, C ₆ H ₄ .CH ₃ .C ₃ H ₇ ^a	183.5	184.46	184
Naphthalene, C ₁₀ H ₈	149.2	—	149

The value 10.5 for nucleus carbon thus adapts itself well either for benzene or its homologues; and in the deducing of such special values for carbon or hydrogen, or for both, the aromatic *hydrocarbons* are certainly the most suitable, as they consist of carbon and hydrogen alone, and do not contain oxygen or nitrogen, the presence of which introduces elements of uncertainty.

The above value of carbon may, however, be employed in the same manner in calculating the molecular volumes of simpler aromatic compounds containing oxygen,

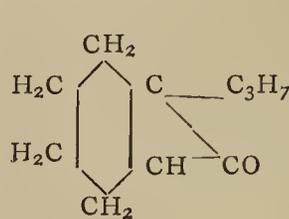
the two values given to this element by Kopp being adopted in the calculation. Thus—

	Observed. (Kopp).	Calculated. C=10.5 & H, H=5.5, O=12.2 & 7.8.
Benzoic aldehyd, C ₆ H ₅ .CHO"	118.4	119.2
Benzoic acid, C ₆ H ₅ .CO'O"H	126.9	127.0
Ethyl benzoate, C ₆ H ₅ .CO'O"C ₂ H ₅	172.4—174.8	171.0
Benzylic alcohol, C ₆ H ₅ .CH ₂ O'H	123.7	125.8

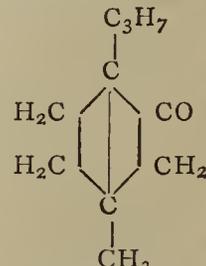
Mr. Kuhara* calculated the molecular volumes for the above bodies, using Löschmidt's constants, and on the supposition that 3 atoms of carbon have the value 14, the rest 11, and that hydrogen, whether of the nucleus or of the side-chain, possesses the constant value 3.5. He will find that his numbers are not more concordant with the experimental values than are those above calculated. If, moreover, he tried his method of calculation upon the aromatic *hydrocarbons*,—bodies which, as I already pointed out, are certainly best suited to test the accuracy or utility of the constants for carbon and hydrogen—he will get very different results, as I have already broadly indicated and as the above Table will show in greater detail.

The above Table clearly shows the fault of the method of calculation employed by Mr. Kuhara, which, when applied to simpler aromatic compounds containing oxygen, gives results (by chance?) fairly agreeing with the experimental values, but which when applied to the aromatic hydrocarbons gives results entirely at variance with those experimentally determined.

Using the same method of calculation, and on the supposition that oxygen is ketonic, Mr. Kuhara finds that the observed molecular volume of camphor agrees almost exactly with the calculated value, and draws therefore a probable conclusion that its constitution is correctly represented by one of the following formulæ:—



(Kachler).



(Kannonikov).

The agreement between the observed and the calculated values for the molecular volume of camphor, viz., 187.42

* *Four. Science College, Imp. Univ., Japan*, vol. ii., Part 4; also *Four. Tokyo Chem. Soc.*, vol. ix., No. 9, and *CHEMICAL NEWS*, vol. ix., p. 14.

† Mr. Kuhara makes naphthalene = 150, but it seems to me that the two possible ways of calculation consistent with those adopted for other bodies are:—

I.	II.
C ₃ = 3 × 14 = 42	C ₃ = 5 × 14 = 70
C ₇ = 7 × 11 = 77	C ₅ = 5 × 11 = 55
H ₈ = 8 × 3.5 = 28	H ₈ = 8 × 3.5 = 28

and 187.2 respectively, is certainly very remarkable, but one does not feel very much inclined to accept any conclusion based upon a method of calculation apparently open to so grave a criticism as I have indicated.

With our present imperfect state of knowledge regarding the relation between molecular volumes of compounds and their "constitution," especially in the case of aromatic compounds, we can neither make a free nor a safe application of it in the discussion of the probable constitution of such bodies as camphor and borneol.

It is probable, for instance, that the atomic volume of carbon may vary not only according as it exists in the benzene nucleus or in the side-chains, but also according as it is combined with 1, 2, 3, or 4 other carbon atoms, and again according to the nature of other atoms directly combined with it. Schiff, indeed, has pointed out that the atomic volume of carbon may vary from 8 to 13, and that of oxygen from 5.6 to 19.

The difference observed between the molecular volumes of—

- (1) Para-chlorotoluene .. $C_6H_4.CH_3.Cl = 134.91$
(2) Benzylic chloride .. $C_6H_5.CH_2.Cl = 133.47$

may, for example, be due to either one or all of the following differences:—

1. Chlorine in (1) is in direct combination with carbon of the nucleus, that in (2) with one in the side-chain.
2. There are four (CH) groups in (1), five in (2); in other words, there are two side-chains in (1), and only one in (2).
3. The carbon to which chlorine is combined in (1) is in its turn directly combined with two other atoms of carbon, while that to which chlorine is combined in (2) is only combined with one other carbon atom.

Such considerations as these make us hesitate very much before making a free application of the very imperfect knowledge we possess at present regarding the relation between molecular volume data and the constitution of chemical compounds.

It is true that the molecular volume of camphor calculated with the use of constants, $C=10.5$ and $H=5.5$, $O=12.2$ or 7.8 , does not agree with the experimental value, but this is simply because we are ignorant of the law which connects together the variation of the atomic volume of an element with its mode of combination. It is possible, for example, that the atomic volume of carbon directly combined with four other atoms of carbon may be considerably lower than 10.5 or 11 ,* and the abnormally low molecular volume of camphor, as actually observed, may be due to the existence in it of two or more of such carbon atoms. The six formulæ of camphor quoted by Mr. Kuhara represent it as containing respectively 0, 0, 2, 1, 2, and 1 such carbon atoms, and it may possibly turn out that either the formula (3) or the formula (5) correctly represents its constitution. Further theoretical speculations upon these points are more than useless at present, and I therefore do not more than broadly make the above suggestions for future consideration.

On the Dioxystearic Acid obtained by the Oxidation of Oleic Acid in an Alkaline Solution by Means of Permanganate.—Nik. Spiridonoff.—In this process there are chiefly formed caprylic, suberic, and azelaic acids. These substances, which are formed during the production of dioxystearic acid, must be in part regarded as products of a further oxidation of the latter acid.—*Journal für Praktische Chemie*, Vol. xl., No. 16.

* It may be remarked that the atomic volume of diamond calculated in the usual manner is $\frac{12}{3.53} = 3.4$.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 16th, 1889.

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

MESSRS. Wallace C. Nickels and J. A. Nettleton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick Alfred Anderson, B.Sc., Lesney House, Erith, Kent; G. Russell Beardmore, Warwick House, Upper Street, Islington; Robert Frederick Blake, 37, Hartington Street, Dublin Road, Belfast; Bertram Blount, Laboratory, Broadway, Westminster; Henry Herbert Bunting, 82, Netherwood Road, Kensington, W.; Paul Alexander Cobbold, Warwick School, Warwick; John S. Lumsden, 5, Paradise Road, Dundee; Frederick Mills, Bevan Crescent, Stockton-on-Tees; Robert Richard Rothwell, 82, Mawson Street, Ardwick Green, Manchester; Edward Sergeant, 75, Park Road, Bolton; Basil William Valentin, Aston Brewery, Birmingham.

The following papers were read:—

1. "A New Method of Estimating the Oxygen Dissolved in Water." By J. C. THRESH, D.Sc., M.B.

The process is based on the observation that whereas, in absence of oxygen, nitrous acid and hydrogen iodide interact to form iodine, water, and nitric oxide; in presence of oxygen the nitric oxide becomes re-oxidised, and, serving as a carrier of the oxygen, an amount of iodine equivalent to the oxygen present is liberated, in addition to that resulting from the initial action of the nitrous acid: hence, deducting the amount liberated by the nitrous acid and by the oxygen dissolved in the solutions used from the total amount, the difference will be that corresponding to the oxygen dissolved in the water examined.

The solutions used are:—(1) A solution containing 0.5 grm. sodium nitrite and 20 grms. potassium iodide in 100 c.c.; (2) a solution of 7.75 grms. sodium thiosulphate in 1 litre, 7 c.c. of which corresponds to 0.25 milligram of oxygen; (3) a clear solution of starch; and (4) diluted pure sulphuric acid (1:3).

The apparatus required is a very simple one. It consists of a wide-mouth white glass bottle of about 500 c.c. capacity, provided with a caoutchouc stopper, through which four holes are bored. Through one passes the neck of a cylindrical "separator" funnel of known capacity, and through the second a tube drawn out to a fine point, which is connected by a short length of caoutchouc tubing with the thiosulphate burette; while inlet and exit tubes for coal-gas are passed through the third and fourth holes, the exit tube having attached to it a sufficient length of caoutchouc tubing to permit of connection being established between the bottle and the separator when the stopper of the latter is withdrawn.

The separator is filled with the water to be examined, and 1 c.c. of the nitrite-iodide and 1 c.c. of the acid solution are added; if the pipette be held vertically, with its end just below the surface of the water, the solutions flow in a sharply defined column to the lower part of the separator, so that an infinitesimally small quantity (if any) is lost in the water which overflows when the stopper is inserted. The admixture of the liquids having been effected by inverting the apparatus several times, a sharp current of coal-gas is passed into the bottle to displace the air, the escaping gas being allowed to burn at a jet attached to the exit tube. Fifteen minutes after adding the solutions to the water the flame is extinguished, a cork is attached in place of the jet and is inserted in place of the stopper of the separator, and the water is then allowed to flow into the bottle; the exit tube having been disconnected from the funnel and the gas set fire to, thio-

TABLE I.
COMPOSITION OF THE MILK.

Yield of milk.		Date.	No. 40.						No. 41.					
			Morning.			Evening.			Morning.			Evening.		
40	41		Fat.	Other solids.	Total solids.									
38 lbs.	37 lbs.	13th Nov.	3.41	8.47	11.88	5.71	8.63	14.34	—	—	—	—	—	—
—	—	19th "	—	—	—	—	—	—	3.80	8.24	12.04	4.54	8.10	12.64
—	—	22nd "	3.39	8.39	11.78	4.50	8.38	12.88	3.80	8.38	12.18	4.61	8.41	13.02
22 "	25 "	5th Dec.	3.44	8.28	11.72	5.12	8.48	13.60	3.07	8.21	11.28	4.50	8.52	13.02
—	—	10th "	2.17	7.87	10.04	4.68	8.30	12.98	3.13	8.19	11.32	5.13	8.25	13.38
15 "	22 "	17th "	2.98	7.58	10.56	3.86	8.14	12.00	3.27	8.27	11.54	4.26	8.26	12.52
8 "	18 "	7th Jan.	2.70	7.50	10.20	3.64	7.68	11.32	3.93	8.13	12.06	4.95	8.19	13.14

TABLE II.

SO_3	$\text{As}_2\text{O}_3, 8\text{SO}_3$	$\text{Sb}_2\text{O}_3, 9\text{SO}_3$
$2\text{H}_2\text{SO}_4, \text{SO}_3$	$\text{As}_2\text{O}_3, 4\text{SO}_3$	$\text{Sb}_2\text{O}_3, 4\text{SO}_3$
H_2SO_4	$\text{As}_2\text{O}_3, 2\text{SO}_3$	$\text{Sb}_2\text{O}_3, 3\text{SO}_3$
$9\text{H}_2\text{SO}_4, 3\text{H}_2\text{O}$ to $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$	$\text{As}_2\text{O}_3, \text{SO}_3$	or $\text{Sb}_2(\text{SO}_4)_3$
$\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$	—	$\text{Sb}_2\text{O}_3, 2\text{SO}_3, \text{H}_2\text{O}$
$\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$	—	or $\text{Sb}(\text{OH})\text{SO}_4$
Action on sulphate of alcohol	—	$\text{Sb}_2\text{O}_3, 2\text{SO}_3, \text{H}_2\text{O}$
Cold water	As_2O_3	or $\text{Sb}(\text{OH})\text{SO}_4$
Hot water	—	$\text{Sb}_2\text{O}_3, 2\text{SO}_3, 3\text{H}_2\text{O}$
		or $\text{Sb}(\text{OH})\text{SO}_4, \text{H}_2\text{O}$
		$\text{Sb}_2\text{O}_3, 2\text{SO}_3$
		or $\text{SbO}(\text{SO}_4)_2$
		$2\text{Sb}_2\text{O}_3, \text{SO}_3, x\text{aq.}$
		$7\text{Sb}_2\text{O}_3, 2\text{SO}_3, y\text{aq.}$

Where, $x=4$ to 16 and $y=2$ to 16.

sulphate is run in until the colour of the iodine is nearly destroyed; about 1 c.c. of starch is then added from the separator and the titration is completed. The effect of the nitrite, dilute acid, and starch solutions is readily determined by removing the separator and adding 5 c.c. of each in succession and then titrating; the effect of the oxygen in the thiosulphate may be allowed for on the assumption that as much oxygen is dissolved in it as distilled water would contain at the same temperature. It appears that there is no advantage in passing the coal-gas through alkaline pyrogallol.

The author states that concordant results are easily obtained, and that the results in the case of freshly distilled water closely agree with those recently published by Sir Henry Roscoe and Mr. Lunt (*cf. Chem. Soc. Proc.*, 1889, 124; *Trans.*, 1889, 552). Thus:—

Temp.	Thresh.	Roscoe and Lunt.
10°	7.81	7.77
15	7.02	6.96
20	6.17	6.22
25	5.69	5.60
30	5.45	5.43

DISCUSSION.

Mr. WARINGTON said that on the occasion of Mr. Holland having suggested in the CHEMICAL NEWS a method of estimating nitrites in water by means of potassium iodide, he had pointed out that the method was fallacious in presence of air; the delicacy of the iodine test for nitrites was doubtless ascribable to the occurrence of the series of changes of which Dr. Thresh had availed himself.

Mr. GREEN stated that he also had called attention to the influence of oxygen about four years ago, in a communication to the University College Chemical Society.

Dr. STEVENSON said that he was not satisfied with the method of estimating nitrites in water proposed by the author; a comparison with other methods would be desirable.

Mr. CHAPMAN JONES drew attention to the use of manganous hydrate in estimating the oxygen dissolved in water.

2. "Note on a Milk of Abnormal Quality." By F. J. LLOYD.

The author is led to give the results of his examination of the milk afforded by two cross-bred shorthorns, as its quality appears to be altogether remarkable (compare table); there being no evidence either that the cows were suffering from disease, or that they were insufficiently or improperly fed, he is of opinion that the normal quality of their milk is such as has never been recorded. Several complete analyses, made with the object of discovering whether the loss fell on any special constituent, show that this is not the case, the caseine, sugar, and other constituents, except the mineral matters, being equally affected (See Table I.).

DISCUSSION.

Dr. STEVENSON expressed the opinion that the animals in question were in some way suffering from malnutrition, or were subject to some latent disease.

Mr. WARINGTON said that the amount of total solids was not below the accepted lowest value; whilst Professor KINCH remarked that equally low results had been obtained in certain cases at the Agricultural College, Cirencester.

Professor THOMSON mentioned the case of a cow having the propensity of eating heather tops affording a milk containing a lower proportion of total solids than that of other cows of the herd which had not the propensity.

Mr. LLOYD, in reply, said that in the cases considered by him the small amount of solids other than fat was what he desired to bring under notice; the total solids often varied, but the variation was chiefly in the amount of fat, not in the solids other than fat.

3. "The Sulphates of Antimony." By R. H. ADIE, B.A.

Having previously studied the compounds of arsenious oxide with SO_3 , the author has now examined those of antimonious oxide. His results are summarised in the following Table, in which is indicated the composition of the products obtained from the two oxides on treatment with the acid formulated in the first column (See Table II.).

On comparing the two series of compounds it appears that:—

(i.) With H_2SO_4 and weaker acids, Sb_2O_3 forms a different order of sulphates from As_2O_3 , while it resembles it in forming acid sulphates when subjected to the action of stronger acids. Thus the former yields the characteristic group salt, $Sb_2(SO_4)_3$, in place of the basic $As_2O(SO_4)_2$ afforded in the latter. The limits of existence, both as regards dilution and temperature, are much narrower for the arsenic than for the antimony salt. The practically complete formation of $Sb_2(SO_4)_3$ in one crystallisation also contrasts with the formation of $As_2O(SO_4)_2$ only by repeated crystallisation.

(ii.) Arsenious oxide does not form any basic sulphates containing water, while the more metallic antimonious oxide does form hydrated sulphates in acids weaker than H_2SO_4, H_2O . This acid is the limit of existence of $Sb_2(SO_4)_3$ in solution, and of any arsenic sulphate whatever.

At the meeting on March 20th, Professor Judd, F.R.S., will deliver a lecture on "The Evidence afforded by Petrographical Research of the occurrence of Chemical Change under great Pressures."

At the next meeting, on February 6th, there will be a ballot for the election of Fellows, and the following papers will be read:—

"The Oxides of Nitrogen." By Professor RAMSAY, F.R.S.

"Studies on the Constitution of Tri-derivatives of Naphthalene." By Dr. ARMSTRONG and W. P. WYNNE.

NOTICES OF BOOKS.

Annual Report of the Public Analyst appointed for the Parish of Kensington for the Year ending March 31, 1889. By C. E. CASSAL, F.C.S., F.I.C. Kensington: J. W. Wakeham.

In this parish the adulteration of milk seems to be progressively declining. In the year 1885—86 the genuine samples were 29.0 per cent; in 1886—87, 37.86; in 1887—88, 55.46; and in 1888—89, 58.33 per cent. The proportion of samples inferior in quality, though not positively adulterated, shows no such progressive decline.

Two of the samples of butter pronounced adulterated contained, respectively, not less than 93 and 90 per cent of foreign fat. From the returns of the Local Government Board it would appear that the sophistication of butter and the sale of butter substitutes as butter are still very extensively practised.

None of the samples of cheese examined were adulterated.

Two samples of tea, certified as inferior, though not demonstrably adulterated, probably contained a proportion of leaves which had been previously exhausted and re-dried. This fraud is difficult to detect analytically. It is to be feared that the servants in hospitals, boarding-schools, hotels, restaurants, &c, dispose of spent tea-leaves to itinerant agents for this purpose.

A sample of lard was found to have been adulterated with cotton-seed oil and another contained portions of light animal membranes distributed through it.

Several cases which have been made the subject of legal proceedings have given room for great dissatisfaction on the decisions of the Bench. In one case of milk the analyst had certified the presence of at least 25 per cent of water, and the public analyst of another parish had arrived at the same result. The defendant, however, applied to have a sample forwarded to Somerset House for analysis. The chemists there certified that not less than 22 per cent of water had been added. The slight discrepancy would doubtless be due to the time that had elapsed before the second analysis could be made. The Bench convicted the defendant, but although

he had given all this trouble, and though he had been previously cautioned for selling adulterated milk, they merely inflicted a fine of £1 and costs, for the singular reason that he had been a long time in business!

Another dealer, who was fined £1 ros., had previously been not merely cautioned, but actually convicted.

It seems to us that the provision of the Act that a dealer is to be informed that a sample purchased of him will be analysed, is a grave mistake. The object of inspection is to secure a portion of the article as sold in the common course of business. If the dealer is acting honestly it can make no difference to him, or to the results of the analysis, whether he is thus cautioned or not.

It would produce much good if convictions were duly advertised, at the cost of the defendant, in the local papers.

The Vestry of the Parish of Saint George, Hanover Square. Public Analyst's Report for the Year ended March 25, 1889. June, 1889. London: Wightman and Co.

This report is presented by the Public Analyst, C. E. Cassal, F.C.S., F.I.C.

If the repression of fraud in the quality of articles of food and drugs sold goes on but slowly, the fault lies, to a great extent, with the foolish leniency of magistrates. Mr. Cassal states, on the authority of the Local Government Board, that in over 80 per cent of the cases taken into Court, the average fine was only about £1. Hence the offender still finds sophistication profitable, and the public generally, as well as the honest tradesman, are taught to think that frauds of this kind are but a very trifling matter. It appears that the samples of coffee and tea submitted to examination in the Parish of St. George were all genuine, but four samples of cocoa were adulterated with starch in quantities ranging from 20 to 35 per cent, and in addition, with sugar from 25 to 35 per cent. Thus, the genuine cocoa present did not reach 50 per cent. If we consider that starch on the large scale is worth about 1d. per lb., the transaction must be exceedingly profitable to the vendor. Two adulterated samples of butter contained respectively at least 95 and 90 per cent of foreign fats.

In milk there has been an improvement. The percentage of genuine samples has risen from 47.06 per cent in 1887—88 to 66.92 in 1888—89. The adulterated and the inferior have, of course, declined. But Mr. Cassal remarks that the word "genuine" does not imply that the milks so described were all of good quality. Of 92 samples returned as genuine, only 49 were of good quality and 37 were pronounced fair.

The adulterated samples of lard contained at least 25 per cent of foreign fat, chiefly beef-stearine, mixed with cotton-seed oil. Of course, neither of these articles can be objected to *per se*, but they should be sold under their own names.

The Vestry of the Parish of St. Mary, Battersea. The Annual Report of the Public Analyst for the Year ending March 25, 1889. By C. E. CASSAL, F.C.S., F.I.C.

In this parish butter figures in a discreditable manner. The adulterated samples were 62.5 per cent. Fifteen samples consisted chiefly of margarine, and were seized under the provisions of the Margarine Act of 1887. Considering that provision dealers can sell margarine without interference if they will only label it as such, this state of things shows a preference for dishonesty.

All the samples of cocoa examined were adulterated with starch and sugar to the extent of from 50 to 60 per cent.

No coffee has been condemned. But it is to be regretted that grocers are able to evade the law by selling an article which is most mendaciously styled "Coffee as

in France," or "French Coffee." An opportunity should be taken by Government of stopping up this loophole.

In this Parish the conduct of the magistrate is much to be regretted. In one case, after the Analyst's report had been confirmed by the Somerset House chemists the magistrate declined to convict on the ground that "*the defendant had been put to sufficient expense in the matter.*" "Case B" was proved, but here also the magistrate declined to convict, and adjourned the case *sine die*. Two other cases in which the facts were similar were then withdrawn under protest from the Vestry.

Calvert's Mechanics' Almanack and Workshop Companion for 1890, containing, in addition to the usual Matter of an Almanack, Practical, Technical, and Industrial Information especially instructive to Artizans and Handicraftsmen. London: John Heywood.

WE notice here a paper on "Oppositions to Patent Applications," which shows that either patent-law or patent practice is in a very unsatisfactory state. Mr. Lloyd Wise, the author of the paper in question, considers that the practice has been wanting in consistency. But how to remedy the mischief is a difficulty not solved either in the paper before us or elsewhere.

In a paper on "Forms and Sizes of Steel and Iron Plate Test Pieces" we find it stated that a certain size is said to be used by "Mr. Jern Kontoret, Stockholm!" Now "Jern Kontoret" is the name not of a man, but of a Swedish periodical devoted to the interests of the iron trade.

Most of the matter contained in this Almanack does not come within our competence.

CORRESPONDENCE.

SILICA IN ANALYSES.

To the Editor of the Chemical News.

SIR,—Can any of your readers enlighten me as regards the following:—

I have a mineral for analysis which consists of aluminium silicates, iron oxides, hydrates, and silicates, magnesium silicates, together with free quartz sand and mica in an extremely fine state, and a little free hydrated silicic acid, probably the result of decomposition. There is also present about 4—5 per cent of alkali, K_2O and Na_2O , combined probably with the aluminium and silica.

The following is an analysis of the gently ignited material?—

SiO_2	66.24
Al_2O_3	18.36
Fe_2O_3	7.77 and trace of manganese.
MgO	2.65 and trace BaO.
Alkalies, &c. ..	4.98 by difference, and includes also traces of $Cl \cdot SO_3 \cdot P_2O_5$.

100.00

I wish to make the analyses so as to show the SiO_2 in a tabulated form, as follows:—

Sand
Free hydrated SiO_2
Combined

I should be much obliged if anyone would tell me the best method of doing so without resorting to tedious and troublesome processes, as the analyses have to be made rapidly.

I can quite confirm Mr. John Tsawoo-White's (CHEM.

NEWS, vol. lix., p. 244) and Mr. Bertram Blount's (CHEM. NEWS, vol. lix., p. 277) suspicions as to the insolubility of "ignited" precipitated SiO_2 in sodium carbonate solution.—I am, &c.,

W. J. COOPER.

High Street, Mitcheldean,
Jan. 21, 1890.

MADDER LAKES.

To the Editor of the Chemical News.

SIR,—I have lately been examining a considerable number of madder lakes with a view of finding whether they had been touched up with cochineal. I have, however, found it a difficult matter to decide, and therefore write to your journal in the hope of eliciting some information from some of its readers. If the adulteration consisted in the addition of a considerable quantity of cochineal lake, it would, doubtless, be easily detected, but I believe that if there is any adulteration it is not so gross; the colour being merely brightened by the introduction of a little cochineal at the end of the process of manufacture.

I have been experimenting on alizarin lakes lately, and my attention was first directed to the rose madders, &c., by their peculiar tint, tending towards violet when rubbed out thin, and very different from the ruby red that I had become accustomed to in working with alizarin. I therefore bought several little tubes of colour from different firms to examine. I found that if I rubbed out a cochineal lake, ground in oil in a porcelain basin, and then poured strong ammonia over it, the lake immediately turned purple.

I then tried the same test for some of my alizarin lakes, and found them very slightly affected. On now trying the madder lakes of commerce, I found that they nearly all turned purple, and those that did not do so were rather brown than violet in tint.

I next proceeded to examine these lakes through the spectroscope, by shaking them up with a little turpentine and allowing the light to pass through that, or by rubbing them out on a glass plate. I found that the alizarin lake, when strong, absorbed everything, except the red, and on diluting gradually allowed more light to pass through, without any bands, unless a possible duskiness in the green, thus differing from an alkaline solution of alizarin itself.

A cochineal lake, on the other hand, allowed the passage of a little violet as well as red, and on dilution three bands in the green appeared; one between the green and yellow, one in the middle of the green, and one, very faint, between the green and blue.

On now examining the suspected lakes, two bands were at once detected, corresponding apparently to the two first bands of the cochineal, and these bands were only found in those lakes which were affected by ammonia. Unfortunately, however, the question was not thus settled, as I found on measuring that these bands were shifted further towards the purple than those of cochineal. Nor has the matter been cleared up by the brightening of an alizarin with cochineal. I find I can easily do so, and the resulting lake is very beautiful, but is not very strongly affected by ammonia, and its bands are in the right place.

Having consequently exhausted my resources, I thought it best to appeal to those of your readers who have special knowledge of this subject, in the hope of being able, in this way, to settle the question.

I should mention, in conclusion, that my lake was prepared from "extreme blue" alizarin, but I also prepared and tested with ammonia lakes from "yellow and "blue" alizarin.

The subject is, I think, of some importance, as, if the ammonia test is reliable, there are hardly any madders

sold for artists' use which have not been touched up with cochineal.—I am, &c.,

A. P. LAURIE, M.A.

King's College, Cambridge,
Jan. 24, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Bulletin de la Société Chimique de Paris.
Series 3, Vol. ii., No. 10.

Preparation of Nitrogen in the Cold from Atmospheric Air.—M. Berthelot.—The author utilises the reaction of copper in presence of ammonia for the absorption of the oxygen. Nitrogen remains, and is displaced by means of water completely freed from dissolved oxygen by the same reactions. The gas is freed from traces of nitrite and from ammonia by a passage over potassa, or better, soda-lime, first in the liquid and then in the solid state, and afterwards over pumice steeped in sulphuric acid.

Thermic Researches on the Isomeric Nitro-Camphors and on Cyanated Camphor.—MM. Berthelot and P. Petit.

Combination-Heat of Fluorine and Hydrogen.—MM. Berthelot and Moissan.—These two papers do not admit of useful abstraction.

New Researches on the Fixation of Nitrogen by Vegetable Mould. Influence of Electricity.—M. Berthelot.

The Fixation of Atmospheric Nitrogen.—M. Berthelot.

Observations on the Formation of Ammonia and of Volatile Nitrogenous Compounds at the Expense of Vegetable Soil and of Plants.—M. Berthelot.—These three memoirs have already in substance appeared elsewhere.

Facts on Mellitose.—M. Berthelot.—The author has re-examined mellitose as extracted from cotton-seed cakes. He assigns to it the formula $C_{36}H_{32}O_{32} + 5H_2O_2$, but he has also obtained another hydrate containing $6H_2O_2$.

New Observations on the Reciprocal Displacements between Oxygen and the Halogens.—M. Berthelot.—A thermo-chemical paper not admitting of useful abstraction.

Observations on the Presence of Nitrous Acid in the Air.—L. Ilosvay.—The author has found nitrous and nitric acid in the atmosphere at every hour of the day, both acids being in combination with ammonia. He considers that they play an important part in supplying nitrogen to the vegetable economy.

Chemical Treatment of Diseases caused by Cryptogams.—Dr. A. B. Griffiths.—A paper on the use of ferrous sulphate as a remedy for the attacks of parasitic fungi. The subject matter will be found chiefly in the author's papers, "Manures and their Uses," in the CHEM. NEWS and in the *Journal of the Royal Agricultural Society*.

Colorimetric Determination of Nitric Acid by Means of a Sulphuric Solution of Diphenylamine.—J. A. Müller.—This paper will be inserted in full.

Thermic Formation of the Salts of the Phenylene-diamines.—Leo Vignon.—This paper does not admit of useful abstraction.

New Apparatus for Fractionated Distillations in a Vacuum.—H. Gautier.—Not intelligible without the accompanying diagram.

Journal für Praktische Chemie.
New Series, Vol. xl., No 16.

Fluorine Compounds of Vanadium and its Nearest Analogues.—E. Petersen.—The result of these researches is that compounds of VOF_2 are formed in neutral or feebly acid solutions. A compound, VF_4 , seems capable of existing in concentrated hydrofluoric acid, but on contact with water or air it is converted into an oxy-fluoride. The compounds in question cannot be directly compared with the known double fluorides of the tetravalent elements, but vanadium approximates more nearly to this stage of oxidation than to any other. The dioxides of niobium and tantalum seem quite indifferent. Among the metals of the iron group, manganese forms a dioxide which possesses feebly acid properties. But it forms, with hydrofluoric acid, sesqui-compounds, and no compounds of tetravalent manganese.

Calorimetric Researches. Nineteenth Memoir: On the Thermic Value of the Acids of the Oxalic Series and of Fumaric and Maleic Acids.—F. Stohmann, Cl. Cleber, and H. Langbein.—The purpose of this investigation was to ascertain how far the numerous isomerisms met with in the so-called adipic acids, $C_6H_{10}O_4$, have an influence on their thermic value.

On Opening up Sulphides, such as Bournonite, Proustite, &c., in a Current of Air charged with Bromine.—P. Jannasch.

A New Method for the Analysis of Pyrites.—Paul Jannasch.—These two papers will appear in full.

Remarks on the Determination of Sulphuric Acid in Presence of Iron.—P. Jannasch.—The proportion of sulphuric acid in a liquid, as found by precipitation with barium chloride, is always too low if salts of iron are simultaneously present. The cause of this fact has been recently examined by the author and Richards, on which occasion they discussed the current methods for the analysis of pyrites, and, in reference to that of Lunge, they remarked that from a purely scientific point of view it must be rejected. Thereby they had only Lunge's earlier method in view, which he himself subsequently pronounced not quite accurate. By a previous precipitation of the iron with a slight excess of ammonia at a moderate heat, Lunge has subsequently rendered his process perfectly accurate.

On Opening up Pyrites in a Current of Oxygen.—P. Jannasch.

The Determination of Sulphuric Acid in Presence of Iron.—G. Lunge.—These two papers will be inserted in full.

On Orthoparadinitrophenyl-phenylhydrazine, Dinitro-, and Nitronitroso-azobenzol.—C. Willgerodt and B. Hermann.—Both dinitroso- and nitronitroso-azobenzol dissolve readily in most organic solvents. Hence the molecular magnitudes of these compounds may possibly be determined by means of Raoult's method.

On Orthobromparatoluylic Acid and Chloronitro-Paratoluylic Acid.—M. Fileti and F. Crosa.—A claim of priority as against Claus and Kunath.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. iv., No. 46.

The only chemical matter contained in this issue is a paper by Mr. Riley on the alloys of nickel and steel, taken from *Engineering*, and a note on the sophistication of lard with cotton-seed oil, a fraud which is detected by the iodine test.

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

Recent Methods for Determining the Non-crystalline Matter in the Products of Sugar-Works.—G. Midavaine.—In place of Fehling's liquid, Degener and Bodenbinder recommend Soldaini's reagent, which is highly sensitive, and undergoes no change on keeping. To prepare this liquid a solution of 40 grms. pure copper sulphate is precipitated by means of a solution of 40 grms. sodium carbonate, and the precipitate of basic sodium carbonate is filtered and washed. This precipitate, which weighs 15 grms., is gradually introduced into a boiling and concentrated solution of potassium bicarbonate and digested for ten minutes in a vapour-bath. The liquid is then poured into a two-litre flask, made up to a total volume of 1400 c.c., and heated for two hours in a steam-bath, with constant stirring. It is then filtered, and yields a deep blue liquid of the sp. gr. 1.185. If this reagent is boiled, even after dilution, there is no deposit. A solution of pure cane-sugar may be boiled for six minutes over a flame, or for twelve minutes in the brine-bath before the reduction of the reagent takes place. With 50 c.c. of this liquor, 0.0014, or even 0.0005 of inverted sugar may be detected in presence of cane-sugar. Soldaini's reagent keeps almost indefinitely. Another reagent, called the "carbonated liquor," is proposed by H. Pellet, Chief Chemist of the Wanze Sugar Works. It consists of:—Salt of seignette, 200 grms.; sodium carbonate (pure and dry) 100 grms.; copper sulphate (pure and crystalline), 70 grms.; ammonium hydrochlorate, 7 grms.; distilled water, 600 c.c. The four salts are placed in a porcelain capsule, the water is added, and heat is applied until all is dissolved, when the volume is made up to 1 litre, filtering if needful.

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 advertising columns.

Sewage.—Will any reader inform me if sewerage treated with "ferrous sulphate" from a district where the water is chiefly of a greasy character—the sediment when dried and subjected to heat produces a gas giving a good light on combustion—can be of any commercial value.—"STAR."

MEETINGS FOR THE WEEK.

- MONDAY, 3rd.—Medical, 8.30.
— Society of Arts, 8. "The Electro-magnet," by Silvanus P. Thompson, D.Sc., M.I.E.E.
— Society of Chemical Industry, 8. "Metallic Compounds of the Phenols," by A. H. Allen. "New Method of Hardening Steel for Projectiles," by Watson Smith. "On Bromanil," by M. Losanitch.
— Royal Institution, 5. General Monthly Meeting.
- TUESDAY, 4th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
- WEDNESDAY, 5th.—Geological, 8.
— Society of Arts, 8. "High-speed Knitting and Weaving without Weft," by Arthur Paget.
- THURSDAY, 6th.—Royal, 4.30.
— Royal Institution, 3. "Sculpture in Relation to the Age," by Edwin Roscoe Mullins.
— Royal Society Club, 6.30.
— Chemical, 8. Ballot for the Election of Fellows. "The Oxides of Nitrogen," by Prof. Ramsay, F.R.S. "Studies on the Constitution of the Tri-derivatives of Naphthalene," by Dr. Armstrong and W. P. Wynne. "On the Action of Chromium Oxochlorides on Nitrobenzol," by G. G. Henderson, B.Sc., and J. Morrow Campbell, B.Sc.

- FRIDAY, 7th.—Geologists' Association, 7.30. (Anniversary).
— Society of Arts, 5. "The Utility of Forests and the Study of Forestry," by Dr. Schlich.
— Royal Institution, 9. "The London Stage in Elizabeth's Reign," by Henry B. Wheatley, F.S.A. Physical, 5. (Annual General Meeting). "On Galvanometers," by Prof. W. E. Ayrton, F.R.S., T. Mather, and W. E. Sumpner. "On a Carbon Deposit in a Blake Telephone Transmitter," by F. B. Hawes.
- SATURDAY, 8th.—Royal Institution, 3. "The Natural History the Horse, and of its Extinct and Existing Allies," by Prof. Flower, F.R.S., &c.

TO CORRESPONDENTS.

F. MacDonald.—Use a moderately strong solution of nitrate of silver.

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THE CHEMICAL NEWS.

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THE COMPOSITION OF THE MILK OF THE
BOTTLE-NOSE WHALE
(*GLOBIOCEPHALUS MELAS*).

By Prof. PERCY F. FRANKLAND, Ph.D.,
and FRED. J. HAMBLY,
Assistant Lecturer on Chemistry in University College, Dundee.

ON the occasion of the recent capture of no less than 160 individuals of this species in Tankerness Bay, near Kirkwall, Orkney, our colleague, Prof. D'Arcy Thompson, received, amongst other specimens, a small quantity of the milk of one of these creatures, the liquid having been scooped directly from the mammary gland after death.

The sample was unfortunately a very small one (but little in excess of 3 grms.), which is the more to be regretted as an almost unlimited quantity must have been available for collection, a large number of the captured whales being females.

The milk presented a thick creamy appearance, globules of fat being clearly discernible in the mass, which was possessed of a strong fishy odour.

Owing to the small quantity of the material at our disposal, we were unable to make an exhaustive analysis, but such determinations as were possible we deemed it advisable to perform in duplicate, although, from the non-homogeneous nature of the substance, it was not to be anticipated that very concordant results would be obtained.

The following are the results of the duplicate analyses:—

	No. 1.	No. 2.
Weight of milk taken..	1·431 grms.	1·678 grms.

Results of Analysis expressed in Parts per 100.

	No. 1.	No. 2.	Mean.
Total solids (dried at 100— 105° C.)	52·13	50·53	51·33
Water	47·87	49·47	48·67
Non-fatty solids (insoluble in ether)	7·72	7·42	7·57
Fat (soluble in ether)	44·41	43·11	43·76
Ash	0·44	0·47	0·46

That the discrepancies between the two analyses were due to want of homogeneity in the sample, and not to any inaccuracy in the determinations, is clearly shown by the fact that the total solids, non-fatty solids, and fat stand in the same proportion to each other in both analyses. Thus, sample No. 2 was apparently more aqueous than No. 1, and if the results of No. 2 be corrected in the ratio of 50·53 : 52·13, then the figures of the analysis No. 2 become practically identical with those of No. 1; thus, the non-fatty solids become 7·65 per cent and the fat 44·45 per cent.

The milk of this species of the bottle-nosed whale is thus enormously rich in fat, whilst the non-fatty ingredients

are rather below than above the average of those present in the milk of ordinary mammals. The only other analysis of the milk of a *Cetacean* with which we are acquainted is that made by Prof. Purdie, of St. Andrews, of the milk of the porpoise, and which yielded the following very similar results (*Brit. Assoc. Report*, 1885, Aberdeen):—

Total solids..	58·89 per cent.
Water	41·11 "
Non-fatty solids..	13·09 "
Albumenoids	11·19 "
Milk sugar (?)	1·33 "
Fat	45·80 "
Mineral matter	0·57 "

The table below exhibits the composition of the milk of some of the commoner mammals.

We examined the ash of the whale's milk qualitatively, and found that it contained a large proportion of phosphoric acid. We also saponified the fat, and on treating the aqueous solution of the resulting soap with ether we obtained a small quantity of extract, which was, however, insufficient for further examination. On decomposing the soap with dilute sulphuric acid the resulting product proved to be only partially soluble in cold alcohol, a residue melting at 51° C. being left. This may possibly be spermaceti (m. p. 49° C.), which had escaped saponification, for, as is well known, it is only saponified very slowly. We were unfortunately unable to further investigate this interesting point owing to the material being exhausted.

A BRIEF SUMMARY ON PRACTICAL
MANIPULATION.

By H. N. WARREN, Research Analyst.

Precipitation.

AMONG the numerous operations that are performed in the laboratory, none are perhaps oftener employed than that of precipitation. Many precipitates, not among the least of which noted for tedious and imperfect filtration may be mentioned those of barium sulphate and calcium oxalate, when recently precipitated, pass in considerable quantity through the pores of the paper. This may naturally be considerably retarded by employing both solutions at the boiling-point. But even then considerable risks are entertained, combined with a grievous waste of time. The addition of starch-paste has been recommended by several experts, but the same investigators omit to state what percentage of sulphide they obtain after ignition. I may mention, as an improvement, the following method:—Employ both the reagent and the solution containing the sulphate at an elevated temperature; at the same time introduce a few drops of ethereal solution of pyroxilin and mix well with the precipitate by stirring; the pyroxilin is at once set free, and, mixing intimately with the precipitate, allows of an immediate filtration. The separation of iron from manganese by means of sodium acetate is well known to be amongst the bulkiest precipitates obtainable for practical purposes; yet, if at the boiling temperature there be added to the precipitate finely powdered glass, it at once mechanically subsides, and, if dexterously performed, may be filtered

Average Percentage Composition, by Weight, of Milk from Various Mammals (Hoppe-Seyler).

	Woman.	Cow (summer).	Ewe.	Mare.	Bitch (meat-fed).	Sow.	Ass.	Buffalo.	Camel.	Hippo- potamus
Water	87·24	86·48	83·30	91·15	71·21	81·80	89·01	80·64	86·34	90·43
Total solids	12·75	13·52	16·70	8·85	28·79	18·20	10·99	19·36	13·66	9·57
Casein	1·90	3·84	5·80	1·05	12·89	5·30	3·57	5·55	3·67	—
Fat	4·32	4·01	6·15	1·27	12·04	6·00	1·85	8·45	2·90	4·51
Sugar	5·97	4·93	3·96	5·75	1·82	6·07	5·05	4·52	5·78	—
Salts.. .. .	0·28	0·74	0·66	0·37	1·63	0·83	0·52	0·84	0·66	0·11

and washed with impunity. As a third instance may be mentioned the effectual separation of precipitates occasioned during the manufacture of the pharmaceutical preparations, one of the most obstinate being the *Tinctura rhei* of the British Pharmacopœia.

A sample of this description which was lately presented to my notice has been, by the manufacturers, several times ineffectually passed through the variè of commercial filters. The sample referred to, which was, when received, of a deep cloudy slate colour, due to suspended insoluble matter, was, after a short digestion with a small quantity of egg albumen, entirely freed from coherent matter by ordinary filtration. I may also mention that paper pulp distributed throughout the solution retains very perfectly any finely divided substances.

Incineration.

In cases where the total ash is required, such as the incineration of organic substances, among which may be mentioned the analysis of beet-sugar, so imperfect is the combustion of the organic matter, on account of the easily fusible salts which impregnate it, that an addition of a small quantity of H_2SO_4 is required in order to convert the inorganic salts present into sulphates, and thus render them less fusible, correction for increased weight being afterwards deducted.

The imperfect combustion of carbon when in contact with phosphates, especially the case of magnesium pyrophosphate, tends to increase errors; in which case I have observed several authors recommend the use of ammonium nitrate as a consumer of the carbon. I have, however, frequently used with success a plug of gun-cotton, omitting altogether a filter-paper.

Precipitation retarded.

Several organic acids or salts of the same are well known to retard the precipitation of metals when in solution. Among the most formidable are the tartrates and oxalates, also the citrates, which are not unfrequently unintentionally formed by the incautious filtration of strongly acid liquors through organic membranes; these may be altogether prevented by the employment of wool-glass; they are not, however, by any means the only acids that present a retarding action, one of the most opposing being hydroferrocyanic acid. So powerful is the action of this acid when in solution towards the salts of tin, so as not only to render the sulphide of tin unprecipitable, but even to immediately decompose it into the ferrocyanide after its formation.

Reading of Definite Quantities from Measured Flasks.

At the moment it may be desirous of denoting the exact capacity of a measured instrument, say, for instance, the reading from a measured flask, it not unfrequently happens that an accumulation of either froth or air-bubbles obliterate the dimension. These may be immediately expelled by the addition of one drop of alcohol.

(To be continued).

ON THE EXAMINATION OF ESSENTIAL OILS BY MAUMENÉ'S TEST.

By ROWLAND WILLIAMS, F.I.C., F.C.S.

MAUMENÉ'S test has been found so useful in conjunction with other methods of analysis as a means of detecting the presence of, and in some cases approximately estimating the proportion of, certain adulterants in fixed oils, e.g., linseed in rape oil and cotton-seed in olive oil, that it seemed to me worth while to apply the test to a number of essential oils which I have at hand.

I have already examined most of these oils by other methods, and published the results of my investigation in the CHEMICAL NEWS (vol. lx., p. 175).

For the benefit of those who are not very familiar with the mode of conducting Maumené's test, I may say that it consists in adding strong sulphuric acid to the oil under examination, generally in the case of ordinary fixed oils, in the proportion of 10 c.c. of acid to 50 grms. of oil, both being at the same initial temperature (preferably about 60° F.), stirring vigorously, and noting the highest point indicated by the thermometer.

In order to avoid loss of heat as much as possible, it is desirable that the operation should be conducted in a beaker surrounded by cotton-wool and packed in a somewhat larger vessel. The increase of temperature is much greater in the case of some fixed oils than of others, and depends upon a variety of circumstances, among others the nature of the oil itself, the strength of acid employed, the exact manner in which the acid is added, and the mode of stirring adopted. If these and other apparently minor details are not rigidly attended to, a considerable discrepancy may occur between duplicate experiments with the same sample of oil. Maumené's test can, therefore, only be regarded as an arbitrary one, and to obtain thoroughly satisfactory results every chemist should, whenever possible, examine samples of oil submitted to him for analysis under precisely the same conditions as a genuine specimen of the kind of oil in question. The results will then, in many cases, be of unquestionable value.

In the annexed table I give the figures obtained from all the essential oils which I have had the opportunity of examining by Maumené's test.

Table of Results.

Name of oil.	Rise of temperature in degrees F.
Aniseed	156
Bergamot—	
1st sample	186
2nd „	178
Cajeput—	
1st sample	91
2nd „	73
Caraway—	
1st sample	120
2nd „	136
Cassia—	
1st sample (pure)	102
2nd „ „	102
3rd „ (adulterated with rosin)	147
4th „ „	158
5th „ „	184
6th „ „	173
7th „ „	200
Cedarwood—	
1st sample	55
2nd „	46
Cinnamon—	
1st sample	136
2nd „	150
Citron—	
1st sample	166
2nd „	166
Citronelle—	
1st sample	152
2nd „	152
Cloves—	
1st sample	122
2nd „	130
Eucalyptus—	
1st sample	97
2nd „	98
3rd „	82
Geranium (finest Spanish)	96
Juniper—	
1st sample (English)	144
2nd „ (Foreign)	190

Name of oil,	Rise of temperature in degrees F.
Lavender, Mitcham—	
1st sample	120
2nd ,,	113
Lavender, Hitchin.. .. .	142
Lavender, French Petale—	
1st sample	112
2nd ,,	108
Lavender, Spike—	
1st sample	102
2nd ,,	162
Lemon—	
1st sample	152
2nd ,,	163
Lemongrass—	
1st sample	114
2nd ,,	104
Mace—	
1st sample	122
2nd ,,	116
Nutmeg—	
1st sample	118
2nd ,,	123
Orange—	
1st sample	152
2nd ,,	144
Pennyroyal—	
1st sample	84
2nd ,,	54
Peppermint, Mitcham—	
1st sample	67
2nd ,,	70
Peppermint, American—	
1st sample	72
2nd ,,	94
Peppermint, Japanese—	
1st sample	68
2nd ,,	78
Rosemary—	
1st sample	109
2nd ,,	134
Rue—	
1st sample	151
2nd ,,	182
Sage—	
1st sample	157
2nd ,,	157
Sassafras—	
1st sample	52
2nd ,,	89
Turpentine—	
1st sample	136
2nd ,,	160
3rd ,,	178
4th ,,	152
Thyme (red)—	
1st sample	108
2nd ,,	132
Verbena—	
1st sample	120
2nd ,,	104

A few words of explanation are necessary in connection with the preceding figures. In the first place I must state that owing to my having only a small quantity of most of the essential oils at my disposal, I decided to perform the test on 100 fluid grains of each sample, with certain exceptions hereafter mentioned. The carefully measured quantity was placed in a small glass beaker surrounded with cotton-wool in the manner previously described. The temperature of the oil having been taken, 20 fluid grains of strong sulphuric acid was added, and the mixture vigorously stirred with the thermometer until a point was reached at which the mercury ceased to rise, and the increase of temperature noted.

The acid which I employed in my experiments was ordinary pure sulphuric acid, previously heated for some time, and then kept in a well-stoppered bottle.

In the case of certain essential oils, addition of sulphuric acid causes so violent a reaction that the utmost care is required to obtain a satisfactory result, and even when every precaution is taken it is difficult to get reliable figures from some oils. This is owing to the frothing up or actual spirting which takes place when strong sulphuric acid is added to certain essential oils, especially to those of caraway, cinnamon, verbena, and lemongrass.

As I considered it advisable to use the same apparatus throughout this investigation, I found it necessary, in the case of the four oils above mentioned, to employ only 50 grains of oil and 10 grains acid; otherwise the action was so energetic as to cause part of the mixture to be violently ejected from the beaker. It is probable that by mixing these oils with olive oil (as is frequently done in the examination of linseed and fish oils by Maumené's test), before the addition of sulphuric acid, the reaction would be moderated and the results thereby rendered more accurate, but I have not applied this modification to any of them.

With regard to the oils of cassia, Nos. 1 and 2 are, I believe, pure. The remaining five samples are grossly sophisticated with various proportions of rosin. These, it will be noticed, give a much greater rise of temperature than the genuine oils. Maumené's test seems likely, therefore, to be useful as a confirmatory test for rosin in cassia and other essential oils when other methods of examination have indicated the presence of that adulterant.

It must be understood that in publishing these results I make no claim for their absolute accuracy, although the determinations were made as carefully as possible under the circumstances. The figures are only put forward now for the purpose of directing attention to the possibility of successfully applying Maumené's test to essential oils for the detection of certain impurities therein. Probably others, working under more favourable conditions as regards the quantity of essential oils at their disposal, will obtain somewhat different results to my own, for which reason I lay special stress on the necessity of each operator examining suspected samples of essential oils side by side with an undoubtedly pure specimen of the oil under consideration.

Laboratory and Assay Office,
28, Pall Mall, Manchester,
January 24, 1890.

THE ANALYSIS OF CHROME IRON.

By R. FRESENIUS and E. HINTZ.

SOME time ago the authors had to execute the analysis of a chrome iron which, as it subsequently appeared, contained 61 per cent chrome, 28 per cent iron, and 9 per cent of chemically combined iron and graphite. As it was scarcely attacked by acid, and could only be dissolved by treatment with hydrochloric acid prolonged for weeks, the investigation presented difficulties which could only be overcome by degrees. It seems, therefore, interesting to describe the method which proved successful, and which we can therefore recommend.

1. Determination of Total Metals and of the Slag.

About 5 grms. of the chrome iron are placed in a porcelain boat, inserted into a tube of sparingly fusible glass, and heated for a long time in a current of desiccated chlorine gas free from air. The portion from the beginning of the tube to the boat is about 20 c.m., and that behind the boat 40 c.m. The end of the tube is bent at a right angle and leads into a Pélilot tube, the other limb of the latter is connected with a Woolfe's bottle. The current of gas issuing from the latter passes

through two more Péligré tubes. The outer limb of the last is connected with a flask containing hydrate of lime in order to absorb the escaping chlorine. All these recipients contain water, but in the Woolfe's bottles only so much that the tube forming the connection between the first Péligré tube and the bottle leads not quite to the surface of the water.

The heat of the porcelain boat is raised very gradually, and that of the back part of the tube is regulated in such a manner that a relatively trifling quantity of the ferric chloride finds its way into the recipients, which are kept cool with water. The operation takes from three to four hours.

After the tube is cold, the recipients are disconnected, and in their place is joined on a Péligré tube containing a little water. The chlorine gas is then expelled from the tube by dry carbonic acid. Desiccated hydrogen gas, free from oxygen, is then passed through the tube, and both the boat and that part of the tube in which there is the greatest portion of sublimed chromic chloride is submitted to a gentle, but prolonged, ignition in order to convert it partly into chromous chloride, and thereby render it soluble in water. When cold the boat is drawn out. It contains the liberated carbon, the graphite, the small quantity of slag, chiefly particles of chrome iron which have escaped the action of the chlorine, also manganous chloride, and sometimes small quantities of iron and chromium chlorides. Its contents are treated with water, the undissolved matter is filtered off, washed, and dried, the filter is incinerated separately, and the residue is put in a porcelain boat, inserted in a glass tube, and heated in a current of dry oxygen, in order completely to burn the graphite. It is then heated in a current of hydrogen to reduce portions of iron oxide.

The boat is introduced into a new glass tube, arranged like that described for the first treatment with chlorine; the receivers which were formerly used are again connected, and the boat is again heated in a current of chlorine, free from air, until no further sublimate is formed, and the contents of the boat appear white. When cold, the boat is drawn out, its contents are heated in water, filtered, the undissolved slag is washed with hot water, dried, ignited, and weighed. If its weight is appreciable it is submitted to further analysis, according to the usual process.

The contents of the glass tube used in the second chlorine treatment are heated, as already indicated, first in a current of hydrogen. The contents of both tubes are heated in them with water, and a measured quantity of hydrochloric acid, of sp. gr. 1.1, and the solutions obtained are added to the contents of the receivers, and the liquid obtained on washing the slag. If the solution does not become clear even on long standing, or if a sediment appears it must be filtered. The contents of the filter are washed into a platinum capsule, the ash of the filter is added, the liquid is evaporated down to a small portion, dried up along with a mixture of equal parts sodium carbonate and potassium chlorate, heated to fusion, softened in water, and evaporated to dryness in a porcelain vessel with the addition of a little hydrochloric acid. The residue is moistened with a measured quantity of hydrochloric acid, of sp. gr. 1.1, water is added, any residue (*a'*) is filtered off, washed, dried, and laid aside. A filtrate here obtained is to be added to the main solution.

The flask containing such solution is then weighed in order to know the weight approximately, and a calculated quantity of pure sodium carbonate is added, *i.e.*, so much that there may remain in the liquid, in a free state, about 4 per cent of hydrochloric acid of sp. gr. 1.1, which can easily be effected as all the hydrochloric acid added has been measured.

The liquid thus prepared is submitted to prolonged treatment with sulphuretted hydrogen, at first at 70°, but afterwards in the cold. It is let settle for some time, the precipitate, which consists chiefly of sulphur, is filtered

off, washed with water, to which a little sulphuretted hydrogen water has been added, treated with hydrochloric acid containing a little bromine, filtered, washed, the excess of bromine is removed with ammonia, acidulated with hydrochloric acid, and the solution is again treated with sulphuretted hydrogen, as above. If no precipitate appears, the solution is added to the main liquid. If there is a precipitate, it is filtered off, and the filtrate is added to the main liquid. The precipitate, which may contain copper, lead, arsenic, antimony, and, in general, the metals of the V.th and VI.th groups, is treated by known methods for their separation and determination. The main liquid, which chiefly contains chromium and iron chlorides, and a moderate quantity of alkaline chlorides, is repeatedly evaporated to dryness in the water-bath to eliminate silica. The residue is moistened with hydrochloric acid, let stand for some time, mixed with water, filtered, and the precipitate (*a'*) is washed, dried, and the filter containing it and that containing the precipitate (*a*), if one exists, are incinerated together. If the ignited residue is white it is weighed, the silica is determined by volatilisation with hydrofluoric acid, any insoluble residue is fused with potassium disulphate, the melt is softened with cold water, and the solution is first tested for titanous acid by prolonged boiling. The solution, if it remains clear (or the filtrate if a deposit has been produced), is tested with ammonia, in order to be certain that there remain no oxides precipitable by this reagent.

If the ignited residue containing silica is not white it need not be weighed. It is fused with sodium carbonate in a platinum crucible, adding a little saltpetre. The melt is moistened with water, rinsed into a porcelain capsule, repeatedly evaporated to dryness with hydrochloric acid, treated with hydrochloric acid and water, filtered, and washed, the filtrate being added to the main solution. The precipitate is ignited, weighed, and treated with hydrofluoric acid, as above.

The main solution is treated with chlorine gas, or mixed with strong chlorine-water until it smells of chlorine, in order to convert the ferrous chloride into ferric chloride, any chromous chloride being at the same time converted into chromic chloride. The liquid is then subjected to prolonged heating in a porcelain capsule until the free chlorine is completely expelled, and the liquid is concentrated down to about 1 litre. It is let cool, introduced into a capacious boiling flask, a solution of sodium carbonate is added until the free acid is nearly neutralised, and to the clear liquid there is added pure barium carbonate ground up in water until a portion remains undissolved. It is repeatedly shaken up, let settle, the supernatant liquid is drawn off with a syphon, and the precipitate is completely washed by decantation. The liquids drawn off are filtered, the trace of precipitate remaining on the filter and the main bulk are dissolved in hydrochloric acid, and the liquid is made up exactly to 1 litre.

The precipitate consists chiefly of chrome and iron hydroxides, and barium carbonate. The liquid, filtered off, may contain manganese, nickel, cobalt, and zinc, if these metals were present in the chrome iron. It is evaporated down with the addition of some hydrochloric acid to about 500 c.c. The baryta is precipitated from the boiling liquid with dilute sulphuric acid, and is filtered and washed in order to free it from traces of the above-mentioned metals; it is placed in a small porcelain capsule with hydrochloric acid, evaporated down to a small quantity, mixed with water, filtered after some hours, and the filtrate is added to the liquid containing the manganese, &c. The whole is concentrated, almost neutralised, with ammonia, a sufficiency of ammonium acetate is added, and the solution is precipitated with sulphuretted hydrogen. The precipitate formed contains nickel, cobalt, and zinc, if present. These metals are separated by the ordinary methods.

The manganese, which is in the filtrate, is precipitated at a boiling heat by bromine and ammonia; but as the

hydrated peroxide thus obtained contains alkali it is dissolved in hydrochloric acid, the solution precipitated with ammonium sulphide after the addition of ammonia, and the manganese determined as manganous sulphide.

There now remains the solution containing the iron and the chrome, which has been brought to the volume of 1 litre. Of this, 200 c.c. are evaporated down to a small residue to expel the greater part of the hydrochloric acid; water is added, and it is raised almost to a boil with the cautious addition of dilute sulphuric acid in order to remove baryta. After long standing the barium sulphate is removed, placed in a porcelain capsule, covered with hydrochloric acid, which is then evaporated down to a small residue; water is added, and after some hours it is filtered and washed with water, repeating this hydrochloric treatment twice more in the same manner in order to remove all traces of ferric and chromic oxide which may adhere to the barium sulphate.

All the liquids thus filtered off from the barium sulphate are evaporated first in a porcelain capsule, and then in a small platinum capsule, down to a small residue. Pure sodium carbonate is then cautiously added up to a slight excess, and then 5 grms. of a mixture of equal parts of sodium carbonate and potassium chlorate. The mixture is completely dried, and gradually heated to fusion. When cold, the melt is treated with hot water, filtered, washed until the washings run off quite colourless; the filter, in which there is a portion of the ferric oxide, is dried and incinerated in the platinum capsule containing the remainder of the ferric oxide; 4 grms. of the mixture of sodium carbonate and potassium chlorate are added, the whole is melted, and the melt, when cold, is treated with hot water until everything soluble is removed. In these operations the use of glass vessels must be avoided, as they are attacked by the strongly alkaline liquids; vessels of platinum or of porcelain are used in preference.

If the final filtrate is colourless, or has only a very faint yellow tint, we have all the ferric oxide in the residue and all the chrome in solution. The ferric oxide is dissolved in hydrochloric acid, precipitated with ammonia, and determined as usual. After it has been weighed, it is dissolved in fuming hydrochloric acid, and the (generally trifling) residue of silica derived from the vessels is determined and deducted from the weight of the ferric oxide. The solution of the ferric chloride is poured into pure hot potassa lye in a platinum capsule to find if any alumina is dissolved; if so, it is determined and deducted from the ferric oxide.

The solution containing the chrome as an alkaline chromate is acidified with hydrochloric acid, and ammonia is added until the liquid is just alkaline. If there appears at once, or after standing, a white flocculent precipitate, it is filtered off, washed, and weighed. It may be alumina, aluminium phosphate, a residue of silica or of titanate, or a mixture of these bodies. Its weight is first determined, and it is then fused with potassium disulphate, and treated by known methods to determine its nature.

The liquid which remained clear on the addition of ammonia, or the solution filtered from the above white precipitate, is mixed with a sufficiency of hydrochloric acid, alcohol is added, and the whole is heated in a porcelain capsule until all the chrome is converted into chloride. The chrome is then precipitated with ammonia as hydroxide, and determined as usual. If the chrome-iron contained phosphorus, and if the phosphoric acid thence arising has not been completely eliminated along with alumina, it goes down along with the chromium hydroxide. The quantity of phosphoric acid thus weighed along with the chromic acid must be deducted from the weight of the ignited precipitate before the quantity of chromium can be calculated.

2. Determination of total Carbon, Phosphorus, and Sulphur.

Five grms. of the mineral are again treated in a current

of chlorine precisely as described under 1. The contents of the boat, with the addition of a little solution, are digested for a long time with hydrochloric acid and water, and decanted through an asbestos filter. If particles of chrome-iron still appear, the undissolved part must again be heated in a current of chlorine free from air, until there is no further formation of a sublimate. In any case, the carbonised residue is washed until the washings no longer give the reaction of chlorine, and the contents of the filter are then treated in the ordinary manner with chromic and sulphuric acids in order to convert the entire quantity of carbon into carbonic acid for its determination.

The contents of all the receivers which contain all the sulphur and phosphorus in the state of phosphoric acid are evaporated to dryness along with some sodium chloride in order to separate silica. The residue is heated with hydrochloric acid and water, filtered, nearly neutralised with ammonia, barium chloride is cautiously added to the clear solution so as to throw down the sulphuric acid. It is let settle for some time, the barium sulphate is filtered off, purified by evaporation with hydrochloric acid thrice repeated, washed with water, as directed under 1, weighed, and the sulphur present in the chrome-iron is thus calculated.

The solution filtered off from the barium sulphate, together with the washings, is evaporated down with repeated additions of nitric acid, until all the hydrochloric acid is driven off. The phosphoric acid is then separated by means of molybdic acid, determined as usual, and from the results the proportion of phosphorus in the chrome-iron is calculated. If the mineral is arseniferous, the washed ammonium-magnesium phosphate is dissolved in hydrochloric acid, and any arsenic acid existing in the precipitate is removed by means of sulphuretted hydrogen. From the filtrate, after concentration, the ammonium-magnesium phosphate is reprecipitated by means of ammonia and a little sodium-ammonium phosphate.

3. Determination of Graphite.

Ten grms. of the sample are digested for weeks with hydrochloric acid—often renewed—until all the iron and all the chrome are dissolved, and the undissolved matter does not follow a magnet held underneath the flask. All the hydrochloric acid poured off is passed through an asbestos filter, the residue of graphite is washed with water, potassa-lye, alcohol, and ether, and treated with chromic and sulphuric acids, as in 2, to determine its carbon. On deducting its weight from that of the total carbon we find the carbon in chemical combination.—*Zeitschrift für Analytische Chemie.*

THE ESTIMATION OF MINUTE QUANTITIES OF GOLD.*

By Dr. GEORGE TATE, F.I.C., F.C.S.,
Principal at the College of Chemistry, Liverpool.

(Concluded from p. 55).

SINCE it might be urged against the utility of the microscopic estimation of gold, that the ordinary crucible or "pot" method of assaying ores, might be incapable of enabling the assayer to isolate the one ten-thousandth of a grain, or that the losses incidental to cupellation, parting, collection, and fusion of the gold, were together in excess of that weight, I have conducted a large number of experiments, which tend to prove that, with care, exceedingly minute quantities of gold are capable of isolation, and that the percentage loss of metal is extremely small. A few of these experiments are here recorded.

* A Paper read before the Liverpool Polytechnic Society, November, 1889.

Distribution of Gold in Lead Alloys.—To determine that my method of obtaining standard gold prills from lead alloys was not appreciably affected in accuracy by want of uniformity in the distribution of the gold throughout the lead, I prepared an alloy of gold with assay lead. After allowing the ingot of metal to slowly cool, portions of 2 grms. (30 grains) were taken from the top, centre, and bottom of the ingot, and separately assayed for gold.

The prills of parted gold measured respectively 15·9, 16·4, and 17·0 divisions, indicating 0·30, 0·32, and 0·36 m.grms., or 0·0046, 0·0049, and 0·0053 grain of gold. When the gold-lead alloys employed for preparing standard prills are well flattened, one may hence feel assured of the uniformity of the alloy.

Loss in Parting.—Gold prills varying from 0·0001 to 0·002 grain in weight according to measurements with the microscope were alloyed with various proportions of silver, parted from this metal, and then collected and fused into beads. In the majority of cases the prills were repeatedly alloyed and parted.

Parting tests A and B:—

Gold prills.	Measure (¼ inch).	Weight in m.grms.	Parting loss in m.grms.
Original	43	0·0772	
1st parting	43	0·0772	nil.
2nd ,,	40	0·0621	0·0151
3rd ,,	37	0·0491	0·0130
Original	43	0·0772	
1st parting	41	0·0670	0·0102
2nd ,,	40	0·0621	0·0049
3rd ,,	36	0·0452	0·0169
4th ,,	35·8	0·0445	0·0007
5th ,,	34·5	0·0388	
6th ,,	35	0·0416	0·0029

Total loss in 3 partings, A 36 per cent.

,, 6 ,, B 46 ,,

Average loss for 1 parting, A 12 ,,

,, 1 ,, B 8 ,,

Parting tests C:—

Original gold	0·000100 grain.
Gold after 1st parting	0·000088 ,,
Gold after 2nd ,,	0·000072 ,,
Loss in 2 partings	0·000028 ,, or 28 p. c.

Parting tests D:—

Gold taken	0·000100 grain.
After cupellation with large excess of silver and 100 grains lead, and parting twice	0·000075 ,,
Loss in 2 partings	0·000025 ,, or 25 p. c.

In the above tests the silver was in each case in excess of the quantity necessary for parting, but had not been weighed.

In the following series silver, in the form of a lead alloy, was added in definite amount. (See next column).

After each parting in these two series the silver solution was filtered through good filter paper. The paper was finally assayed for gold and found to contain 0·193 m.grm. gold, showing that 0·0196 m.grm. gold was presumably in the acid solution, and that one-half of the loss only was due to minute particles of float-gold being mechanically carried away in the washing.

Parting test G.—Gold 0·0193 m.grm., parted from 2500 times its weight of silver (0·05 gm.), yielded:—

Gold	0·0143 m.grm.
Loss on parting	0·0050 ,, or 25 per cent.

Parting test H.—Gold 0·0126 m.grm., parted from 16,000 times its weight of silver (0·200 gm.), yielded, after a second parting from a small excess of silver, necessitated by want of purity of the first prill:—

Gold	0·0071 m.grm.
Loss on parting	0·0055 ,, or 43 per cent.

Parting tests E:—

Parting No.	Gold measure 1-in. objective.	Parted from silver. M.grms.	Weight of gold. M.grms.	Loss in weight. M.grms.	Loss per cent.	Ratio gold: silver.
—	8·75	—	0·0491	—	—	—
1	8·75	0·25	0·0491	0	0	1:5
2	7·9	0·25	0·0350	0·0141	28	1:5
3	8·0	0·25	0·0374	0	0	1:7
4	8·0	0·50	0·0374	0	0	1:13
5	7·5	1·0	0·0309	0·0065	17	1:27
6	6·9	1·0	0·0239	0·0070	22	1:30

Parting tests F:—

—	9·9	—	0·0708	—	—	—
1	9·8	0·25	0·0685	0·0023	3	1:3·5
2	9·7	0·25	0·0662	—	—	1:3·5
3	9·8	0·25	0·0685	0	0	1:3·5
4	9·7	0·50	0·0662	0·0023	3	1:7
5	9·2	1·0	0·0571	0·0091	15	1:15

Average loss for each parting 8 per cent

Maximum loss 28 ,,

Minimum loss 0 ,,

Total loss on the combined weights of the original prills 0·0389 m.g. or 32%

From these and other parting tests I conclude that the average loss in parting the one-thousandth of a grain of gold from silver is about 5 per cent; in parting the one-tenth-thousandth of a grain, between 10 and 20 per cent; that the loss increases with the proportion that the silver bears to the gold, and that this loss is partly mechanical and partly owing to the solvent action of the nitric acid upon the gold when in presence of silver or of products of the reduction of the nitric acid.

The variations that I have noted in the loss on parting I attribute either to the variable molecular conditions of the alloys (dependent possibly upon rates of cooling) or to variations in the heating during the action of the acid, giving rise to variable products of reduction of the acid. Experiments are in progress to determine more accurately the cause of the solvent power of nitric acid upon minute quantities of gold.

Loss in Cupellation.—That gold suffers at most only an infinitesimal loss when cupellated with pure lead (free from silver) is satisfactorily proved by the accuracy with which the standard prill, the one-millionth of a grain, has been obtained by cupellation.

I will here briefly detail four experiments that show the gold suffers no appreciable loss during cupellation with antimony and copper.

Portions of gold, each 0·1 m.grm. (0·00154 grain), were alloyed with 15 grms. (300 grains) of lead containing a trace of silver, and cupellated separately with—

- (1). 0·5 gm. (8 grains) copper.
- (2). 0·5 ,, (8 ,,) antimony.
- (3). 2 ,, (30 ,,) copper.
- (4). 0·5 ,, (8 ,,) antimony after scorification.

After parting, the residual gold was estimated to be in m.grms. respectively 0·098, 0·111, 0·097, and 0·100 in the four experiments.

Loss of Gold in Extraction from Siliceous Ores.—To enable me to experiment with ores containing proportions of gold equivalent to 2 dwts. or less per ton (0·0003 per cent), I obtained from a rich gold ore siftings through a very fine sieve that gave fairly constant results on assay. This ore, in weighed quantity, was mixed with a large excess of sand and substances commonly occurring in quartz ores that were themselves free from gold. The mixtures thus prepared, representing poor gold ores of

Total weight of ore, grms.	Weight of gold in m.grms. introduced according to average.	Average content of gold in grains per ton.	Constituents of ore other than gold.	Lead alloy from crucible, in grms.	Gold obtained in m.grms.†	Gold obtained in grains per ton.	Apparent error in weight of gold.	Apparent error in grains per ton.	Remarks.
25	0.084	53	Silica.	17	0.103	63	+0.019	+10	10 grms. only of litharge used.
25	0.084	53	"	9	0.060	37	-0.024	-16	
60	0.084	22	"	20	0.085	23	+0.001	+1	2½ grms. arsenical copper precipitate.
15	0.084	87	Silica, Arsenic, Copper.	10	0.103	106	+0.019	+19	
15	0.084	87	Silica, Zinc, Sulphide.	11	0.093	97	+0.009	+10	Zinc blende, 2½.
20	0.084	65	"	23	0.093	73	+0.009	+8	Zinc blende, 5 grms., calcined.
15	0.093	97	{ Silica, Copper, Antimony, Sulphur. }	20	0.094	98	+0.001	+1	2½ grms. ore containing chiefly copper, antimony, and sulphur.

known content of gold, were assayed by the crucible method.*

The fine rich ore gave the following results on assay; in the first three tests the gold obtained was weighed, in the last six tests the gold was measured:—

5 grms. ore gave gold	4.1 m.grms.	or 0.082 p. c.
2 " " "	1.7 " "	or 0.085 " "
1 " " "	0.8 " "	or 0.080 " "
0.5 " " "	0.394 " "	or 0.0788 " "
0.5 " " "	0.442 " "	or 0.0884 " "
0.1 " " "	0.0885 " "	} averaging 0.0877 " "
0.1 " " "	0.0938 " "	
0.1 " " "	0.0980 " "	
0.05 " " "	0.0353 " "	

I concluded that a fair average for the gold in 0.1 grm. would be 0.084 m.grm., with probable minimum and maximum amounts respectively of 0.0788 and 0.0980.

By means of 0.1 grm., gold, according to the above average, to the amount of 0.084 m.grm. was added to various materials, which were then assayed with the results given in Table above.

In the second assay the gold was purposely separated under disadvantageous conditions, only 9 grms. of lead being produced in the fusion, but even here 70 per cent of the total gold was isolated.

The above results indicate that one-tenth of a m.grm. or 1½ thousandths of a grain of gold can be isolated from weights of siliceous ore, ranging from 15 to 60 grms. or from 200 to 1000 grains in weight, even in the presence of copper, arsenic, antimony, zinc, and sulphur compounds.

Finding that a millionth of a grain of gold could be cupellated from lead without loss, I successfully attempted the recognition of the millionth of a grain of the metal, when in alloy, with a trace of silver. The parting was conducted with a small drop of nitric acid upon a microscope slide. The black sponge of gold that was left was distinctly visible under the microscope. Washing was performed by adding drops of water and carefully applying to the edge of the liquid small pieces of bibulous paper. By watching the sponge, this separation of the silver solution can be successfully performed without loss of

* It would appear from my own observations and from the experience of other assayers that the method of fusion with litharge in a crucible gives results of greater accuracy than the method of scorification with lead. This is probably due to the difference in form of the two vessels, and no doubt accounts for the greater favour buyers show towards the latter method.

† The weights of gold in these test assays were estimated by comparison with 0.1 m.grm. standards only. These standards were some of the earliest prepared, and were cupellated upon ordinary (somewhat rough) cupels. The estimate of diameters of 0.1 m.grm. standards since prepared is such as to make these weights of gold about 12 per cent less than those given. The same error applies to the last four tests in the preceding table. Reference is made, and this chiefly to impress the necessity for employing smooth cupels for obtaining prills.

gold. After drying the slide it was again brought upon the stage of the microscope, and the gold picked up by means of a minute piece of pure lead fixed upon the point of a stout needle. By cupellation a distinct visible bead of yellow gold was obtained. It is thus possible, under favourable conditions, to recognise in a complex mixture even the millionth of a grain of gold.

This method of working under the microscope should be of value to geological science, by permitting of the search for gold in rocks neighbouring gold deposits, and thus throw light upon the "origin of gold in veins and lodes."

Data Useful in Assaying.

Parts of ore.	yielding	part of gold =	Per ton.		
			ozs.	dwts.	grains.
100	0.00001		0	0	1.5
"	0.0001	"	0	0	15.6
"	0.001	"	0	6	12
"	0.01	"	3	5	8
"	0.1	"	32	13	8
"	1.0	"	326	13	8
24 grains	..	equal to 1 pennyweight	} troy.		
20 pennyweights	..	1 ounce			
1 milligram. (m.g.)	..	equal to 0.0154 grain.			
1 thousandth grain	..	0.0648 milligram.			

Table of Cubes.

Number.	Cube.	Number.	Cube.
1.0	1	10.0	1000
1.5	3.3	10.5	1157
2.0	8	11.0	1331
2.5	15.6	11.5	1521
3.0	27	12.0	1728
3.5	42.9	12.5	1953
4.0	64	13.0	2197
4.5	91	13.5	2460
5.0	125	14.0	2744
5.5	166	14.5	3049
6.0	216	15.0	3375
6.5	275	15.5	3724
7.0	343	16.0	4096
7.5	422	16.5	4492
8.0	512	17.0	4913
8.5	614	17.5	5359
9.0	729	18.0	5832
9.5	857	18.5	6332

For figures that are not given in the table, and that are higher than 8, approximate cubes may be obtained by taking proportionate differences.

For cubes of numbers higher than those given, many can be obtained by taking the cube of half the figure and multiplying by 8. Thus, the cube of 24 will be 8 times

the cube of 12, or $1728 \times 8 = 13824$. The cube of 19 would be 8 times the cube of 9.5, viz., $857 \times 8 = 6856$.

The decimal points in the cubes have been omitted.

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLET, F.R.S.,

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UNTIL lately gold ranked among the elementary substances of which the general properties had been well ascertained, but in regard to the atomic weights of which our knowledge was least satisfactory. That this constant should be determined as accurately as possible for gold was desirable, in view of its bearing on the precise place assigned the metal in the "periodic" classification of the elements based on the ideas of Newlands, Odling, Mendeleeff, and L. Meyer. Furthermore, an exact knowledge of the atomic weight of gold might be conveniently applied in the determination of the atomic weights of some of the other elements. A practical laboratory reason for desiring to possess a trustworthy value for this constant was also presented by the facility with which gold compounds of many organic substances may be prepared, and the ease with which their composition may be ascertained by simple ignition in the air and weighing of the residual gold, the results leading to a knowledge of molecular composition when the atomic value of the weight of the metal obtained is assumed to be known.

For the last three years and a half I have been occupied, during a large part of such time as has been available for original work, in devising and carrying out experiments aiming at the re-determination of the constant in question. The difficulties met with have been greater than were at first looked for, and have led to much time and labour being consumed in attempts to overcome them. About two years ago, when this work was already well under way, but still in progress, there appeared the results of experiments aiming at the same end, by Krüss in Germany and by Thorpe and Laurie in England—experiments made with the care and accuracy of modern methods, and apparently deserving of much confidence. My own work, however, was continued, as we cannot have too many careful independent determinations of atomic weights by different workers, and as I had used to a considerable extent other processes than those on which the newly published determinations were based, while the chemists named had employed, in the main, one and the same method. A preliminary notice of my work was read in the Chemical Section of the British Association at the Manchester meeting of 1887. The details of my experiments and the results which I have reached are now laid before the Royal Society.

Earlier Determinations of the Atomic Weight of Gold.

In the work of L. Mulder, "Historisch-kritisch Overzigt van de Bepalingen der Æquivalent-Gewigten van 24 Metalen," Utrecht, 1853, and in the recent papers of Krüss and of Thorpe and of Laurie, there are abstracts of reports upon a number of experiments by chemists of the earlier part of this century, bearing on the value to be assigned to the atomic weight of gold, such as those of Proust,† Richter, ‡ Dalton,§ Thomson,|| Oberkampf,¶ Pelletier,** Figuier,†† and Javal;‡‡ but of these, none

deserve any attentive consideration at the present day, the methods used having, in some cases, been such that accurate results could not be expected from them, and the actual figures obtained in other cases differing so widely from each other that no importance can be attached to them.

Before the year 1887 but two chemists—Berzelius and Levol—had published the results of experiments furnishing fairly admissible data for calculating the atomic weight in question.

a. *Experiments of Berzelius, 1813.**—The method adopted was the precipitation of a solution of auric chloride by metallic mercury, determining the quantities of mercury dissolved and gold thrown down. In the original paper but a single experiment is reported, but later the author appears to have made a second,† so that for the two, Meyer and Seubert, in their re-calculation of the atomic weights of the elements,‡ give, as the sums of the amounts of mercury and gold found to be equivalent to each other, 24.240 grms. of the former and 15.912 grms. of the latter. Taking these quantities to represent the ratio between the weights of three atoms of mercury and two atoms of gold, we have for the weight of the single atom of the latter ($H=1$).

If we assume Hg = 199.8 (L. Meyer and Seubert†)	196.73
If we assume Hg = 199.712 (F. W. Clarke§)	196.65

This method recommends itself as advantageous on several grounds, and the experiment deserves repetition as soon as the atomic weight of mercury becomes known with greater certainty than at present. But until this condition is fulfilled the result for gold cannot be depended upon as of the first rank in exactness. In any renewed attempt to apply this method several questions would have to be examined as to the precise nature of the solution used and of the reaction itself.

(Berzelius|| also precipitated gold by means of a known quantity of phosphorus from a solution of the chloride used in excess, and his results, as calculated by F. W. Clarke,¶ lead to the atomic weight 195.303 for gold; but this process appears ill adapted to give very exact results, even in such hands as those of the great Swedish chemist, and the value obtained is certainly too low in the light of more modern researches).

b. *Experiments of Berzelius, 1844.***—In these experiments potassium aurichloride, which, it was found, could not be completely dried without loss of chlorine, was ignited in hydrogen, and the residue was treated with water to dissolve potassium chloride, the quantity of which was determined, as well as that of the metallic gold left undissolved. Five experiments were made, and the aggregate amounts obtained of potassium chloride and gold were 3.7800 grms. and 9.9685 grms. respectively. These figures, if we assume $K = 39.03$ and $Cl = 35.37$, give, for the atomic weight of gold, 196.20, the lowest result from one of the individual experiments being 196.11, and the highest 196.27.

Among possible sources of error in this process we may note, as deserving consideration, the conceivable retention, by the potassium aurichloride of hydrogen aurichloride, and the difficulty of directly determining with accuracy the potassium chloride extracted by water. The former would lead to a higher result for gold than should be obtained; the latter might either give too low a result in consequence of imperfect drying, or too high if there

* A Paper read before the Royal Society, May 9, 1889.

† *Journal de Physique*, vol. lxii., 1806, p. 131; N. Gehlen, *Journal*, vol. i., 1806, p. 477.

‡ *Schweigger, Journal*, vol. vii., 1813, p. 43

§ "New System," Part II., 1810, p. 253.

|| "First Principles," vol. i., 1825, p. 440.

¶ *Annales de Chimie*, vol. lxxx., 1811, p. 140.

** *Ibid.*, vol. xv., 1820, pp. 5, 113.

†† *Ibid.*, vol. lix., 1821, p. 177.

‡‡ *Ibid.*, vol. lvii., 1821, p. 337; *Schweigger, Journal*, vol. xxxiii., 1821, p. 238.

* *Stockholm Kgl. Vetensk. Akad. Handl.*, 1813, p. 185.

† Berzelius, *Lehrbuch*, vol. iii., p. 1212, str. 70.

‡ Lothar Meyer u. Karl Seubert, "Die Atomgewichte d. Elemente aus d. Originalzahlen berechnet," Leipzig, 1883, p. 191.

§ "The Constants of Nature," "Smithsonian Miscellaneous Collections," Washington, D.C.

|| Berzelius, *Lehrbuch*, 5 Aufl., vol. iii., p. 1188.

¶ "The Constants of Nature," "Smithsonian Miscellaneous Collections," Washington, D.C.

** Berzelius, *Lehrbuch*, 5 Aufl., vol. ii., p. 1212.

were partial loss by volatilisation, either during the ignition in hydrogen, or in subsequently recovering the potassium chloride from solution. The quantities of material used were smaller than is probably desirable.

*c. Experiments of Levol, 1850.**—A weighed quantity of gold was dissolved as auric chloride, the metal reduced from the solution by means of sulphur dioxide, and the sulphuric acid formed was determined as barium sulphate. In two experiments, reported as giving exactly the same result, 1 grm. of gold gave 1.782 grms. of barium sulphate. Hence, if Ba be taken = 136.86, S = 31.98, and O = 15.96, we have, for the atomic weight of gold, the number 195.86.

Of the sources of error to which this method is liable, probably the most important are atmospheric oxidation of sulphurous to sulphuric acid and imperfect washing out of soluble compounds of barium from the barium sulphate. Both would tend to give too low a result for gold.

For all these earlier experiments details are wanting as to the exact mode of purification of the gold and other materials used, and in the weighings there appears to have been no correction introduced for atmospheric buoyancy; the results doubtless represent apparent, not absolute weights.

(There is also to be quoted the statement of Julius Thomsen,† that he found in hydrogen bromate (AuBr₃.HBr.5H₂O) 32.11 per cent of gold and 52.00 per cent of bromine, from which he concluded that Au = probably about 197. Taking Br = 79.76, and calculating from the ratio of Br₄ : Au, the number is 197.01.)

Recent Careful Determinations of the Atomic Weight of Gold.

a. Experiments of Gerhard Krüss, 1886.‡—The author has described in detail the means resorted to for the preparation of pure metallic gold, and especially for its separation from silver and the metals of the platinum group, with an account of the spectroscopic examination of the gold employed. He has then given a full account of:—(a) His determinations of the gold and chlorine (the former reduced by a stream of sulphur dioxide; the latter precipitated and weighed as silver chloride) in a neutral solution of auric chloride, prepared by the action of water on the so-called auro-auric chloride (Au₂Cl₄),§ itself, prepared by the direct action of chlorine on metallic gold; (b) Like determinations of gold and chlorine in sublimed auric chloride, made by direct action of the elements on each other with careful regulation of the temperature. (c) Determinations of the gold in a weighed quantity of potassium auribromide (KAuBr₄), the metal in some experiments reduced from a solution of the salt by sulphurous acid, in others reduced from the dry salt by heating in a stream of hydrogen; (d) Determinations of the gold and bromine (the former thrown down by sulphurous acid; the latter precipitated as silver bromide) in the same salt, potassium auribromide; (e) Determinations of the loss of weight (representing 3 atoms of bromine for 1 of gold) undergone by heating potassium auribromide gradually to 320° C., towards the end, in a stream of hydrogen; (f) Determinations of the quantity of potassium bromide recovered from the residue left in the experiments of (e) by treatment of this residue with water, separation of the metallic gold, careful evaporation of the liquid, and final cautious heating of the potassium bromide over a free flame. In the experiments of series *a* account was taken of the somewhat different processes of purification of the gold used, but no corresponding

differences being observable in the results obtained, no further record was made in the remaining series of the history of the gold used in these.

After correction of the weighings for atmospheric buoyancy in such cases as seemed to the author to involve a correction worth noticing, the following results were calculated from the figures obtained, these figures agreeing in general closely with other in each series:—

Series.				
<i>a.</i>	Mean of 8 experiments.	Atomic wt. of gold	=	196.622
<i>b.</i>	" 4	" "	" "	= 196.143
<i>c.</i>	" 9	" "	" "	= 196.741
<i>d.</i>	" 5	" "	" "	= 196.743
<i>e.</i>	" 4	" "	" "	= 196.619
<i>f.</i>	" 4	" "	" "	= 196.620

Leaving out the results of series *b*, on the ground of the very small quantity of sublimed auric chloride available, and the considerable discrepancy of one of the results (that in which most material was used) from the rest, the author calculates from the remaining 30 experiments the general mean 196.669; but, taking into account the greater or less closeness of agreement of the figures obtained by the several methods, he comes to the conclusion that 196.64 may better be assumed as the true atomic weight of gold. In these calculations Ag was assumed = 107.660, Cl = 35.368, Br = 79.750, and K = 39.040.

As regards possible sources of constant error in Krüss's experiments, it may be observed that—

1. In series *b* very small quantities of sublimed auric chloride were used—the whole amount available for all four experiments being only about seven-tenths of a grm.—and it is probable that a little free chlorine may have been physically retained by the chloride in spite of the long-continued passage over it of dry air. The experiment in which the largest quantity of material was used gave the atomic weight = but 194.79. On these grounds the author himself excludes the series from consideration in calculating his general mean.

2. In series *c*, *d*, and *e* the evidence is pretty strong, but perhaps not conclusive, to show that potassium auribromide can be rendered absolutely dry by exposure to air in a vessel containing phosphorus pentoxide, either at ordinary or higher temperatures, without, at the same time, undergoing any loss of bromine. The attainment of constant weight by the salt does not positively prove the entire removal of water. If moisture were retained the atomic weight of gold found would be brought out lower than it should be.

3. Krüss himself observed that in all cases in which he dissolved potassium auri-bromide in water, a small residue of metallic gold was left, and, determining in a single experiment the amount of this (about 0.05 per cent), he used it as a correction for all his results. As pointed out by Thorpe and Laurie,* this partial decomposition of the salt was probably due to the action of dust from the air. If the results obtained from the solution were used, without any correction, to establish the atomic weight of gold, the tendency would, of course, be to a value lower than the truth. Although the correction introduced is small, it can hardly be supposed that it should be taken as constant in amount in all the experiments.

4. In series *e* it may be questioned whether traces of potassium bromide may not have been volatilised at the highest temperature used, or the residual potassium bromide may not have, to a small extent, exchanged bromine for oxygen while heated in air (before the use of the stream of hydrogen), the latter change being one to be guarded against whenever haloid salts are strongly heated in the presence of free oxygen. The tendency in both cases would be to a lower atomic weight for gold.

5. In series *f* there was risk of slight loss of potassium bromide during filtration and evaporation of its solution,

* *Annales de Chimie* [3], vol. xxx., p. 355.

† *Journ. Prakt. Chem.*, vol. xiii., 1876, p. 345.

‡ *Liebig's Annalen*, vol. ccxxxviii., p. 30; and separate publication, G. Krüss, "Untersuchungen über das Atomgewicht des Goldes," München, 1886.

§ Krüss has, in a later paper (*Berichte Deutsch. Chem. Gesell.*, vol. xx., p. 2634) denied the existence of auro-auric chloride as a definite compound, but admits that the substance so described by Julius Thomsen yields, on treatment with warm water, a solution of pure neutral auric chloride, with separation of metallic gold.

* *Chem. Soc. Journ.*, Dec., 1887, p. 866.

and during exposure of the salt to the heat of a free flame, when there might possibly have been again slight replacement of bromine by oxygen, thus causing the atomic weight sought to come out too high, or else, on the other hand, risk of imperfect drying, which would give too low a value for the atomic weight in question.

On the whole it seems probable that the tendency of most of the constant errors to be suspected in connection with Krüss's experiments—experiments carried out with remarkable patience, skill, and apparent freedom from merely "fortuitous" errors—was in the direction of an atomic weight for gold somewhat below, rather than above, the true value.

*B. Experiments of Thorpe and Laurie, 1887.**—In these experiments potassium auri-bromide was used, and determinations were made:—*a.* Of the weight of the residue left on heating the salt over a Bunsen flame till bromine ceased to be given off (this residue consisting of metallic gold and potassium bromide), and the weight of the gold left by such residue after all potassium bromide had been washed out of it by water; *b.* Of the weight of silver necessary to be added as nitrate to the solution of potassium bromide obtained in *a* in order to just precipitate the bromine present; *c.* Of the weight of the silver bromide so precipitated. All suitable experimental precautions seem to have been taken, and the weighings were corrected for atmospheric buoyancy. The individual results in each series agreed with each other even more closely than in Krüss's research.

The results obtained were as follows, using in calculation the numbers $Ag = 107.66$, $Br = 79.75$, and $K = 39.03$:—

Series.

<i>a.</i>	Mean of 8 experiments.	Atomic wt. of gold	=	196.876
<i>b.</i>	" 9 "	" "	=	196.837
<i>c.</i>	" 8 "	" "	=	196.842

The general mean of these values, giving equal weight to the different series, is 196.852.

As regards possible sources of constant error specially belonging to these experiments, it is to be noticed—

1. There is an advantage, as observed by the authors themselves, over the greater part of the experiments of Krüss in the nature of the relations employed not requiring that the potassium auri-bromide should be perfectly dry, the exact quantity of the original salt not needing, in fact, to be known.

2. In series *a* it is conceivable that there might have been slight volatilisation of potassium bromide, or interchange in it to a small extent of bromine for oxygen, during the heating of the original salt, or retention of traces of potassium bromide by the metallic gold when washed—the latter but little probable. Any of these defects, if existing, would cause the method to give a higher value for Au than the true one.

3. In series *b* the probability seems to be in favour of not quite the whole of the original potassium bromide being actually used, and minute loss of silver solution having perhaps occurred, so that rather more of this solution was counted as used than the true quantity. If so, the former defect would tend to raise, the latter to lower, the atomic weight of gold.

4. In series *c*, in view of the evidence adduced to prove complete drying of the silver bromide, it is more likely that its weight as obtained was below, rather than above, the truth. Hence we should suspect, if any constant error exist, that it would rather tend towards an unduly high value for Au.

On the whole, there seems to be less reason to fear sources of constant error of any considerable amount in connection with the experiments of Thorpe and Laurie than with those of Krüss, and the drift is in the opposite direction, tending rather to give too high than too low a value for the atomic weight to be determined.

It should be mentioned that Krüss* has claimed that in the potassium auri-bromide used by Thorpe and Laurie there was probably as much free gold as he considered to exist in the salt used by himself, and on this assumption has calculated that the three series of experiments by the English chemists should, if corrected on this account, lead to the numbers 196.616, 196.559, and 196.575 respectively for Au. From this conclusion the latter chemists altogether dissent,† and express their confidence that in none of the preparations used by them was there free gold sufficient to account for the difference between their own results and those of Krüss

(To be continued).

OBITUARY.

THE LATE M. G. A. HIRN.

M. G. A. HIRN, correspondent of the Physical Section of the Academy of Sciences, died at Colmar on January 14, in his seventy-fifth year. He was carried off by the prevailing epidemic. The deceased *savant* was born at Logelbach, August 21, 1815, and was nominated as a correspondent of the Academy in the Physical Section in 1867. In his twenty-sixth year, in conjunction with his elder brother, Ferdinand, he undertook the direction of the extensive tissue-printing works of Haussmann, Jordan, and Co., at Logelbach. He made a series of remarkable investigations on superheated steam, the use of steam-jackets, the exchange of heat through metal walls, &c. He also undertook studies on lubricating oils, and introduced the use of mineral oils which had been considered unfit for lubrication. One result of his labours was to make him a fervent believer in the mechanical theory of heat. He installed, in the region of the Vosges, posts of meteorological observation at different altitudes, and the results obtained formed the substance of several communications to the Academy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 3, January 20, 1890.

The Different States of Graphitic Carbons, and on the Corresponding Chemical Derivatives.—M. Berthelot and P. Petit.—The study of the isomerism of simple bodies, otherwise called allotropy, is one of inquiries which enable us to penetrate furthest into the constitution of matter and of the chemical elements, and that of the allotropies of carbon is particularly interesting. In examining the multiple states of carbon one of the authors has sought to explain them by the polymeric condensations of the true element designated by that name, which has no permanent existence in the free state of a simple molecule. The graphites in particular, when oxidised by the moist way at a low temperature, form ternary compounds, one of the terms of which have been discovered by Brodie. M. Berthelot has since shown that there are several different states or graphites chemically distinct, forming each a special graphitic oxide, which produces a corresponding hydrographitic and pyrographitic oxide, and may be reproduced from them with

* *Chem. Soc. Journ.*, June, 1887, p. 565, and Dec., 1887, p. 866.

* *Berichte Deutsch. Chem. Gesell.*, vol. xx., p. 2365.

† *Chem. Soc. Journ.*, Dec., 1887, p. 868.

the speciality of its primitive characters. There are three distinct graphitic oxides; that of the graphite of cast-metal contains 62.7 per cent of carbon; that of amorphous graphite (plumbago) contains 56.2 per cent; and that of electric carbon 51.9 per cent. The comparison may be made by admitting that one and the same proportion of oxygen, such as O_{16} , is combined in the three bodies to carbons differently condensed, *i.e.*, $2C_{28}$ in the first, $2C_{22}$ in the second, and $2C_{16}$ in the third. Each graphite would thus represent a different simple radicle, which is permanent in its combinations, as Brodie has already shown for one of them.

Combustion- and Formation-Heat of the Graphitic and Pyrographitic Oxides.—M. Berthelot and P. Petit.—A thermo-chemical paper, which does not admit of useful abstraction.

Remarks on the Formation of Nitrates in Plants.—M. Berthelot.—M. Heckel has shown that the caffeine contained in the seeds of Kola disappears progressively along with the formation of potassium nitrite. M. Lundström has also shown that saltpetre takes its rise in special organs of the coffee and other trees. These observations seem to throw a new light on the formation of saltpetre in the Amaranths observed some years ago by M. André and M. Berthelot. These facts establish the likeness and the connection between the life of microbia inhabiting the soil and that of microbia which inhabit plants, and which often there intensify their specific chemical activity.

The Combinations of the Alkaline Metals with Ammonia.—H. W. Bakhuis-Roozeboom.—This paper constantly refers to an accompanying diagram.

The Absorption of the Ultra-Violet Rays by Certain Organic Substances belonging to the Fatty Series.—J. L. Soret and A. A. Rilliet.—The author communicates the conclusions to which they have been led in researches on the absorption of the ultra-violet rays. Many of their results agree with those of MM. Hartley and Huntington (*Phil. Trans.*, 1879, Part I.). The alcohols of the fatty series are generally very transparent for ultra-violet rays. They estimate that the degree of absorption of these rays constitute a very delicate means for recognising the purity of organic bodies.

The Refractive Powers of Double Salts in Solution.—E. Doumer.—In general the molecular refractive power of a salt, whether simple or double, is proportional to the number of valencies of the metallic portion of the salt. The facts observed afford a means of determining the molecular refractive power of simple salts which are not easy to prepare in a state of purity, but which are capable of yielding double salts, soluble and easily purified.

The Substitution-Derivatives of Ammonium Chloride.—J. A. Le Bel.—Certain chemists consider this salt as a chloride of nitrogen pentahydride, ascribing to the five atoms linked to the nitrogen a part exactly identical. Others consider it as an ammonium hydrochlorate. The author's views do not admit of abridgment.

Reactions between Salts of Copper and Metallic Cyanides.—Raoul Varet.—The haloid salts of copper undergo double decomposition with all the cyanides. The oxalates are without action upon the mercury and silver cyanides only.

The Different Dextro-, Levo-, and Racemic Bornylphenylurethanes, and on the Isobornylphenylurethanes.—A. Haller.—Not adapted for useful abstraction.

The Physiological Action of Selenious Acid.—C. Chabrié and L. Lapicque.—The organic sulphides yield neutral oxides, whilst the oxides of the selenides of the fatty series are strongly basic. A dose of selenious acid a little above two-thousandths is necessary to prevent the fermentation of beef-broth under the action of the microbia of the atmosphere. Sulphites, if injected into the blood

of an animal, are transformed into sulphates, which possess no poisonous action. The selenites are not oxidised under these conditions. An aqueous solution of selenious acid accurately neutralised with soda is fatal to dogs if introduced in the proportion of 3 m.grms. per kilo. of the weight of the animal. The heart is arrested in systole, and all the viscera are intensely congested.

MISCELLANEOUS.

Royal Society of New South Wales.—*Original Researches.*—The Royal Society of New South Wales offers its Medal and a Money Prize for the best communication (provided it be of sufficient merit) containing the results of original research or observation upon each of the following subjects:—

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No. 32. On the Silver Ore Deposits of New South Wales. The Society's Medal and £25.

No. 33. On the Occurrence of Precious Stones in New South Wales, with a Description of the Deposits in which they are found. The Society's Medal and £25.

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The competition is in no way confined to Members of the Society, nor to residents in Australia, but is open to all without any restriction whatever, excepting that a Prize will not be awarded to a Member of the Council for the time being; neither will an award be made for a mere compilation, however meritorious in its way. The communication, to be successful, must be either wholly or in part the result of original observation or research on the part of the Contributor. The Society is fully sensible that the money value of the Prize will not repay an investigator for the expenditure of his time and labour, but it is hoped that the honour will be regarded as a sufficient inducement and reward. The successful Papers will be published in the Society's Annual Volume. Fifty reprint copies will be furnished to the Author free of expense. Competitors are requested to write upon foolscap paper—on one side only. A motto must be used instead of the writer's name, and each Paper must be accompanied by a sealed envelope bearing the motto outside, and containing the writer's name and address inside. All communications to be addressed to the Honorary Secretaries, Mr. F. B. KYNGDON and Mr. W. H. WARREN, The Society's House, 5, Elizabeth Street, Sydney.

New Process for the Preparation of Alumina and Alkaline Aluminates.—Dr. K. J. Bayer.—The author's process is based upon the fact that a solution of sodium aluminate (obtained by treating bauxite with sodium carbonate or sodium sulphate and carbon) is decomposed on agitation with alumina.—*Chemiker Zeitung.*

NOTES AND QUERIES.

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

Phosphorescence.—Will any of your readers kindly inform me of the cause of the gleam of light seen when some finely powdered limestones are projected on to a heated surface; as, for example, into a platinum crucible heated so as to show just dull red in the dark? I have noticed this in the case of a great number of limestones, the gleam of light varying much in intensity and colour, from white to dark yellow and yellowish green.—W. J. COOPER.

MEETINGS FOR THE WEEK.

- MONDAY, 10th.—Medical, 8.30.
— Society of Arts, 8. "The Electro-magnet," by Silvanus P. Thompson, D.Sc., M.I.E.E.
- TUESDAY, 11th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
— Institute of Civil Engineers, 8.
— Photographic, 8. (Anniversary).
— Royal Medical and Chirurgical, 8.30.
— Society of Arts, 8. "Cast-iron and its Treatment for Artistic Purposes," by W. R. Lethaby.
- WEDNESDAY, 12th.—Society of Arts, 8. "Modern Improvements in Facilities for Railway Travelling," by George Findlay.
— Microscopical, 8. (Anniversary).
— Pharmaceutical, 8.
- THURSDAY, 13th.—Royal, 4.30.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
— Royal Institution, 9. "The Three Stages of Shakspeare's Art," by Rev. Canon Ainger, M.A., LL.D.
- FRIDAY, 14th.—Quekett Club, 8.
— Astronomical, 3. (Anniversary).
— Royal Institution, 9. "Problems in the Physics of an Electric Lamp," by Prof. J. A. Fleming, M.A., D.Sc.
- SATURDAY, 15th.—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.

A Gentleman (age 40) holding Advanced Science and Art Certificates in the following subjects wishes for appointment:—Mathematics (Second Stage); Sound, Light, and Heat; Electricity and Magnetism; Inorganic Chemistry; Organic Chemistry (Hon.); Geology; Human Physiology; Botany; Biology; Metallurgy; Steam and Applied Mechanics; National Medallist in Physiology; Trained in Chemistry, Physics, and Biology at Normal School of Science, London. Good Demonstrator and Lecturer.—Address, "Science," CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1577.

ON THE GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR.

ON the strength of Dumas's famous "Recherche sur la Composition de l'Eau" (*Ann. Chim. Phys.* (3), vol. viii., p. 189) all chemists, until lately, agreed in assigning to the atomic weight of oxygen the value $O = 16$ ($H = 1$); and it is on the strength, chiefly, of the same evidence that many of us now hold that $O = 15.96$ is a closer approximation to the truth.

In these circumstances it is surely worth while to look into Dumas's work with the help of critical experiments, and to try and see whether the great master was not right in thinking that, all his great efforts notwithstanding, the difference lies within the influence of his *method* errors, the more so as all these errors (as far as one can see without experimenting) tend to raise the experimentally ascertained value of the ratio $H : O$ above its true value.

I accordingly, some time ago, caused my private assistant, Mr. J. B. Henderson, to join me in this inquiry, and, thanks to his youthful energy and enthusiasm, we have already made considerable progress in our experiments, and hope, before long, to lay a complete account of them before the Society. Meanwhile, I content myself with stating that we have succeeded in so modifying Dumas's *modus operandi* as to give a higher degree of constancy to the weighings, and to reduce the trouble and loss of time involved to far less than it was with the original form of the method.

The principal object of the present communication, however, is to direct attention to an oversight which Dumas made himself guilty of, and which, as far as I am aware, has never been noticed before. What I allude to is that Dumas, while weighing his oxygen (virtually) *in vacuo*, weighs his water in air, and forgets to reduce this latter weight to the vacuum.

That the correction tells very appreciably on the calculated weight of the hydrogen, a very little reflection is sufficient to show; I prefer to at once give the results of my re-calculation of Dumas's results, and apply the correction to my "most probable" value.

In his tabular statement of results (p. 200 of his memoir) Dumas gives, in the case of each of his nineteen experiments, two values for what he calls the equivalent of hydrogen (the term meaning, with him, the weight of hydrogen which unites with 10,000 parts of oxygen into water), viz.: firstly, the value as calculated from the uncorrected weights of water and oxygen, and secondly, the "equivalent as corrected for the air in the sulphuric acid" (employed for the evolution of the hydrogen from zinc). For reasons which will be stated in our memoir I have left these corrected values on one side, and reduced only the "*equivalents bruts*."†

Taking S as a symbol for the weight of oxygen consumed in a given synthesis, and W as representing the uncorrected weight of water produced, I formed the nineteen equations:—

$$\begin{aligned} W_1 - kS_1 &= \delta_1. \\ W_2 - kS_2 &= \delta_2. \\ W_3 - kS_3 &= \delta_3. \\ \dots \dots \dots \end{aligned}$$

and solved these in respect of k , firstly, in the way which reduces the algebraic sum of all the errors δ to nil; and secondly, so as to reduce the sum of the squares of the errors δ to its minimum. The first method gave $k = 1.125, 43$; the second gave $k = 1.125, 47$. The two values, as we see, are almost identical. Adopting the second, it may be read as stating that 1000 grms. of oxygen take up hydrogen to form a quantity of water whose apparent weight in air is 1125.47 grms. But, assuming the air to have the density corresponding to $15^\circ C.$, and 760 m.m. (which probably is not far removed from the air density which actually prevailed during Dumas's work), the air displaced by the water amounts to 1.38 grms., whence we have, in reference to any given quantity of water, the following relative values for the weights of—

Oxygen.	Hydrogen.	Water.
1	0.126 85	1.126 85
8	1.014 8="H."	
15.767="O."	2="H ₂ ."	

The results of our own experiments tend to show that the true value of "H" ($O = 16$) is probably not quite so high as 1.0148, but it is higher than the 1.0024 demanded by the customary " $O = 15.96$."

I venture to hope that the publication of this notice will cause those chemists, who hitherto (after having become convinced that $O : H$ is less than 16) have persisted in referring their atomic weights to $H = 1$, will give up this absurd practice, and, as sensible people, adopt $O = 16$ as their standard. The sixteenth part of the atomic weight of oxygen, surely, is as good a unit as one could desire to have.

P.S.—The above had already been forwarded to the secretary of the Royal Society, when a friend directed my attention to a passage in Dumas's memoir, which I must confess had escaped my attention. In the course of his critical remarks on Berzelius's quantitative syntheses of water (by means of the oxide of copper method), Dumas points out that Berzelius ought to have reduced his water weights to the vacuum, but neglected this important correction.

With this sentence before one it is difficult to think that Dumas should have forgotten the very same correction in his own experiments, and yet I feel quite convinced he did, for the following reasons:—

1. While minutely describing his mode of weighing the oxide of copper, and the copper obtained therefrom in the same evacuated vessel, he is silent on this point in connection with the determination of the weight of water obtained.

2. Had he used the same method for the water which he adopted for the oxygen, the air-pump would have had to be attached to the last U-tube of the water apparatus, and, as at his time vulcanised indiarubber was not invented yet, we should see a stopcock at that U-tube in his very complete and detailed drawing of the apparatus. But no such thing is to be seen.

3. After having allowed his reduced copper to cool in hydrogen he detaches the bulb containing it, pumps out the hydrogen, and then weighs the evacuated apparatus. While this is being done a current of dry air is made to pass through the apparatus containing the water, to displace the hydrogen, and render the apparatus fit for the balance. If the water vessel was meant to be evacuated before being weighed, why not pump out the hydrogen?

4. Had Dumas weighed the water in the ordinary way, and then added on the weight of the displaced air, then, on the table of results (p. 200) the numbers given as representing the weights of water obtained could not agree with the differences between the weights of the water receptacle before and after the experiment.

5. Last, not least, the experiments made by Mr. Henderson and myself agree very nearly with Dumas's; but

* Read before the Royal Society of Edinburgh, February 3, 1890.
† As already pointed out by Lothar Meyer and Seubert, Dumas's table includes quite a number of misprints. These, however, are all easily spotted and set right without much fear of error.

they do so only as long as we neglect to correct our water weights for the displaced air.

ADDENDUM.—Not wishing to conceal anything that tends to invalidate my hypothesis, I will point out that Erdmann and Marchand, in their well-known syntheses of water, by means of the oxide of copper method (Erdmann's *Journ. f. Prakt. Chem.*, 1842, vol. xxvi., p. 461), obtained almost exactly the same value for H as Dumas did, although they *did* reduce their water-weights to the vacuum. But from their memoir it appears that, while they used (recently fused?) caustic potash for drying their hydrogen before it entered their oxide of copper tube, they dried the outgoing excess of hydrogen (and air at the end) only with (fused?) chloride of calcium. Now it is fair to assume that the caustic potash dried the gas *completely*, while we know, on the other hand, by Fresenius's experiments, that *fused* chloride of calcium leaves about one milligram of water in every litre of gas that enters the U-tube in a moist state. Hence, although Erdmann and Marchand, like Dumas, *produced* the correct amount of water from a given weight of oxygen, the German investigators had less water on the balance than Dumas, and came up to his number only by adding on the weight of the displaced air, which Dumas did not. As soon as we have completed our own experiments we shall try and see whether my premisses are correct.

Anderson's College Buildings,
February 10, 1890.

ESTIMATION OF FATTY ACIDS IN ALIZARIN OIL.

By ROWLAND WILLIAMS, F.I.C., F.C.S.

As one who has had a good deal of experience in the determination of fatty acids in oleine (alizarin or Turkey-red oil), perhaps I may be permitted to point out certain sources of error in the process proposed by Mr. Fred. Guthrie for this purpose (*CHEM. NEWS*, vol. lxi., p. 52). I think it only right to do this, because if Mr. Guthrie's process were generally adopted by chemists in calico printing and dye works, a serious injustice would be inflicted upon makers of and dealers in alizarin oil.

As ordinarily prepared, alizarin oil contains a small proportion of alkali combined with part of the fatty acids, the remainder of the fatty matter being present mainly in the form of free sulpho-fatty acids. In the case of oleine made from castor oil, the fatty matter consists largely of sulpho-ricinoleic acid, which, as everyone knows who has worked with this substance, is comparatively soluble in water.

The idea upon which Mr. Guthrie apparently bases his process is, that if alizarin oil be heated first with soda and then with a slight excess of sulphuric acid, the sulpho-compounds are decomposed, and may be removed by filtration and washing with boiling water. This idea is, I believe, quite erroneous. I am of opinion that if a fatty acid, *e.g.*, sulpho-ricinoleic, be treated as described above, sulpho-ricinoleic acid would be again liberated. According to Mr. Guthrie, however, this is not the case, as he states that by working in the above-mentioned manner "the sulpho-fatty acids are decomposed, the sulphuric acid washed away; therefore the fatty acids do not blacken and decompose on drying at 212° F.," thereby implying that, in the case of oleine made from castor oil, ricinoleic, and not sulpho-ricinoleic, acid is the final product of his method of analysis. Even if this assumption were correct, the figures obtained by such a process would be totally unfair to the vendors of alizarin oil, and they would naturally decline to accept such results, for the simple reason that when they guarantee, say, 50 per cent fatty acids, they mean sulpho-fatty acids; whereas, if Mr. Guthrie's statement be accepted, his method would

indicate the percentage of ricinoleic acid—an altogether different thing.

One of the advantages which Mr. Guthrie claims for his process is that "the fatty acids are practically insoluble in boiling water." Now, I venture to say that this expression of opinion is contrary to the experience of all who have had occasion to work upon the fatty and sulpho-fatty acids of castor oil. Even ricinoleic acid is somewhat soluble in hot water, while sulpho-ricinoleic acid forms a white emulsion, some of which would certainly be carried away with the wash-water employed. It seems to me, therefore, that whether the result obtained be moderately near the truth, or decidedly too low, depends almost entirely upon the amount of washing to which the fatty acids are submitted.

The great objection to Mr. Guthrie's process is that he makes no attempt to substantiate its accuracy by comparison with other well known and reliable methods. Not a single figure is brought forward, nor the result of any experiment recorded, which might prove that the "threefold advantages" which the process is alleged to possess have any real foundation on fact.

It seemed worth while, therefore, to test the accuracy of the process on two samples of oleine, which I have just examined by my usual method. The results, which are given below, were, as I anticipated, much too low.

	Fatty acids, per cent.	
	Guthrie.	Williams.
No. 1 sample	38·4	46·9
No. 2 ,,	44·3	50·8

These figures are, I think, sufficient to convince anybody of the inaccuracy of the process which Mr. Guthrie recommends.

I may say, however, that the process failed still more signally when tried on a sample of 75 per cent oleine, such as is manufactured for export. The result was more than 12 per cent too low, the solubility of the fatty acids being very apparent in this particular case. There are one or two other points in the process to which exception might reasonably be taken, but I trust I have said enough to prove the unreliability of the proposed method.

Laboratory and Assay Office,
28, Pall Mall, Manchester,
Feb. 4, 1890.

THE DETERMINATION OF SULPHURIC ACID IN PRESENCE OF IRON.

By G. LUNGE.

As far back as 1881 the author found that opening up iron pyrites in the wet way, for which he had proposed an especial method, did not give perfectly accurate results if the sulphuric acid is precipitated in the ferriferous solution. The precipitate always contains arsenic, and the results are rather too low (on an average, 0·18 per cent of sulphur in ordinary pyrites). The precipitate may, indeed, be obtained perfectly free from iron, but only by using great quantities of acid in washing, which dissolves away about $\frac{1}{2}$ per cent of sulphur in the state of barium sulphate. This may, indeed, be recovered, but it is better, before precipitating the barium sulphate, to throw down the ferric oxide by means of a moderate excess of ammonia, and to wash upon the filter with boiling water. Even with a single precipitation it is quite possible to render the precipitated ferric oxide perfectly free from sulphur, which was ascertained by drying the precipitate, fusing with soda, and testing the solution for sulphuric acid, of which not even a trace was ever found.

This method, after its description in the "Pocket-Book for the Alkali-Manufacturer" (1883), was brought into very general use both in Germany and England for the valuation of iron-pyrites,

Though the experiments of Jannasch and Richards did not relate to this latter improved method, but to the author's former one (which he had himself pronounced not perfectly accurate), the suspicion might arise among the many chemists interested whether the more recent method (of 1881) was in question. To remove this doubt and to satisfy himself that no error had occurred in his experiments, he caused the question to be independently re-examined by Herr Barbezat and Obregia.

H. Barbezat showed that the precipitation of the ferric hydroxide must be effected exactly as laid down by the author in 1881, *i.e.*, the moderately warm liquid must be mixed with ammonia in moderate excess, let stand for about ten minutes, then filtered and washed upon the filter with boiling water, keeping the precipitate constantly stirred up. In this case the ferric hydroxide retains no sulphur. But if the operator proceeds—as it is elsewhere directed for the precipitation of the iron—by adding a very slight excess of ammonia and removing this by prolonged boiling, there remains behind a very appreciable quantity of basic ferric sulphate, up to 3.6 per cent of the total sulphur. Hence this method should not be adopted.

H. Obregia made direct comparative experiments on very pure Spanish pyrites, in which there was no reason to fear any complication in the comparison of the methods from the presence of galena, &c. He determined the sulphur according to the three following methods:—A, by opening up with a mixture of 1 part hydrochloric acid, 3 parts nitric acid, and direct precipitation with barium chloride (*i.e.*, according to Prof. Lunge's earlier method, which he had pronounced not perfectly accurate as far back as 1881); B, opening up as above, precipitating and washing the ferric hydroxide, and afterwards precipitating with barium chloride (*i.e.*, Prof. Lunge's method of 1881). Here he generally succeeded when operating upon 1 grm. pyrites to obtain not more than 200—250 c.c. of liquid *before* adding the barium chloride, so that the precipitation of the sulphuric acid could be effected at once without concentration. C., by opening up with soda, exactly according to the method of Fresenius employed by Jannasch and Richards.

In the series of experiments, B, the iron precipitate was also fused with soda and tested for sulphuric acid, not a trace of which was ever found, exactly as in the experiments of Prof. Lunge in 1881.

The following are the proportions of sulphur found:—

A. Lunge's old method.	B. Lunge's method of 1881.	C. Method of Fresenius.
52.38	52.70	52.46
52.38	52.41	52.49
51.94	52.22	52.31
	52.26	
	52.39	
Mean.. 52.23	52.40	52.40

Hence the following conclusions may be safely drawn:—

1. The author's method of 1881, above described, gives results which quite agree with those of the saltpetre-soda melting process of Fresenius. If we reject the first of the experiments B as probably too high, the mean of the series is 52.32, *i.e.*, only 0.1 per cent lower than the mean of the Series C.

2. It is fully proved that the iron precipitate, if properly treated, retains no sulphuric acid.

3. The former opinion of Jannasch and Richards, that the Lunge process, from a purely scientific view, must be rejected, is not applicable to the process described in 1881. This is found quite as accurate as that of Fresenius, and has the advantage of requiring less time and less skill, and of not ruining platinum crucibles. In the rare cases when it is requisite to determine the sulphur present in

heavy spar and galena, this can be effected by fusing the residue insoluble in acids with soda.—*Journal für Praktische Chemie.*

ON THE
DECOMPOSITION OF ORGANIC MATTER
IN WATER.*

By MARK POWERS.

THE experiments herein detailed were undertaken with a view to obtain more exact information in regard to the decomposition of organic matter in water. While we have experimental evidence bearing on many points in connection with the subject, a review of this evidence will show that in many cases conclusions have been drawn which can be scarcely justified by the facts already known. We find many conflicting statements in the literature of the subject, and because of this fact and of the undoubted importance of the question, I have thought it worth while to repeat certain experiments with such modifications as would be most likely to reveal the truth in each instance. I have also endeavoured to obtain further facts to aid in the solution of the problem.

The organic matter dissolved by water or held in suspension is derived from the decay of the proximate constituents of plants and animals, and may be taken up at any stage of this process. The compounds which enter into the composition of this matter are more or less unstable, undergoing change with ease, and very little is known concerning their individual properties. The element of danger does not arise from any inherent toxic properties of these compounds, but from the fact that water containing such matter serves as an excellent means for the development and distribution of disease germs. Certain products of decay are much more harmful than others in this respect, and certain conditions lend special power to bring about harmful results.

Simple oxidation, putrefaction, and the different varieties of fermentation are the chief agencies which effect this decomposition. Carbon dioxide, water, and ammonia are the principal ultimate decomposition products of organic matter. Ammonia may undergo the further transformation into nitric acid. The intermediate products are quite numerous and complex. Carbohydrates yield by fermentation a large number of alcohols, aldehydes, ethers, and acids of the fatty series. Vegetable matter in contact with moist soil is converted into a brownish black mass or humus which contains a great many unstable organic compounds. The fat yields glycerin and fatty acids. Fæcal matter contains undigested food and numerous decomposition products of albuminous matter and other proximate constituents of food. The albumenoids, including egg albumen, casein, blood-fibrin, peptones, &c., and the closely related bodies, such as gelatin and chondrin, yield a large and very important class of compounds. The principal products are the amido-derivatives of the fatty acid series—leucine, glycocoll, aspartic and glutamic acids, &c., members of the fatty acid series—formic, acetic, propionic, butyric, &c., the compound ammonias—methylamine, ethylamine, propylamine, &c., members of the aromatic group—phenol, cresol, skatol, indol, tyrosin, hydroparacumaric acid, alphatoluic acid, &c. These compounds yield simpler products by further decomposition. Albuminous matter enters largely into the composition of the animal body, and is found in small quantity in nearly all parts of the plant, with the exception of the seed, where it occurs more abundantly. It is the decomposition of these highly complex nitrogenous compounds in water that introduces the element of danger, as the organic nitrogen results almost entirely from the decomposition of albuminous

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matter and derived products. The amount of free ammonia and nitric acid indicates with more or less accuracy the extent of changes which have already taken place. In the following experiments an attempt has been made to furnish data from which more accurate conclusions may be drawn concerning the organic matter in water by the study of individual department in case of the principal constituents of this matter. Each compound, when subjected to the tests, decomposes in a manner peculiar to itself.

Total Conversion of the Nitrogen of Albumen into the Form of Ammonia.

Wanklyn's statements upon this subject are rather indefinite. This author mentions experiments of his own by which almost all of the nitrogen of albumen is converted into the form of ammonia, but does not give the details of his work. He was at first inclined to believe that the ammonia obtained was a definite portion of the total amount. According to other chemists, only a fraction of the total nitrogen of albumen will yield ammonia when boiled with permanganate solution. The details of my own experiments are given for the purpose of showing under what circumstances the total nitrogen of albumen is evolved in the form of ammonia.

Fresh White of Egg Solution No. 1.—Containing 30 grms. of fresh white of egg dissolved in 2500 c.c. water. 10 c.c. of this solution were diluted to 500 c.c., 5 c.c. of a strong solution of Na_2CO_3 , free from ammonia, were added, and the mixture distilled. Four distillates of 50 c.c. each were removed for the estimation of "free ammonia," then 50 c.c. of a solution containing 8 grms. potassium permanganate and 200 grms. potassium hydrate per litre were added, and four more distillates of 50 c.c. each were nesslerised for the "albumenoid ammonia." By continued boiling of the same portion of this solution with permanganate mixture on successive days, the total nitrogen in egg albumen appears in the form of ammonia. Before each distillation 200 c.c. of pure water was added to the contents of the retort. The retort was kept tightly stoppered during intervals between successive distillations in order to preserve the solution free from atmospheric impurities. Care was taken to wash the condenser thoroughly with water free from ammonia before being used. An aliquot part of the first distillate was taken for comparison with standards where depth of colour would interfere with accuracy.

In calculating the amount of ammonia which by theory should be obtained from a certain weight of white of egg, I have taken the values usually given (see König's "Nahrungsmittel"), viz., 12.5 per cent of albumen with 15.7 per cent of nitrogen. Under theory, the values so obtained are given below.

	Free Ammonia. M.grm. NH_3 .	Albumenoid Ammonia. M.grm. NH_3 .
First distillation	0.0675	1.420
Second	..	0.270
Third	..	0.146
Fourth	..	0.095
Fifth	..	0.061
Sixth	..	0.037
Total amount	2.029
Theory..	2.85

Solution of Egg Albumen No. 2.—Containing 48.710 grms. fresh white of egg dissolved in 2500 c.c. water. 10 c.c. of this solution were taken for distillation. The same precautions as given above were taken with this series of distillations. (See next column).

Egg Solution No. 3, made by dissolving dried albumen in distilled water, was decomposed much more slowly.

It will therefore be observed that it is possible, by continued distillations with alkali-permanganate solution to convert the total nitrogen of albumen into the form of ammonia. Egg solution No. 2 yields nearly 95 per cent

	Albumenoid Ammonia. M.grms. NH_3 .
First distillation	2.620
Second	0.475
Third	0.210
Fourth	0.208
Fifth	0.153
Sixth	0.122
Seventh	0.095
Eighth	0.099
Ninth	0.075
Tenth	0.070
Eleventh	0.060
Twelfth	0.050
Thirteenth	0.038
Total amount	4.275
Theory..	4.63

of this element. The decomposition is, however, very slow under the conditions of the experiment. The rate depends upon a variety of circumstances—the concentration and quantity of permanganate solution, shape and size of retort, rapidity of distillation, &c. In egg solution No. 1 about 50 per cent of the nitrogen in the form of ammonia was evolved during the first distillation; in solution No. 2 a larger proportion, while from a solution of dry albumen in water only a little over 35 per cent of the total amount was obtained.

Decomposing Solution of Egg Albumen.

Fresh white of egg solution No. 1 was allowed to putrefy, and the process of decomposition was traced from the beginning by means of the amount of free and albumenoid ammonia evolved. 10 c.c. were taken for each test. Precautions were taken to keep the room as free as possible from ammonia vapour or other substances liable to contaminate the solution. I am not aware that anyone has traced the process of decomposition of albumenoid material in this way. The conditions simulate those that exist in natural waters. Tiemann and Preusse have traced the process of decomposition of egg albumen by means of the oxidation test with standard solution of potassium permanganate, but only for a short time.

	Free Am. m.grms. NH_3 .	Alb. Am. m.grms. NH_3 .
Feb. 19..	0.072	1.420
„ 26..	0.067	1.120
Mar. 5..	0.110	1.113
„ 12..	0.442	1.068
„ 19..	0.623	1.055
„ 26..	0.890	1.015
April 2..	0.940	0.958
„ 9..	0.978	0.838
„ 16..	1.013	0.763
„ 23..	1.327	0.700
„ 30..	1.375	0.680
May 7..	1.525	0.595
„ 14..	1.635	0.578
„ 21..	1.680	0.541
„ 28..	1.785	0.496
June 4..	1.904	0.455
„ 11..	1.965	0.444
„ 18..	2.035	0.413
„ 25..	2.206	0.352
July 2..	2.127	0.355
„ 9..	2.129	0.304
„ 16..	2.140	0.298
„ 23..	1.990	0.320
„ 31..	2.092	0.320
Aug. 13..	1.915	0.322
„ 27..	2.124	0.332

Putrefying solution of egg albumen yields a gradually increasing quantity of free ammonia, while the albumenoid ammonia regularly diminishes. The free ammonia plus

the albumenoid ammonia is an increasing quantity, and near the latter part of the time occupied by experiment is above 90 per cent of the total nitrogen.

Urea.

There are, perhaps, more conflicting statements in regard to the decomposition of this compound than any other. Wanklyn states that urea, when quite pure, may be boiled for a long time with alkalis without evolving a trace of ammonia, and again, in presence of permanganate and excess of potash, urea is doubtless decomposed, but it yields no ammonia. Tiemann obtains, on the other hand, the total nitrogen in the form of ammonia. Other chemists assert the possibility of obtaining the total amount. In one of Wanklyn's experiments, by boiling for a long time with strong permanganate mixture, only 22 per cent could be obtained. The details of my own experiments with this compound are given below.

The total nitrogen of urea is converted into ammonia if a simple solution in water is boiled during a sufficient length of time. The decomposition is more rapid if strong solution of alkali permanganate be added.

Experiment 1.—2.5 m.grms. urea were dissolved in 500 c.c. water, and 5 c.c. of a strong solution of Na_2CO_3 added, and the mixture distilled for free ammonia, after which 50 c.c. of permanganate solution were added for the albumenoid ammonia.

Free ammonia = 0.028 + 0.014 + 0.012 + 0.011 m.grm.
 $\text{NH}_3 = 4.5$ per cent NH_3 .

Albumenoid ammonia = 0.033 + 0.022 + 0.021 + 0.027 + 0.056 m.grm. $\text{NH}_3 = 11$ per cent NH_3 .

Total = 15.5 per cent of theoretical yield of NH_3 .

Experiment 2.— $\frac{1}{2}$ m.grm. urea — otherwise same as in Experiment 1.

Free ammonia = 0.022 + 0.012 + 0.0015 + 0.001 m.grm.
 $\text{NH}_3 = 12$ per cent NH_3 .

Albumenoid ammonia = 0.022 + 0.007 + 0.005 + 0.003 m.grm. $\text{NH}_3 = 13$ per cent NH_3 .

Total = 25 per cent of theoretical yield of NH_3 .

Experiment 3.— $\frac{1}{2}$ m.grm. urea — 100 c.c. permanganate solution.

Free ammonia = 0.022 + 0.012 + 0.0015 + 0.0015 m.grm.
 $\text{NH}_3 = 13$ per cent NH_3 .

Albumenoid ammonia = 0.020 + 0.012 + 0.012 + 0.0125 m.grm. $\text{NH}_3 = 19$ per cent NH_3 .

Total = 32 per cent of theoretical yield of NH_3 .

Experiment 4.—1 m.grm. urea—2 grms. potassium permanganate and 40 grms. potassium hydrate added for albumenoid ammonia.

Free ammonia = 0.034 + 0.025 + 0.012 + 0.0075 + 0.005 m.grm. $\text{NH}_3 = 16$ per cent NH_3 .

Albumenoid ammonia = 0.068 + 0.023 + 0.021 + 0.0225 + 0.030 m.grm. = 28 per cent NH_3 .

Total = 44 per cent of theoretical yield of NH_3 .

Experiment 5.—1 m.grm. urea in 450 c.c. water with 50 c.c. permanganate solution added. Boiled during ten hours in retort with inverted condenser and bulbs containing dilute solution of sulphuric acid attached at other end. Two sets of bulbs were employed and blank experiments were made in order to test the connections of the apparatus, and to ascertain if any other sources of error might be present in the experiment. The amount of ammonia obtained in the blank trial was so small as to be neglected altogether. The albumenoid ammonia obtained from urea was 78 per cent of the total amount. By distilling off four distillates of 50 c.c. each for four successive times, the remaining 22 per cent of the ammonia was obtained.

Experiment 6.—2 m.grms. urea. Boiled solution during twenty hours—otherwise same as in Experiment 5. Albumenoid ammonia obtained, 101 per cent.

Experiment 7.—2 m.grms. urea. Boiled during twenty-two hours in 500 c.c. water only. Ammonia obtained, 95 per cent of the theoretical amount.

In this connection the results obtained by Dr. Charles Smart are of interest (*Sanitarian*, Nov., 1886). He states:—"Since 1 m.grm. urea in 500 c.c. of water gives a persisting and equable evolution of 0.01 m.grm. of ammonia when distilled alone or with sodium carbonate, and an evolution of 0.02 in each measure when subsequently treated with alkaline permanganate, a water sample which yields such results must have contained urine equivalent to, at least, 1 m.grm. of urea," and again "a water which yielded in successive distillates of 50 c.c. each 0.47, 0.25, 0.15, and 0.15 m.grm. of free ammonia, and afterward, 0.54, 0.34, 0.32 and 0.32 m.grm. of albumenoid ammonia, might be set down as having contained urine equivalent to, at least, 15 m.grms. of urea in the 500 c.c. of water used in the experiment." If these statements expressed the real facts in the case the observation would doubtless be of great value. The equable evolution refers to the third, fourth, and subsequent distillates, and the results are in direct proportion to the amount of urea present. The experiments I have made with urea prove that no set or combination of conditions can concur to produce such an evolution of ammonia. The decomposition of urea takes place very slowly, even with strong solution of permanganate, but wide variations result from apparently slight changes in the conditions of the experiment. My experiments were made in as nearly uniform a manner as possible, with reference to the time in collecting distillates. Experiments 2 and 3, with one-fifth as much urea as in Experiment 1, gave, on the other hand, nearly twice the quantity of total ammonia, and furthermore, a comparison of the third, fourth, and subsequent distillates in each case reveals the fact that the amount of albumenoid ammonia evolved is from two to six times the quantity of free ammonia, and is not in the constant ratio of 2 : 1. The evolution of ammonia from urea is quite variable, and being associated in natural waters with other nitrogenous compounds of unknown character, there is no trustworthy evidence that will determine the quantity of the substance with the degree of precision stated by this author.

(To be continued).

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLET, F.R.S.,
Professor of Chemistry in the University of Virginia.

(Continued from p. 72).

General Results of former Determinations most deserving Confidence.

THESE recent researches, unquestionably by far the most valuable up to the present time, give us, when taken separately and together, the following values for the atomic weight of gold:—

1. General mean of 5 series by Krüss, as calculated by himself 196.640
2. General mean of 3 series by Thorpe and Laurie, as calculated by themselves 196.852
3. 1 and 2, giving equal value to each 196.746

Difficulties to be overcome in Determining the Atomic Weight of Gold.

Besides the special difficulties connected with each method which may be adopted, the determination of any high atomic weight with a degree of accuracy which enables the result to be accepted to a given decimal place is clearly a much less easy matter than would be the

* A Paper read before the Royal Society, May 9, 1889.

attainmen of an apparently equal degree of precision for an atomic weight represented by a small number. In obtaining the atomic weight of lithium, the first with which, many years ago, I had any personal experience, a difference of unity in the first decimal place corresponded to about $\frac{1}{70}$ th of the whole value considered to be correct. In getting the atomic weight of aluminum, worked on later, a like difference represented approximately $\frac{1}{270}$ th of the whole value. But, in the case now considered, of the atomic weight of gold, unity in the first decimal place means but about $\frac{1}{170}$ th of the whole value. So that, looking at the matter in this light, it may be said that a degree of precision is demanded more than seven times as great as in the case of aluminum, and twenty-eight times as great as in the case of lithium.

There is also to be noticed, as the most obvious *general* difficulty to which all methods for determining the atomic weight of gold are more or less exposed, the instability of compounds of this metal; not merely the ease with which complete decomposition occurs, with separation of free gold, but the much more insidious and less easily detected trouble arising from the comparative ease with which aurous pass into auric compounds, and the reverse.

New Experiments by the Author.

The general difficulties just alluded to, and the special points to be investigated in regard to each method of determination tried, have demanded much time and work, and I cannot feel even now that all has been done that is desirable and possible; but the experiments projected have been so far completed as to seem to justify publication, and I am not likely soon to be able materially to extend them.

General Principles kept in View.

The improvements made of late years in manipulative methods and apparatus have tended to reduce very much the magnitude of what are commonly called "fortuitous" errors in our quantitative determinations of matter, and to increase greatly the accuracy of such determinations. Probably no modern work has had more influence in this direction than the classic researches of Stas on certain atomic weights—the precautions taken by him, and his remarkable manipulative skill, causing his results to bear almost the same relation to those of his immediate predecessors as did those of Berzelius to the work of the chemists of his earlier day. No one nowadays would undertake the determination of the atomic weight of one of the better known elements without taking such elaborate precautions as practically ensure pretty close concordance of results, when obtained by the same method, applied in the same hands. In the present state of the question of atomic weights and improvement in their determination, advances in mere delicacy of manipulation and success in merely securing close agreement of results by the same method are not alone sufficient. It cannot be too much insisted upon that we need, besides, well-directed and laborious investigation of possible sources of *constant errors*, and the adoption of means to guard against them. Careful preliminary study is required, in a general way, of the precise nature of each reaction employed, and how it may be influenced by the conditions of the experiment. We learn more and more of late that many of the reactions—perhaps it should rather be said all of the reactions—which have been generally supposed to be of the simplest nature are in reality complex.

The following are among the general principles which seem to be most important, as tending to greater accuracy and trustworthiness in atomic weight determinations; they have been in part stated in the author's earlier paper on the atomic weight of aluminum:—

1. In purifying the materials used, both the element of which the atomic weight is to be investigated (or any special compound containing it) and all substances used to react thereupon, resort should in all cases be had to

"fractional" methods, assuming materials to be pure only when earlier and later fractions give no signs of any constant difference in the results which they yield.

2. Different and independent processes should be applied to the determination of the same atomic weight, and the results used to check each other. It is desirable that as many such different processes be applied as can be devised, provided each be reasonably free from apparent sources of error, even though it be usually impossible to properly assume that all are equally advantageous in this respect, and therefore of equal value. In the comparison of results obtained it should be noticed whether a given method tends on the whole to yield results probably higher or lower than the truth, though it may be gravely doubted whether the practice is commendable of attempting any numerical estimate of relative value, by so-called "weighting" of the results in calculation.

3. In connection with each process there should be careful study of the reactions depended upon for the final determination of an atomic weight, looking especially to the possibility of the occurrence of secondary or subsidiary reactions.

4. Each process adopted should be as simple as possible, both in the nature of the chemical reaction or reactions, and in the known liability to merely manipulative errors.

5. Each process should be carried out with, in some experiments larger, and others smaller, quantities of material. But, on the whole, the quantities used should be kept within such limits as are most likely to admit of most accurate determinations being had under the conditions of the special process.

6. In the reactions depended upon, only such other elements should be concerned as may be counted among those of which the atomic weights are already known with the nearest approach to exactness.

7. It is particularly desirable that, if possible, the atomic weight to be investigated shall be, by at least one process, compared directly with that of hydrogen, now almost universally taken as the basis for the whole list of the elements. It is remarkable for how very few of the elementary substances—not more than three or four—this direct comparison has been accurately made.

8. In the greater number of the processes available for atomic weight determinations the comparison with hydrogen must perforce be made indirectly. When this is the case, it is desirable that as few other elements as possible the assumed atomic weights of which will have to be taken into account shall be involved in each single reaction depended upon.

9. In selecting *different* processes to be applied to the determination of the atomic weight of a given element, in order that the results may check each other, it is desirable that, not the same, but as many different other elements as possible, shall be concerned in the several reactions, provided all such elements count amongst those of which the atomic weights may be considered in the first rank as to the accuracy with which they are known.

Means and Methods of Weighing Employed.

These were in the main the same as those which I had in former years used in determining the atomic weight of aluminum.

The balance chiefly used, made by Becker, was carefully cleaned, and all its parts adjusted, especially as to the position of the centre of gravity for each load to be used. A second balance, by the same maker, of larger size, capable of taking a load of a kilogram. in each pan, was employed in weighing certain of the solutions experimented on, and was in like manner carefully adjusted and tested. All weighings were made by observation of the oscillations of the index on either side of the position of rest. A difference of weight of 0.0001 grm. with the smaller balance, and 0.0002 grm. with the

larger instrument, was easily and distinctly observable with any load which the research required.

The same kilogram weight was made the basis of a comparison with all my other weights which had been before used in the same way. This had been compared at Washington with the "star kilogram" of the United States Coast Survey, the value of which is known in terms of the original "kilogram of the Archives" at Paris. All the smaller weights were carefully re-checked against this and against each other, and their real values ascertained as referred to a vacuum. The necessary determinations were made of the specific gravity of all materials and vessels which were to be weighed, and the barometer and thermometer were read at the time of each weighing, so that all weights recorded in this paper represent real values *in vacuo*. In order to reduce to a minimum errors due to varying deposition of hygroscopic moisture, vessels of like material, shape, and size with those used to contain substances to be weighed were used as tare.

History and Mode of Purification of the Gold used in this Research.

Most of the metal needed was prepared by myself, with precautions presently to be mentioned; a part was obtained as "proof gold," from the United States Mint at Philadelphia; another part from the United States Assay Office at New York; and a single specimen of English "trial plate" gold from the Royal Mint in London.

1. *Purification of Gold by the Author.*—It may fairly be concluded from the general history of the gold of commerce, that the impurities most to be suspected, and most requiring special precautions for their removal, are silver and the metals of the platinum group. My preliminary experiments led me to believe that the greatest difficulty in the way of obtaining perfectly pure gold consists in getting rid of the last traces of silver, the chloride of this metal not being quite insoluble in a solution of auric chloride. For the removal of silver, I have chiefly depended upon evaporation of the gold solution with a little hydrobromic acid, followed by large dilution with water, and long-continued clearing by subsidence. As regards the platinum metals, my results agreed substantially with those of Hoffmann and Krüss,* but I have been inclined to lay some stress on reduction of the gold from its solution *with exclusion of light*, and on *fractional* reduction, using only the middle portion thrown down. I avoided altogether the use of ferrous salts as reducing agents, in view of the difficulty of preparing them in large quantity with assurance of their purity, and the trouble of thoroughly washing the precipitated gold. For the final precipitation of the gold, formic acid seemed to offer real advantages; its volatility admits of easily getting it free from any metallic contamination, and the reduction is more easily effected than with oxalic acid.

Starting with United States gold coin, it was first heated to bright redness in a muffle, as a precaution against the presence of any traces of mercury, and to remove any grease, &c., from the surface, and then dissolved in a mixture of pure hydrochloric and nitric acids in the right proportions. The solution was evaporated with excess of hydrochloric acid nearly to dryness, the auric chloride re-dissolved in a considerable quantity of water, and the solution allowed to settle for four or five days. The greater part of the clear liquid, drawn off with a syphon, and filtered through very siliceous sand,† was again evaporated nearly to dryness, adding towards the end a few drops of pure sulphuric acid, in case of the conceivable, though unlikely, presence of such traces of lead as this might reveal; much pure water was added, the

solution again cleared by subsidence for several days, and the greater part of the clear liquid again drawn off and filtered. This solution was now rendered pretty strongly acid with hydrochloric acid, and fractionally precipitated by sulphurous acid (SO₂ was evolved from sodium sulphite), at as low a temperature as possible, and *in the dark*, putting aside the first and last portions of the metal thrown down, and reserving for further treatment the (largest) middle portion. The gold thus obtained was well washed with water, boiled with nitric acid alone, again washed, boiled with hydrochloric acid alone, again washed, dried, and heated strongly with fused acid sulphate of potassium in a porcelain crucible, boiled with dilute hydrochloric acid, and then with water. The metal was re-dissolved in aqua regia, the solution evaporated nearly to dryness, with addition of pure hydrobromic acid towards the end, very largely diluted with water, and allowed to stand for two days, well protected from dust, before again syphoning off as much of the clear portion as could be safely removed without risk of disturbing the remainder at the bottom, using a conical precipitating jar with greatest diameter below, and filtering the liquid through siliceous sand as before. The evaporation with hydrobromic acid was repeated twice more, and the clear solution—allowed the last time to stand a month before being syphoned off and filtered—was then reduced, once with oxalic acid (neutralising the liquid with pure sodium hydroxide from the metal), once (after re-solution) with sulphurous acid, and once with formic acid, washing the reduced metal well each time before re-dissolving in aqua regia. In the first and second of these reductions a little of the metal first and last thrown down was rejected, and in the final reduction with formic acid the first portion precipitated, about one-fifth of the whole, was reserved for use, labelled A, *a*, the middle portion, about three-fifths, was labelled A, *b*, and the last portion, the remaining one-fifth, was also preserved for use, marked A, *c*, so that it might be seen whether any difference in the character of the metal could be detected in the atomic weight determinations. All of these fractions received a very thorough final washing with water.

Such part of the purified metal as was to be used in the preparation of gold compounds was not fused, but was heated in a glazed porcelain tube to a moderate redness in a Sprengel vacuum. A small part of the metal used in the free state, and desired in compact form, was fused in a perfectly clean Beaufaye crucible with a little acid sulphate of potassium and borax, the button flattened, boiled with strong nitric and then strong hydrochloric acid, thoroughly washed with water, and, finally, heated in the Sprengel vacuum. Throughout the long process of purification, and especially towards its close, the most scrupulous care was taken to exclude dust, and to prevent grains of sand from the bottoms of beakers or any other impurities getting into the precipitated gold, upon which the acids used would not act, so as to obviate the risk of merely mechanical contamination, which, if overlooked, might lead to that being weighed as part of the gold which was, in fact, foreign to it.

2. *Purification of "Proof Gold" obtained from the United States Mint at Philadelphia.*—I owed to the kindness of Mr. J. B. Eckfeldt, Chief Assayer to the Philadelphia Mint, a liberal supply of the "proof gold" used in checking the gold assays there made, and he furnished me the following statement of the manner in which this purest metal is prepared, under his directions:—"The best cornets from the gold assays selected and dissolved in aqua regia. Solution evaporated, with additions of HCl, to nearly crystallisation, diluted largely with water, and allowed to stand for three or four weeks. About seven-eighths of the solution drawn off from the silver chloride, and passed through several thicknesses of various filters. Solution somewhat concentrated, and alcohol and potassium chloride added, allowed to stand

* *Liebig's Annalen*, vol. cxxxviii., p. 66.

† The sand was carefully purified beforehand by boiling with nitric and hydrochloric acid, thorough washing with water, and heating to redness in the air.

for some time (precip. traces of platinum*), and carefully filtered. Gold precipitated by addition of pure ferrous sulphate. Reduced gold washed repeatedly in boiling HCl, until washings show no iron, then well washed in pure water. Gold dissolved, and solution evaporated to crystallisation, with repeated additions of hydrobromic acid,† diluted, and again allowed to stand for some time; filtered. Through the solution was passed pure SO₂ until all the gold was reduced; washed. Gold again dissolved, evaporated with HCl, diluted, and oxalic acid added, and heated until all gold is down, melted in white clay crucible with potassium chlorate and nitrate, afterwards with pure sodium carbonate and borax." Mr. Eckfeldt also informed me verbally that the proof gold thus purified is cast into a small bar in a perfectly clean and bright cast-iron mould; the bar is boiled in nitric acid, washed, and dried, rolled between fine steel rolls quite free from grease, and the strip finally cleaned for use with hot hydrochloric and then nitric acid.

In a letter of later date he wrote:—"In preparing the 'proof' I seldom make over 10 ozs. in one lot; from 8 to 10 ozs. is the usual amount. There is comparatively little trouble in making 999.9 fine, but beyond that it is rather troublesome; and it seems that, with all the care, the final result is sometimes a little in doubt."

The fine gold received from the Philadelphia Mint is designated as B in this paper, in connection with the experiments in which it was used.

3. *Purification of "Proof Gold" obtained from the United States Assay Office at New York.*—Dr. H. G. Torrey, Chief Assayer in this Office, was obliging enough to let me have several samples of his finest proof gold, used in checking the regular assays in his department. He informed me that this proof gold was independently prepared at New York, but was occasionally compared with that of the Philadelphia Mint. He furnished the following brief statement as to its preparation:—"The process used in preparing the gold is to dissolve 'cornets' (or gold from assays) in nitro-hydrochloric acid, and after filtration precipitating by oxalic acid, and after thorough washing, melting under borax. The operation is conducted with the utmost care throughout.

The gold from this source is designated as C in this paper.

4. *Gold from the "Trial Plate" of Fine Gold of the English Mint.*—Professor Roberts-Austen, Chemist to the Royal Mint, was so kind as to let me have a specimen of a few grms. of gold cut from the trial plate of the pure metal prepared by him in 1873. In its preparation use was made of potassium chloride and alcohol to separate any platinum present in the original material, a long period of subsidence was allowed for the deposit of any silver chloride from the solution, and the whole process was applied on a large scale, resulting in the purification of some 70 ozs. of fine gold, of which Professor Roberts-Austen himself has said:—"I have not been able to prepare, or to obtain from any source, gold of greater purity, even in small quantities." It seems, however, that the apparent standard of this gold was slightly reduced in rolling, the finished plate being counted as 999.95 fine in comparison with the same gold before rolling. A memorandum given me by Professor Roberts-Austen states that this trial plate gold is 999.98 fine as compared with the purest gold obtained by Stas for the Belgian Mint.

This specimen of English trial plate gold is designated as D in the present paper.

All the samples of gold received from others—B, C, and D—were, before using them, carefully boiled in nitric

acid to remove any possible traces of silver or other metal derived from the shears used in cutting the plates. They were also previously well washed with ether, to remove any grease, and afterwards with pure water, and were finally heated to redness in the Sprengel vacuum.

It may be remarked, in advance, that I have not been able to trace any probable connection between the history of the several samples of gold used and the values obtained for the atomic weight of the metal. Within the limits of accuracy attained, the results appear to have been sensibly the same by each method for all the gold used. Nor is there apparent in the results of Krüss, or those of Thorpe and Laurie, any evidence of a difference fairly traceable to the nature of the metal employed by them.

A considerable part of the gold prepared by myself was, after having once served for a determination of the atomic weight, re-dissolved and re-precipitated, and was afterwards more than once used in subsequent determinations, and yet no sign was obtained of any resulting influence upon the later values of the atomic weight as obtained, evidence being thus furnished of the purity, not only of the gold itself, but of the reagents used to act upon it, so far as any contamination of the metal was concerned. It may, therefore, be concluded with reason that the gold used in these experiments was of uniform character, and uniformly free from any known impurities, to such an extent, at any rate, as to sensibly change the results obtained.

It is to be noted that the only known elements having higher atomic weights than that of gold are mercury, thallium, lead, bismuth, thorium, and uranium. The presence of any of these in the gold experimented on, even in traces too minute to weigh, is in a very high degree unlikely. The presence of any other element or elements than these would, for analogous compounds, tend to lower the value obtained for the atomic weight of gold; so that, in considering the chances of error due to the nature of the metal used as gold, we should be inclined to say that the risk was rather in the direction of too low than too high a result being reached. But, if the possibility be observed of compounds not analogous being erroneously compared, the contrary error will be seen to be possible. Thus, in case the composition of an auric haloid salt obtained from a given amount of metallic gold should be examined, if any unsuspected silver were present there would be required for the same amount of the halogen three atoms of silver instead of one atom of gold, and, therefore, the apparent weight of gold as compared with that of the halogen would be increased instead of diminished, and a higher value obtained for the atomic weight sought.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Annual General Meeting, February 7th, 1890.

Prof. REINOLD, F.R.S., President, in the chair.

The Reports of the Council and of the Treasurer were read and adopted. The former stated that there had been a very satisfactory increase in the number of members during the year. The number now exceeds 360, of whom 80 are Fellows of the Royal Society.

During the year the Council had proposed to change the time of meeting of the Society from Saturday afternoon to Friday evening. The change was adopted by the members by a vote of 129 to 30, and had resulted in a larger attendance at the meetings.

During the year the second part of Volume I. of the translations of important foreign memoirs had been issued

* The platinum of South American native gold, and of scrap gold from dentists, is at the Philadelphia Mint separated solely by alloying with enough silver, and dissolving out the latter metal with nitric acid. The platinum dissolves with the silver.

† I had, many months before, independently adopted and used hydrobromic acid to remove traces of silver more effectually than by hydrochloric acid, when I learned from Mr. Eckfeldt that he had thus habitually employed it.

to the members, and it was hoped that a third part would be published early in the present session.

The Council had to regret the loss by death of three well-known members—James P. Joule, Warren de la Rue, and Father Perry.

A valuable collection of books had been given the Society by the Royal Astronomical Society.

From the Treasurer's Report it appeared that the balance of the Society had been increased by £120 during the year.

Prof. Hittorf, of Münster, was, at the recommendation of the Council, elected an Honorary Member of the Society.

The result of the new election of officers was declared as follows:—

President.—Prof. W. E. Ayrton, F.R.S.

Vice-Presidents.—Dr. E. Atkinson, Walter Baily, M.A., Shelford Bidwell, F.R.S., and Prof. S. P. Thompson, D.Sc.

Secretaries.—Prof. J. Perry and T. H. Blakesley, M.A., M.Inst.C.E.

Treasurer.—Prof. A. W. Rücker, F.R.S.

Demonstrator.—C. V. Boys, F.R.S.

Other Members of Council.—W. H. Coffin, Sir John Conroy, Bart., M.A., Conrad W. Cooke, Major-General Festing, F.R.S., Prof. J. V. Jones, M.A., Prof. O. Lodge, D.Sc., F.R.S., Prof. W. Ramsay, Ph.D., F.R.S., W. N. Shaw, M.A., H. Tomlinson, B.A., F.R.S., and G. M. Whipple, D.Sc.

Votes of thanks were then passed (1) to the Lords of the Committee of the Council on Education for the use of the room in which the Society met; (2) to the Auditors, Prof. Minchin and Dr. Fison; (3) to the President and Officers of the Society for their services during the year.

The Meeting was then resolved into an Ordinary Science Meeting.

Messrs. E. W. Smith and C. E. Holland, B.A., were elected Members of the Society, and Mr. Sidney Evershed was proposed as a Member.

The paper on "Galvanometers," by Prof. W. E. AYRTON, F.R.S., Mr. T. MATHER, and Dr. W. E. SUMPNER, was then resumed by Prof. AYRTON.

A long table of numbers accompanying the paper, and representing the result of experiments on many galvanometers, was explained. From this it appears that galvanometers of the D'Arsonval type were exceedingly efficient in proportion to the amount of wire used in the coils. It was for this reason that voltmeters with strong permanent magnets could be made sensitive, even with an exceedingly large external resistance in series, so as to diminish the power absorbed by the instrument. The space occupied by the wire was so exceedingly valuable that the extra resistance did not too much diminish the sensibility. The most sensitive galvanometers should therefore be made of the permanent magnet type. If, however, the magnets were to form part of the moving system, as in most galvanometers, the experiments showed that instruments of the Rayleigh, Gray, or Rosenthal type were the best. The coils should be numerous and small, as Mr. Boys had previously shown. As an astatic system of needles sets itself perpendicular to the earth's field, it was recommended that astatic galvanometers should be placed so that the needles pointed east and west. The controlling magnet would then not need to be turned round as it was raised or lowered. It was recommended to calibrate low resistance ballistic galvanometers for quantity by measuring the deflection for a known current. This obviates the necessity for large condensers or high potentials. The method, although not new, is not described in ordinary text-books. In conclusion, Prof. Ayrton asked for information with regard to microscope galvanometers.

Mr C. V. Boys, F.R.S., thought that the factor of merit of galvanometers should not be given in scale divisions per micro-ampère under the condition of constant controlling

moment. This gave too great an advantage to instruments of the Gray or Rosenthal type. Great sensibility could be obtained by diminishing the moment of inertia of the suspended parts, the practical limit being determined by the trouble due to the silk fibre. Spider lines, when used in place of silk fibres, gave better results. It was possible, by using a good suspending arrangement, to use needles $\frac{1}{2}$ " long, and a period of twenty seconds, and to gain a sensibility far greater than those indicated in the paper. Ballistic galvanometers should be made with needles as light as possible. The method proposed of winding the central part of the coil in the opposite sense to the rest would probably not be good, owing to the unevenness of the field produced. The conclusion come to by the authors that D'Arsonval galvanometers of great sensibility should be made with small coils placed in a very strong field, was one he had himself come to, but had finally abandoned, owing to difficulties caused by diamagnetism in the copper and to excessive damping due to Foucault currents.

Mr. SWINBURNE thought that the factor of merit of a galvanometer should be determined differently, according as it was to be used for the measurement of current, or quantity, or for null methods merely. He saw no great advantage in making practical instruments proportional. The name D'Arsonval should be dropped, as the instrument denoted by it was invented by Varley years ago. He would like to know the relative sensibility of the telephone and the Lippmann galvanometer.

Prof. FITZGERALD stated that Lord Rayleigh had shown that the microscope method of observing angular deflections was as sensitive as the ordinary method of mirror and scale, even when only the mirror was used as a pointer, so that if a pointer were attached it would be far more sensitive. The drawback, however, was that it was impossible to distinguish, with the microscope, between lateral displacements of the needles and the angular motion whose measurement was required. To get over this error it was necessary to read both ends of the pointer, but this was hard to do.

Prof. AYRTON replied to the different points raised in the discussion.

NOTICES OF BOOKS.

The Year-Book of Photography and Photographic News Almanack for 1890; containing the Results of Photographic Experimenting during the past Year, and Special Contributions by leading Photographic Authorities, Professional and Amateur; with a Portrait of Prof. E. Becquerel. London: Piper and Carter.

ONCE again the great and growing popularity of photography is brought to our notice, and once again we are compelled to admit that this art is being too little applied in one of the most desirable directions. We are told, indeed, that photography is "the handmaid of all the sciences, the servant of the geographer, engineer, and practical arts." But we find here nothing recorded as to any advances either in celestial or biological photography.

It may be asked whether M. Becquerel is not too strongly glorified in the passage:—"By studying with the spectroscope the light emitted by phosphorescent bodies he established a new method of spectrum analysis, which has of late been largely developed, and is employed to discover traces of substances which other methods of analysis do not suffice to make manifest." The development of phosphorescence spectroscopy, to which its great analytical value is due, may fairly be called a new departure.

Photography in natural colours, which, among photographers, plays the part of the decomposition of the elements among chemists, or the production of life *de novo* among biologists, is treated at some length. The writer's

point of view is to determine the relative merit of experimentalists in this direction, the palm being awarded to Becquerel as against Niepce de St. Victor.

The subject of Amateurs *v.* Professionals again comes forward. This question has its very life in the unfortunate predominance of portrait-photography. The more the art is applied to other purposes the more the difference between the two classes will fade away.

In connection with portraits we find some merited strictures on the growing evil of "re-touching." A photograph which has undergone this process neither throws any light on the character of the original, nor serves to prove his identity. Many of the articles here produced have so little bearing upon science and so much upon Art, that we feel incompetent to pronounce upon them. Did we make the attempt, we might lay ourselves open to severe castigation from the "Levites of Culture," who are waxing exceedingly rampant.

CORRESPONDENCE.

FRENCH ACCOUNTS OF JOSEPH PRIESTLEY.

To the Editor of the Chemical News.

SIR,—National jealousy and false pride prompt French historians of chemistry to belittle the work of Priestley and to magnify that of Lavoisier. Impartial and candid persons are willing to admit the claims for Lavoisier, who certainly had a genius for generalising and constructing an edifice of materials gathered by his contemporaries; but why the French writers so persistently distort certain facts in the life of Priestley which have no bearing on the scientific aspect is unaccountable. Georges Cuvier's attempt to show that Priestley's prime discovery—oxygen—was suggested by, or in consequence of, his hearing a memoir of Bayen on the reduction of mercuric oxide in closed vessels at the time of his visit to Paris, in company with Lord Lansdowne, is in accordance with the spirit of French historians (Cuvier, *Hist. des Sciences Naturelles*, Paris, 1843, vol. ii., p. 23).

Henri Gautier makes the following extraordinary statement; we give it in the original that we may not be charged with mistranslation:—

"Une larme aux malheurs de Priestley, qui fut persécuté toute sa vie. A Birmingham la populace pille et incendie sa maison puis court brûler sa campagne et sa bibliothèque. Son crime était de vouloir fêter dans un dîner notre 14 juillet. Réfugié au fond de l'Amérique du nord, il ne trouve pas le refuge même aux sources silencieuses de l'Usquehannah et demande un asile aux *peaux rouges*; enfin il meurt empoisonné avec toute sa famille" (*Essai sur l'Hist. Chimie*, Paris, 1837).

That Priestley was "persecuted all his life," that he "demanded a refuge at the hands of red-skins," and that "he and his whole family died by poison," are startling additions to our knowledge, and the latter clause must surprise his numerous descendants still living in England and America.

Gautier's statement is doubtless based on somewhat similar expressions of Dumas. In his "Leçons sur la philosophie chimique" (Paris, 1837), Dumas writes of Priestley thus:—"Incertain s'il ne devra pas aller demander l'hospitalité aux *Peaux rouges*"; and again: "Aux sources de Susqueannah, ou il acheta une terre de 200,000 acres. La, sous la protection du président Jefferson, il passa tranquillement le reste de ses jours, qui furent brusquement interrompus par un accident. Il fut empoisonné dans un repas avec toute sa famille, par une méprise dont ou ne s'est jamais rendu compte. Personne ne succomba, mais lui, déjà vieux et affaibli, ne put résister longtemps à l'inflammation d'estomac qui en fut la suite" (Second Edition, p. 131, Paris, 1878).

One need but consult the "Continuation of the Memoirs of Priestley by his Son" (London, 1806, two vols.), in which minute details of the chemist's last illness are given, to note how ridiculous is the account of his having died by poison (see pp. 207—222).

Ferdinand Hevefer repeats the story of the poisoning, but says this cause of illness was attributed without sufficient proof (*sans preuve suffisante*) (*Hist. de la Chimie*, Paris, 1869, vol. ii., p. 476).

Frémy, in his "Discours préliminaire sur le développement . . . de la chimie" (Paris, 1881), says Priestley died "dans une ferme isolée près des sources du Susquehannah," giving us a third variety of orthography for the rather puzzling Indian name Susquehannah.

The climax of absurdity is, however, attained by Benjamin Gastineau in his "Génies de la science" (Paris, n.d., 1870). After referring to his unhappy persecution in Birmingham, this author writes of Priestley:—"Dégoûté de son pays par ces scènes de cannibalisme il s'exila en Amérique où il s'éteignit paisiblement, après avoir été l'ami de Jefferson Davis" (p. 100).

The Birmingham riots of 1791 were assuredly disgraceful enough, and we would be the last to defend the instigators and their crimes, but to attribute *cannibalism* to Englishmen in 1791 is certainly a gross libel. Since, however, the author shows in the next sentence that he confounds President Thomas Jefferson with the late Jefferson Davis, what better things can be expected of him?

Though rather severe, we are almost ready to agree with the English librarian who remarked, when a certain bibliography was commended, "Is it by a Frenchman?" and receiving an affirmative reply, added "Then it must be a bad one!"—I am, &c.,

H. C. B.

ESTIMATION OF FATTY ACIDS IN ALIZARIN OIL.

To the Editor of the Chemical News.

SIR,—The CHEMICAL NEWS (vol. lxi., p. 52) contains a note on the above subject by Mr. F. Guthrie. There are several processes in use for the estimation of the oily matter, which is a factor in the valuation of the said oil, and these methods are liable to give very erroneous results, due to various causes. The one, I believe, mostly used is extraction by immiscible solvents, ether, chloroform, &c., and drying the immiscible layer on the bath *in vacuo*. Chloroform is, from various reasons, to be preferred, but it does not separate well. These methods, depending on extraction with solvents, give results in excess of the truth, due to mineral matter, which are more or less counterbalanced by the solubility of the sulpho-acids in water; nevertheless, in experienced hands, the results are not far from the truth. The method proposed by the writer is by no means new, and his procedure is improved as follows:—

The saponification of glycerides is ensured by digesting with alcoholic potash (on the steam-bath), instead of aqueous caustic soda, evaporation of the alcohol, and prolonged boiling with 20 c.c. of 1—5 H₂SO₄. Fatty acids are washed in usual manner.

After weighing, the fatty acids are then in a fit state for using in determining the acetyl and iodine values.

This process, if adopted, would give the best, and most accurate, results, and there could be no possible discrepancy between different operators as at present; but we must remember that the fatty matter is recovered in an entirely different form.

I shall have more to say on this subject when my work on Turkey Red Oil is completed.—I am, &c.,

J. ARTHUR WILSON.

Tottington, near Bury,
Feb. 3, 1890.

THE IGNITING-POINT OF SULPHUR.

To the Editor of the Chemical News.

SIR,—Recently, in the course of conversation, a remark was made on the low temperature at which sulphur ignites. My interlocutor fixed it as not far above the melting-point of the substance; I was incredulous, and we appealed to the authorities. The result of our joint investigation is as follows:—

- (1). "Gmelin," ii., 169. "Sulphur takes fire at 260° (C.) according to Dalton, at 294° according to Thomson."
- (2). Thomson, "System of Chemistry," i., 278. "When sulphur is heated to the temperature of 560° (F. = 293° C.) it takes fire spontaneously."
- (3). Pelouze et Fremy, "Cours de Chimie Général," i., 23. "Il" (sulphur) "brûle dans ce gaz" (oxygen) "ou dans l'air à une température d'environ 150°" (C.).
- (4). Dumas, "Traité de Chimie," i., 127. "A 107° (C.) le soufre se liquéfie, et lorsqu'il est parvenu à 150°, sa surface, exposée au contact de l'air, s'enflamme."
- (5). "Watts," v., 532. "When heated in air or oxygen to a temperature of 250° C. takes fire."
- (6). "Miller," ii., 188 (Sixth Edition). "When heated in air it takes fire at between 235° and 260° (C.)."
- (7). "Tidy," Second Edition, p. 174, states that the octahedral variety fires at 239° F. = 115° C., and the prismatic at 248° F. = 120° C.

Thus, according to these chemists, sulphur ignites at quite a number of temperatures, ranging from 115° C. to 293° C., from which one is led to conclude that either it must be as protean in this respect as in its physical state, or (as a barely admitted alternative) one or more of these statements must be erroneous. It is possible that some one has it in his power to resolve this point, and to him I appeal, asking anyone who has actually determined the igniting-point of sulphur to give us the result, and indicate the method employed.—I am, &c.,

BERTRAM BLOUNT.

Laboratory, Broadway,
Westminster, S.W.
February 2, 1890.

TEA AND LARD.

To the Editor of the Chemical News.

SIR,—The CHEMICAL NEWS, vol. lxi., p. 59, contains a notice of the "Annual Report of the Analyst appointed for the Parish of Kensington for the year ending March 31, 1889," and in it remarks are made on the adulteration of tea, and the following words occur:—"Though not demonstrably adulterated, probably contained a proportion of leaves which had been previously exhausted and dried.

I should not have taken any notice of this were it not for the fact that I happen to know something of the cultivation and growth of tea, and its subsequent preparation for the market; and having examined this article in cities and towns under many circumstances, peculiar and otherwise, I think I can speak a little on the subject. Bearing in mind that good tea can be bought at a low price, I do not think it would pay for the trouble of collecting, drying, colouring, &c., of spent tea leaves, and I have never heard of these being collected for this purpose. It must be borne in mind that they (the leaves) must be manipulated in some way, otherwise they would be easily distinguished from other portions of a good tea. I know this sophistication was practised some twenty years ago; but if we find a little dirt, poor growth of leaves, and a little facing, it is about all we are likely to come across now-a-days. Yes, I think the faking up of exhausted tea leaves would hardly pay for the trouble, and we may consider ourselves fortunate that this article does not find more favour at the hands of the adulterator.

Then there is the aroma. I think the grateful herb is fairly treated in these times by the arch-fiend

sophisticator, and the poor may safely rely upon getting a pretty pure article, although at times it may be rather poor in quality, but this does not proceed from adulteration.

But with regard to lard, I can believe anything of this commodity; nothing would surprise me. It was but the other day that I had an interview with an individual who required some information respecting the refining of lard and the manufacture of margarine, and in the course of conversation I was asked whether it was possible to incorporate from 20 to 25 per cent of water in addition to "other matter," with lard. The addition was not considered an adulteration. I was told this lard was required for quick use in hotels, &c. I do not want to make a confession as to what I said, neither do I require absolution, but mention the matter as a fact. Most of us know that the lard we receive from America and elsewhere is, as a rule, a mysterious compound; its common adulterant is cotton-seed oil, but we may look for many other foreign bodies and find them, I would sooner use a common grade of margarine than most of the so-called refined leaf lard. Housekeepers and others may be pretty sure what they get in the former case, but in the latter a shroud of mystery is around it, and I am surprised that more prosecutions do not take place; there's something wrong somewhere.—I am, &c.,

JOHN H. SWINDELLS, Ph.D.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 2, January 13, 1890.

Some New Fluorescences.—Lecoq de Boisbaudran.—The author has examined the fluorescence of mixtures of zirconia and $Z\beta$, of stannic acid and samaria, of tantalitic acid and samaria, of the same two acids with $Z\alpha$ and $Z\beta$. He considers that the fluorescences described supply new instances of the plurality of the spectra obtained with one and the same active matter in different solid solvents.

The Relation between the Electric and Thermic Conductivities of the Metals.—Alphonse Berget.—The author does not believe that there is any absolute proportionality between the electric and thermic coefficients of conductivity. In a previous paper he has studied the variation of the thermic conductivity of mercury between 0° and 300°. He has found that the mean coefficient of variation is, for 1°, 0.00046, a number differing from the corresponding coefficient of variation of electric conductivity, which is 0.00085. The law of the proportionality of the two conductivities is therefore only approximately exact.

Formation-Heat of Platinic Chloride.—L. Pigeon.—The formation-heat of solid chloroplatinic acid, $PtCl_4 \cdot 2HCl + 6H_2O$, is 20.5 cal.

The Combinations of Gaseous Hydrogen Phosphide with Boron and Silicon Fluorides.—M. Besson.—Gaseous hydrogen phosphide, when very dry, seems to be without action upon boron fluoride at the ordinary temperature; but if the two gases are let come in contact in a refrigerated receiver, combination takes place at about -30°. At -50° a white solid is deposited, which takes a yellow tint as the temperature rises, and becomes decomposed. The compound may be represented by the formula $2BF_3 + PH_3$. A direct combination of hydrogen phosphide with silicon fluoride requires a temperature of -22° and a pressure of about 50 atmospheres. These

compounds increase the analogy between hydrogen phosphide and ammonia.

Observation on the Rotatory Power of Mitezite and Mitezodambose.—Aimé Girard.—The identity of the rotatory power of mitezite and mitezodambose is absolutely confirmed.

On a New Inosite, Racemo-inosite.—M. Maquenne and Ch. Tanret.—The two inosites have an exactly equal rotatory power, but in opposite directions. This equality of rotatory power in an inverse direction is found in their acetic ethers, which are equally amorphous, and soften at the heat of the hand. They melt at 247°. They behave exactly in the same manner with reagents.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. viii., No. 1.

Recent Improvements in the Electro-Metallurgy of Aluminium, and on the Influence of this Metal upon Siderurgic Products.—Van Langhen.—Aluminium renders iron softer, and naturally increases considerably the force of transverse resistance of white cast-iron, which is ordinarily porous. It also improves grey cast-iron, though to a less extent. The presence of aluminium has a still greater effect in augmenting the resistance to shocks. Aluminium augments the elasticity and diminishes the strain due to internal tension.

New Process for Carbonising Wood for the Manufacture of Powder.—Herr Güttler proposes to inject into the retorts hot carbonic acid during the process of manufacture and cold carbonic acid during the refrigeration. The gases from lime-kilns may be used for this purpose.

Journal für Praktische Chemie.
New Series, Vol. xl., No. 17.

Researches from the Laboratory of the University of Freiburg.—These researches comprise a memoir by Fr. Kehrmann on the Influence of the Nature and Position of certain Atoms and Atomic Groups in the Benzol Nucleus upon the Replaceability of Quinone-Oxygen by the Isonitroso-Group, and a paper by C. Willgerodt on the Symmetric Nitrophenyl Hydrazines of the Aromatic Series.

Fluorine Compounds of Vanadium and its Nearest Analogues.—Emil Petersen.—The author describes the potassium and ammonium double fluorides of vanadium.

Action of Nascent Nitrous Acid upon Various Amines and Pheneloid Bodies.—A. Deninger.—The author gives an account of the reaction of nascent nitrous acid with aniline, orthotoluidine, paratoluidine, parabenzidine, paratolidine, the naphthylamines, sulphanilic acid, salicylic acid and its esters, and paraphenolsulphonic acid.

On Oxymiazine (Oxypyrimidine).—E. von Meyer.—The author corrects two errors in his paper on the polymerisation of the nitriles (*Journal Prakt. Chemie*, xxxviii., p. 336; and xxx., 188 and 202), *i.e.*, the statements on the melting-points of amido- and of oxymethyldiphenylmiazine. The former melts, not at 172°, but at 168°, and the latter not at 256°, but at 250°.

MEETINGS FOR THE WEEK.

- MONDAY, 17th.—Medical, 8.30.
— Society of Arts, 8. "Stereotyping," by Thomas Bolas, F.C.S.
TUESDAY, 18th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 5. "Ocean Penny Postage and Cheap Telegraph Communication between England and all parts of the Empire and America," by J. Henniker Heaton, M.P.

WEDNESDAY, 19th.—Society of Arts, 8. "The Organisation of Secondary and Technical Education in London," by Prof. Silvanus P. Thompson, D.Sc.

- Meteorological, 7.
THURSDAY, 20th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "The Three Stages of Shakespeare's Art," by Rev. Canon Ainger, M.A., LL.D.
— Chemical, 8. "The Behaviour of the more Stable Oxides at High Temperatures," by G. H. Bailey, D.Sc., and W. B. Hopkins. "The Influence of Different Oxides on the Decomposition of Potassium Chlorate," by G. J. Towler, M.Sc., and J. Grant.
FRIDAY, 21st.—Royal Institution, 9. "Magnetic Phenomena," by Shelford Bidwell, M.A., F.R.S.
— Geological, 1. (Anniversary).
— Physical, 5. "On a Carbon Deposit in a Blake Telephone Transmitter," by F. B. Hawes. "The Geometrical Construction of Direct Reading Scales for Reflecting Instruments," by A. P. Trotter, B.A. "A Parallel Motion suitable for Recording Instruments," by A. P. Trotter, B.A. "On Bertrand's Refractometer," by Prof. S. P. Thompson.
SATURDAY, 22nd.—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.

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- Four 27-inch 36 Chamber High-Pressure Filter, Pressers, and Receivers, with Iron Columns, Stand-pipes, and Connections.
Seven Wood Vats, 11 feet 10 inches long, 3 feet 10 inches wide, and 3 feet 6 inches deep.
Two Wood Vats lined with Sheet Lead, 11 feet 9 inches long, 3 feet 9 inches wide, and 3 feet 7 inches deep.
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Two Wrought-Iron Tanks, 10 feet long, 3 feet wide, and 3 feet deep.
One Hoist with Chains and Fittings complete.
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Quantity of Iron Racks suitable for Drying Stoves.
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Two Round Wrought-Iron Tanks, 10 feet long, 3 feet wide, 3 feet deep, with Covers.
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One Automatic Air-Compressor.
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TAR AND LIQUOR.

- The Directors of the SOUTHAMPTON GAS LIGHT AND COKE COMPANY desire to receive Tenders for Surplus TAR and AMMONIACAL LIQUOR for One Year from the 6th March, 1890.
Estimated yearly make:—Tar, 250,000 gallons; Ammoniacal Liquor, 500,000 gallons.
The Contractor must agree to remove the same whenever required, and not to allow an accumulation of more than 10,000 gallons of either Tar or Liquor. Tank trucks and barges can be loaded at the Company's wharf.
Prices to be given for Liquor from 8 to 16 ounces per 1000 gallons. Strength to be ascertained by the Distillation Process of Mr. F. W. Hartley, A.I.C.E.
Prices for Tar to be per gallon.
Payments to be made in cash, fortnightly.
The successful Contractor will have to sign Agreement and Bond for the due performance of his Contract.
Tenders to be delivered to the undersigned not later than 10 o'clock in the morning of the 5th March, 1890. The Directors do not pledge themselves to accept the highest or any Tender.
C. CROWTHER SMITH, Secretary.

Ogle Road, Southampton,
February 12, 1890.

Silicates of Soda and Potash in the state of Soluble Glass, or in CONCENTRATED SOLUTION of first quality, suited for the Manufacture of Soap and other purposes, supplied on best terms by W. GOSSAGE and Sons, Soap Works, Widnes, Lancashire.

London Agents, COSTE and Co., 19 and 20, Water Lane, Tower Street, E.C. who hold stock ready for delivery.

FOR SALE.—THE CHEMICAL GAZETTE.
Complete Set (unbound and uncut), 17 volumes; from November, 1842, to December, 1859.—Address, "Publisher," CHEMICAL News Office, Boy Court, Ludgate Hill London, E.C.

THE CHEMICAL NEWS

Vol. LXI. No. 1578.

NOTE ON THE
DISPLACEMENT OF SILVER BY PLATINUM
AND PALLADIUM.

By FRANK P. PERKINS, F.I.C.

I HAVE observed that it is sufficient to add to a slightly acidulated solution of platinic chloride a fragment of sodium sulphite, and then brush the liquid over a well-washed silver print produced on plain salted paper, for the silver to be almost immediately displaced by platinum. This is a simple method of "toning" for such as have not the ready formed platinous salt at hand.

I have also noticed that a slightly acidulated solution of palladous chloride may be used in the same way, and with similar results.

Exeter, Feb. 13, 1890.

CELLULOSE AND ALKALIES : CELLULOSE
BENZOATES.

By C. F. CROSS and E. J. BEVAN.

A RECENT observation that the hydrated modifications of cellulose precipitated from solution either in the ammonia copper reagent, or in $ZnCl_2$.Aq. (50 per cent), are soluble in strong solutions of sodium hydrate, has afforded a ready means of preparing benzoates of cellulose. By treatment of the alkaline solution with benzoic chloride (Baumann, *Ber.*, xix., 3218) these derivatives are formed and precipitated. They are soluble in glacial acetic acid. On adding water to the solution they are precipitated in voluminous white flocks. The analysis of these compounds by alkaline hydrolysis, and estimation of the benzoic acid by titration, has occasioned some difficulty, and we defer, for the present, any statements as to their composition. They are fusible at high temperatures; on continuing to heat, benzoic acid sublimes. We hope to complete our present investigation of these compounds at an early date.

A noteworthy property of these hydrated modifications of cellulose is that they are assimilable by microscopic organisms. That they form an excellent nidus, *e.g.*, for moulds, appears from the fact that a quantity of the moist substance, well washed after precipitation, squeezed, and kept in a loosely covered jar, has developed an abundant growth of several varieties of these organisms.

In relation to any definitions of cellulose involving resistance to alkalies, these results have a special significance. Growing plants certainly afford an infinite variety of such hydrates, which, not less certainly, will be less or more soluble in alkaline solutions.* The cellulose isolated as the residue of processes of oxidation and hydrolysis must therefore be to that extent an arbitrary quantity. Believing these facts to be generally recognised, we are not a little surprised to read a paper by Lange in the *Ztschr. Physiol. Chemie*, p. 281 of the current issue, basing "A Method for the Quantitative Estimation of Cellulose" upon the observation of Hoppe-Seyler that cellulose resists the action of strong solutions of the alkaline hydrates at 200°! The essential part of the author's proposed process—as applied to woods—consists in a digestion with three to four times the weight of alkaline hydrate dissolved in an equal weight of water, with a

gradual increase of temperature to 180°, at which point it is maintained for one hour.

Of course, in view of the fact that the wood substance is a complex anhydride and a compound of cellulose and lignone "residues," the net product of the complex changes which must take place may very well be a cellulosic aggregate, approximating in weight to that of the pure cellulose isolated by the simple and definite process of converting the lignine into its chloride and removing the derivative by treatment with the specific solvent, sodium sulphite (solution). The author's results are interesting as a study of the action of the alkalies upon the ligno-celluloses (these results, as regards the soluble products, form, in fact, the substance of two valuable communications in the same journal); but we fail to see, more especially in absence of any evidence as to the composition of the residues ("cellulose"), that such a process of estimating cellulose is anything but a retrograde advance.

In view of the results described in this communication, and the solubility of the typical cotton cellulose, when hydrated, in alkalies, the author will probably see fit to revise some of his conclusions.

A PTOMAINE EXTRACTED FROM URINE
IN A CASE OF INFECTIOUS DISEASE
("MUMPS").

By A. B. GRIFFITHS, Ph.D., F.R.S.E., &c.

IN a case of "mumps" where the kidneys were involved an alkaloid was extracted from the urine by what may be called the "ether-tartaric acid" or the Luff method. The process is as follows:—

(a) A considerable quantity of the urine is made alkaline by the addition of a solution of sodium carbonate, and then agitated with half its volume of ether.

(b) The ethereal solution (after standing) is filtered and agitated with a solution of tartaric acid. The tartaric acid combines with any alkaloids present, forming soluble tartrates; and the solution of tartrates forms the lower layer of the liquid mass.

(c) The tartaric acid solution (after being separated from the ether) is also made alkaline by the addition of sodium carbonate, and is once more agitated with half its volume of ether.

(d) The ethereal solution (after standing) is separated, and the ether allowed to evaporate spontaneously.

(e) The residue (after drying over sulphuric acid) is finally examined for alkaloids (ptomaines).

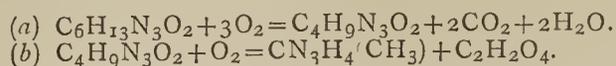
The alkaloid extracted by the above method (in a case where the parotid and submaxillary glands were both affected) crystallises in white prismatic needles, which are soluble in water, ether, and chloroform. It has a neutral reaction and a slightly bitter taste. It forms a yellow crystalline platinochloride, a pale yellow aurochloride, and a white crystalline hydrochloride. It combines with phosphomolybdic acid, forming a golden yellow precipitate. This alkaloid produces a white precipitate with phosphotungstic acid, a slight yellow precipitate with mercuric-potassic iodide, a brown precipitate with iodine solution, and a flocculent precipitate with picric acid. Analyses of the alkaloid in question gave the following results:—

	Found.			Calculated for $C_6H_{13}N_3O_2$.
	I.	II.	III.	
Carbon	45.34	—	45.29	45.28 p.c.
Hydrogen	8.22	—	8.20	8.17 "
Nitrogen	26.39	26.42	—	26.41 "
Oxygen	—	—	—	20.12 "

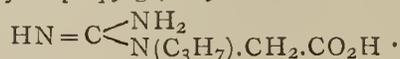
The above figures correspond with the formula $C_6H_{13}N_3O_2$.

* *cf.* "Hydration of Cellulose," *J. Soc. Chem. Ind.*, 1885, p. 7.

When boiled with mercuric oxide this base yields creatine (methylglycocyanine), and finally methylguanidine and oxalic acid:—



Therefore this alkaloid is related to creatine (an animal product) or methylglycocyanine, as well as guanidine. It may possibly be *propylglycocyanine*:—



Further research will settle this point.

If the alkaloid is propylglycocyanine we have the basis of a homologous series of oxygenated bases related to the ureides. Thus—

$\text{C}_3\text{H}_7\text{N}_3\text{O}_2$	Glycocyanine.
$\text{C}_4\text{H}_9\text{N}_3\text{O}_2$	Methylglycocyanine (creatine).
$\text{C}_5\text{H}_{11}\text{N}_3\text{O}_2$	Ethylglycocyanine (?).
$\text{C}_6\text{H}_{13}\text{N}_3\text{O}_2$	Propylglycocyanine (the new base).

The new animal alkaloid is poisonous. When administered to a cat it produced nervous excitement, cessation of the salivary flow, convulsions, and death.

The alkaloid in question is not found in normal urines, therefore there is no doubt that it had been produced within the system during the course of the disease.

It is difficult to say how this alkaloid is formed; it may be a morbid leucomaine (a product of vital physiological or rather pathological processes), or it may be formed from the decomposition of albumenoid molecules by the agency of pathogenic and other microbes.

THE TREATISE OF DEMOCRITUS ON THINGS NATURAL AND MYSTICAL.

Translated by ROBERT R. STEELE, F.C.S., &c.

LITTLE apology is needed to English readers for publishing the earliest known chemical treatise for the first time in English. It is a work on the manufacture of gold and silver, and the receipts are entirely practical ones, which can be followed out at the present time, and which produce alloys or superficial imitations of those metals. The idea of transmutation does not explicitly occur in the work.

Democritus lived in the Fourth Century, B.C. The work proceeds from writers of his school, and is certainly not later than the first centuries of our era. A somewhat magical introduction is prefixed in the text of M. Berthelot.

There were originally four books on the tincture of purple, gold, silver, and stones. Of these, we have the second and third and a fragment of the first.* The text I translate from is the Latin translation of Pizzimenti, published at Cologne, 1574, and Padua, 1575, with ancient commentaries. The English reader may see a sample of these at the end of the translation of Basil Valentine, London, 1678, 8vo. The commentators have well fulfilled their aim; they have explained words and letters, until the plain statements of their author are buried under a mountain of verbiage.

I have chosen this text to bring out the differences between it and the Greek text, first published by M. Berthelot in his "Collection of Ancient Greek Alchemists," Paris, 1888, a work to which I am under great obligations, and to which I would refer any student interested in the study of alchemy. The variations (not merely verbal) I have indicated by italics. A glossary, with references to Pliny's "Natural History," is appended.

ROBERT R. STEELE.

3, Blomfield Terrace,
Shepherd's Bush, W.

* Published in the CHEMICAL NEWS, vol. xlviii., p. 279.

FRAGMENT OF ANCIENT INTRODUCTION.

"Nature rejoices with Nature; Nature conquers Nature; Nature restrains Nature."

We (his disciples) greatly wondered at how briefly he had bound up the whole science. I come into Egypt, bearing the treatises of nature,* that thou mayest cast off confused and superfluous matter.

I. COPPER IS WHITENED WITH MERCURY-AMALGAM OR ARSENIC, AND IS THEN COLOURED GOLDEN BY ELECTRUM OR POWDERED GOLD.

Taking mercury, thrust it into the body† of magnesia, or into the body of Italian antimony, or of unfired sulphur, or of *silver spume*, or of quick lime, or to alum from Melos, or to arsenic, or as thou knowest, and throw in *white earth of Venus*,‡ and thou shalt have clear *Venus*; then throw in yellow *Luna*, and thou shalt have gold, and it will be chrysocoral reduced into a body.

Yellow arsenic also makes the same, and prepared sandarach, and well bruised cinnabar, but quicksilver alone makes brass shining; for nature conquers nature. §

II. SULPHIDE OF SILVER IS TREATED WITH SULPHIDES OF LEAD OR ANTIMONY, AND THE RESULTING ALLOY IS COLOURED GOLDEN.

Treat silver marcasite, which is also called siderites, and do what is usual that it may be melted. It melts with *yellow* or white litharge, or in Italian antimony, and cleanse it with lead (not simply, say I, lest thou err, but with that from *Scissile*, and our black litharge), or as thou knowest; and heat, and throw it made yellow to the material,§ and it becomes coloured; for nature rejoices with nature.

III. COPPER PYRITES IS ROASTED AND TREATED WITH SALT AND ALLOYED WITH SILVER OR GOLD TO FORM GOLD-COLOURED ALLOYS.

Treat pyrites till it becomes incombustible, casting off darkness, but treat with brine, or fresh urine, or sea water, or oxymel, or as thou knowest, until it becomes an incombustible shaving of gold; and as it becomes so, mix with it unfired sulphur, or yellow alum, or Attic ochre, or what thou knowest, and add to *luna* for *sol*, and to *sol* for auriconchylum; for nature conquers nature.

IV. CLAUDIAN METAL IS RENDERED YELLOW BY SULPHUR OR ARSENIC, AND ALLOYED ON GOLD OR SILVER.

Taking claudianum, thou shalt make a marble, as of custom, until it becomes yellow. Thou shalt not render the stone yellow, I say, but that which is useful of the stone. Thou shalt yellow it with alum burnt with sulphur, or with arsenic, or sandarach, or lime, or that thou knowest, and if thou apply it to *luna* thou makest *sol*, but if to *sol* thou makest auriconchylum; for victorious nature restrains nature.

V. SILVER OR BRONZE ARE TREATED WITH AN AMALGAM OF IRON TO PRODUCE GOLD OR ELECTRUM.

Make cinnabar white by oil, or vinegar, or honey, or brine, or alum, then yellow by *misy*, or *sory*, or *chalcant*, or live sulphur, or that thou knowest, and add to *luna* and it will be *sol* if thou colourest golden, or to bronze for electrum. Nature rejoices with nature.

VI. A YELLOW GOLDEN VARNISH FOR METALS.

Whiten, I say, *copper*, *cadmia*, or *zonytes*, as of custom, afterwards make it yellow. But you will yellow it with the bile of a calf, or terebinth, or castor oil, or radish

* "Nature" seems to be used for the specific qualities of a substance; those which differentiate it from others.

† Probably, the reduced metal of.

‡ Berthelot's text rarely used these alchemical names, never in the case of copper.

§ For colouring the alloy—not expressed.

oil, or yolks of eggs, which can render it yellow, and add to *luna*, for it will be gold for gold* ; for nature conquers nature.

VII. THE TREATMENT OF SILVER BY SUPERFICIAL SULPHIDATION TO RENDER IT GOLD COLOURED.

Treat androdamas with bitter wine, or sea water, or acid brine, which things can attack its nature, melt with Chalcidonian antimony, and treat it again with sea water, or brine, or acid brine ; wash until the blackness of the antimony goes away, heat or roast it until it begins to grow yellow, and thou shalt treat with untouched *divine*† water, and lay it on silver, and when thou addest live sulphur thou makest chrysosomium into *golden liquid* ; for nature conquers nature. This is the stone called chrysites.

VIII. AN ALLOY OF COPPER AND LEAD IS FORMED, WHICH IS TURNED YELLOW.

Taking white earth from ceruse, I say, or from the *scoria* of silver, or of Italian antimony, or of magnesia, or even of white litharge, whiten it with sea water, or acid brine, or with water from the air under the dew, I say, and the sun, that it, when dissolved, may become white as ceruse. Heat then this in the furnace, and add to it the flowers of copper, or scraped rust of copper, worked up by art, I say, or burnt bronze sufficiently corroded, or chalcites, or *cyanum* ; then it becomes compact and solid, but it becomes so easily. This is molybdochalium. Test it therefore, whether it has cast off its blackness, but if not, blame not the bronze, but rather thyself, since thou hast not conducted the operation rightly ; therefore thou shalt brighten it, and dissolve it, and add what is necessary to yellow it, and roast till it begins to grow yellow, and throw it into all bodies ; for bronze colours every body where it is shining and yellow ; for nature conquers nature.

IX. COPPER AND SILVER ARE MADE YELLOW BY SULPHATE OF IRON ; WITH A PROCESS OF CEMENTATION.

Rub up sory and chalcant with unfired sulphur ; but sory is, as leprous cyanus, always found in misy ; they call it green chalcant. Roast it, therefore, in the middle of coals for three days, until it becomes a *red* drug, and throw it into Venus, or Luna made by us, and it will be Sol. Place this, cut up in sheets, in vinegar, and chalcant, and misy, and alum, and sal cappadociæ, and red nitre, or as thou knowest, for three, or five, or six days, until it becomes a rust, and it tinges ; for chalcant makes sol a rust. Nature rejoices with nature.

X. AN ALLOY OF GOLD IS HEATED BY SUPERFICIAL CEMENTATION.

Treat Macedonian chrysocola, which is like the rust of bronze, by dissolving it in the urine of a young girl until it entirely changes ; for the nature is hidden within. When, therefore, it is changed, dip it into castor oil, often heating it, and tinging it, afterwards roast with alum, first dissolving with misy or unfired sulphur ; render it yellow, and colour the whole body of gold.

(To be continued).

Combinations of the Alkaline Metals with Ammonia.—M. Joannis.—The author has already shown that an excess of ammoniacal gas gives, with the alkaline metals, a solution possessing a variable tension as long as the concentration does not reach $\text{Na} + 5.3\text{NH}_3$ at 0° , then a constant tension whilst ammonia is withdrawn, and NH_3Na crystallises. The results of experiments do not agree with the theoretical conclusions of M. Bakhuis Roozeboom.—*Comptes Rendus*, Vol. cx., No. 5, February 3, 1890.

* Greek reads:—"Gold, for it will be golden through gold and the golden liquor."

† A curious mistranslation, the words *divine* and *sulphur* being similar in Greek. It is probably a polysulphide of calcium.

ON THE
DECOMPOSITION OF ORGANIC MATTER
IN WATER.*

By MARK POWERS.

(Concluded from p. 79).

Other Nitrogenous Substances.

IN the following Table I have given the results of my experiments, showing how much of the total nitrogen can be evolved as ammonia by the ordinary Wanklyn method from an important class of nitrogenous compounds.

1 m.grm. substance.	M.grms. NH_3 evolved.	Theoretical amount.
Leucine, $\text{C}_6\text{H}_{13}\text{NO}_3$	0.130	0.130
Glycocoll, $\text{C}_2\text{H}_5\text{NO}_2$	0.225	0.226
Aspartic acid, $\text{C}_4\text{H}_7\text{NO}_4$	0.125	0.130
Indol, $\text{C}_8\text{H}_7\text{N}$	0.144	0.145
Skatole, $\text{C}_9\text{H}_9\text{N}$	0.120	0.130
Tyrosine, $\text{C}_9\text{H}_{11}\text{NO}_3$	0.094	0.094
Urea, $\text{CH}_4\text{N}_2\text{O}$	0.060	0.058
Hippuric acid, $\text{C}_9\text{H}_9\text{NO}_3$	0.090	0.095
Asparagine, $\text{C}_4\text{H}_8\text{N}_2\text{O}_3 + \text{H}_2\text{O}$	0.200	0.226
Quinine sulphate, $(\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2)_2\text{H}_2\text{SO}_4 + 8\text{Aq}$..	0.040	0.080
Quinidine sulphate, $(\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2)_2\text{H}_2\text{SO}_4 + 2\text{Aq}$..	0.043	0.071
Strychnine, $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$	0.097	0.101
Trimethylamine chlor., $\text{C}_3\text{H}_7\text{NH}_2\text{HCl}$	0.180	0.178
Aniline chloride, $\text{C}_6\text{H}_5\text{NH}_2\text{HCl}$	0.060	0.131
Albumen	0.149	0.157

In this list of compounds the intention has been to include the important decomposition products of albumen, such as leucine, tyrosine, aspartic acid, glycocoll, indol, and skatole, as the greater portion of the organic nitrogen of natural waters occurs as a constituent of derived products from albuminous matter. Tiemann and Preusse have obtained the total amount of nitrogen in leucine, tyrosine, and aspartic acid in the form of ammonia. My own experiments gave similar results in case of each substance mentioned, the total nitrogen being obtained by the first distillation.

Hippuric acid decomposes in a very peculiar manner. 3 m.grms. of this acid were dissolved in 500 c.c. of water, 200 c.c. were distilled for free ammonia, 50 c.c. permanganate solution added, and the albumenoid ammonia obtained was 0.02, 0.03, 0.042, 0.05, 0.043 m.grms. in the different distillates ; a second distillation gave 0.065, 0.008, 0.002 m.grms., thus completing the evolution of the total nitrogen in the form of ammonia.

Wanklyn states that quinine, quinidine, strychnine, &c., yield one-half their nitrogen in the form of ammonia. I have obtained similar results in case of quinine and quinidine, but the sample of strychnine tested gave nearly the whole amount.

The Oxidation of Organic Matter in Water by Means of Permanganate Solution.

The extent to which a large number of important organic compounds are oxidised, especially the principal

* *Journal of Analytical Chemistry*, Vol. iii., Part 4, October, 1889.

decomposition products of albumen, is shown in the following table. The methods of Schulze and Kubel are compared by giving the results of each. In Schulze's method 100 c.c. of water containing a definite amount of the compound is boiled during ten minutes with constant excess of standard potassium permanganate solution (containing 320 m.grms. per litre) and a definite quantity of pure sodium hydrate, while in Kubel's method the substance is boiled during ten minutes in solution acidified with sulphuric acid. By either method the amount of oxygen consumed varies from a mere trace to almost the total amount necessary for complete oxidation. The correction necessary in Schulze's method was determined by making blank experiments.

1 m.grm. substance.	Schulze's method. M.grms. oxygen consumed.	Kubel's method. M.grms. oxygen consumed.	M.grms. oxygen required for com- plete oxidation.
Leucine, $C_6H_{13}NO_3$	0.216	0.208	2.015
Tyrosine, $C_9H_{11}NO_3$	1.224	1.320	1.812
Clycocol, $C_2H_5NO_2$	0.100	0.100	0.960
Aspartic acid, $C_4H_7NO_4$	0.368	0.368	0.902
Asparagine, $C_4H_8N_2O_3 + H_2O$	0.112	0.08	0.960
Indol, C_8H_7N	1.252	2.080	2.666
Skatole, C_9H_9N	1.696	1.720	2.748
Benzoic acid, $C_7H_6O_2$	0.026	0.096	1.967
Urea, CH_4N_2O	trace	trace	0.800
Hippuric acid, $C_9H_9NO_3$	0.224	0.228	1.743
Trimethylamine chloride, $C_3H_7NH_2HCl$	0.024	0.032	1.761
Aniline chlor., $C_6H_5NH_2HCl$	1.312	1.320	1.916
Salicylic acid, $C_7H_6O_3$	1.392	1.480	1.623
Quinine sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 8Aq$	0.480	0.820	1.798
Quinidine sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 2Aq$	0.416	0.752	2.046
Cinchonine sulphate, $(C_{19}H_{22}N_2O)_2H_2SO_4 + 2Aq$	0.440	0.744	2.127
Cinchonidine sulphate, $(C_{19}H_{22}N_2O)_2H_2SO_4 + 6Aq$	0.400	0.640	1.964
Strychnine sulphate, $(C_{21}H_{22}N_2O_2)_2H_2SO_4 + 6Aq$	0.872	1.048	1.867
Morphine chlor., $C_{17}H_{19}NO_3HCl + 3Aq$	1.016	1.062	1.726
Tannic acid, $C_{14}H_{10}O_9 + 2Aq$	0.768	0.797	1.073
Citric acid, $C_6H_8O_7$	0.504	0.490	0.750
Tartaric acid, $C_4H_6O_6$	0.368	0.432	0.533
Starch, $C_6H_{10}O_5$	0.540	0.544	1.185
Cane sugar, $C_{12}H_{22}O_{11}$	0.628	0.636	1.123
Lactose, $C_{12}H_{22}O_{11} + H_2O$	0.640	0.640	1.066
Glucose, $C_6H_{12}O_6$	0.650	0.648	1.066

From the results of these experiments, Kubel's method being simpler, has the preference. The results obtained by the two methods are in most cases approximately the

same. A large number of the above compounds require over one-half of the amount of oxygen necessary for complete oxidation. In several instances these results accord with those given by Tiemann and Preusse, while in others, different figures were obtained. Without doubt, the application of the principle of oxidation, according to the methods detailed above, yields more satisfactory information than any other so far proposed. Dr. Frankland states that cane-sugar and starch do not require so much as one-hundredth of the oxygen necessary for total oxidation; by Kubel's method, the quantity is over one-half the amount required. In other cases the oxidation would be slight at the ordinary temperature, while at the boiling point of water a large amount of oxygen would be consumed.

In conclusion, several statements may be made in reference to the results obtained by these experiments.

Albumen, urea, and some other compounds will evolve their total nitrogen in the form of ammonia by prolonged boiling with strong solution of alkali permanganate.

No definite portion of the total nitrogen of these compounds is obtained in the first distillation, the amount depending upon a number of conditions, of which the quantity of substance used and the rapidity of distillation are the chief factors that vary the result. Albumen gave in one experiment by the first distillation 1.42 m.grms. ammonia, while the total amount was 2.8 m.grms.; in a second experiment 2.63 m.grms.—total, 4.63 m.grms. In one instance, thirteen successive distillations were made, collecting four distillates of 50 c.c. each, the total amount obtained being about 95 per cent. Egg albumen undergoing putrefaction yields a gradually increasing quantity of free ammonia, while the albumenoid ammonia decreases in a regular manner.

The principal decomposition products of albumen give up readily their total nitrogen in the form of ammonia. Indol and skatole are carried over in the distillation of free ammonia, and give a milkiess to the solution when nesslerised. This fact may account in part for the "haziness" frequently observed in nesslerising.

2.5 m.grms. urea gave of free and albumenoid ammonia 15.5 per cent, while $\frac{1}{2}$ m.grm. yielded 25 per cent. Urea was boiled ten hours with strong solution of alkali permanganate, but not completely decomposed. Complete decomposition was effected, however, by boiling 2 m.grms. during twenty hours with 50 c.c. of permanganate solution. On the other hand, 2 m.grms. of this compound were almost completely decomposed by boiling in water alone for same length of time. The amount of ammonia evolved from urea by the ordinary method depends upon the amount of this substance in solution, a smaller quantity yielding a relatively larger quantity of both free and albumenoid ammonia.

Hippuric acid yields more albumenoid ammonia in the last distillate than in the first. It is, however, completely decomposed by a second distillation.

Quinine and quinidine yield apparently about one-half of their total nitrogen in the form of ammonia. The sample of strychnine tested gave nearly the total amount.

The amount of oxygen consumed varies from a mere trace to almost the total amount required by theory. About one-half the number of compounds studied required from one-half to seven-eighths of the total amount of oxygen. Indol, skatole, and tyrosine strongly reduce the permanganate solution. A large number of organic compounds containing no nitrogen, such as the sugars, alcohols, vegetable acids, &c., are stronger reducing agents than some nitrogenous compounds which may be considered more dangerous.

No compounds were examined, except urea, which did not consume more or less oxygen.

For many valuable suggestions while engaged in the study of these compounds, I am deeply indebted to Dr. John H. Long, in whose laboratory these experiments have been made.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 6th, 1890.

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

CERTIFICATES were read for the first time in favour of Messrs. Percival Babington, Elmfield, Rotherham, Yorks; Richard Berncastel, 38, Ventnor Villas, Brighton; William Burton, 18, Victoria Steet, Basford, Stoke-on-Trent; John Dennant, Lyndhurst Crescent, Glenferrie, Melbourne; Frank Gosling, Waldegrave Road, Teddington; John Charles Jackson, 51, Wellington Road, St. John's Wood, N.W.; Alfred E. Macintyre, Saint John, N.B., Canada; Ira Moore, Sutton Crosshills *via* Keighley; John Myles, Butterburn Park, Hamilton.

The following were elected Fellows of the Society:—

Edward Whitley Allsom, James Munro Taylor Anderson, Frederick Graham Ansell, George Frederick Brindley, Sydney Hoare Collins, John B. Coppock, Thomas Southall Dymond, Alexander Charles Farquharson, Cuthbert Chapman Gibbes, James Grant, William Winson Haldane Gee, B.Sc., P. J. Hartog, Joseph H. Heywood, Arthur Hutchinson, Robert Law, James Guthrie Mactaggart, Arthur Hotham McConnell, Hugh Marshall, Francis Herbert Mason, William Samuel Newman, Edgar Philip Perman, B.Sc., Edward Russell, William Charles Sayers, Saville Shaw, Harry Wood Smith, B.Sc., Henry Heron Smith, John Stokes, John Wade, James Walker, Sydney Russell Wells, B.Sc.

The following papers were read:—

4. "Observations on Nitrous Anhydride and Nitrogen Peroxide." By Professor RAMSAY, Ph.D., F.R.S.

The author recommends as the best method of preparing pure nitrogen peroxide that the deep blue-green liquid, supposed to be a mixture of this oxide and nitrous anhydride, which is obtained by condensing the products of the interaction of arsenious oxide and nitric acid, be added to a solution of nitric anhydride in nitric and phosphoric acids, prepared by adding phosphoric anhydride to well cooled nitric acid; after agitating the mixture, the upper layer is decanted and distilled. He assumes that the two oxides interact thus: $N_2O_5 + N_2O_3 = N_2O_4$.

The melting-point of the peroxide was found to be 10.14° , in agreement with Deville and Troost's statement. The depression in the freezing-point caused by one part of chloroform in 100 parts of the peroxide was 0.35° , and by one part of chlorobenzene, 0.37° : the molecular depression is therefore 41° .

The heat of fusion (W) of the peroxide, calculated from this number and the observed fusing-point by Van't Hoff's formula—

$$W = \frac{0.02T^2}{t},$$

where T is the freezing-point of the solvent in absolute degrees and t the molecular depression, is 33.7 cal.; a direct determination gave 32.3 .

To determine the molecular weight of nitrous anhydride, a known weight of nitric oxide was passed into the peroxide, and the depression of the freezing-point determined; assuming that an amount of nitrous anhydride equivalent to the nitric oxide was formed, the results gave the values 80.9 , 92.7 , and 81.0 , instead of 74 , the value corresponding to the formula N_2O_3 . The author was unsuccessful in freezing nitrous anhydride, even at -90° , by means of liquefied nitrous oxide. It was found to be soluble in this liquid, and it was further observed that as evaporation took place nitric oxide gas was given off, together with the nitrous oxide: it would therefore appear that N_2O_3 is unstable, even at the very low temperature at which nitrous oxide is liquid.

DISCUSSION.

Referring to Professor Ramsay's determination of the heat of fusion of nitrogen peroxide, Mr. PICKERING said that observations on substances which exercise an appreciable influence on each other cannot be safely used in deducting the heat of fusion. Thus, in the case of mixtures of water and sulphuric acid solutions containing respectively the values 37.4 , 58.3 , 79.9 , 74.9 , and 56.3 as the heat of fusion of water, instead of 79.6 . In strong solutions the lowering of the freezing point is always abnormally great; in such solutions, according to the theory of osmotic pressure, the dissolved molecules, being more subject to each other's attraction, should exercise less attraction on the molecules of the solvent, and these latter, therefore, should coalesce more readily to form a solid.

Mr. GROVES remarked that sulphuric acid might be used in preference to phosphoric anhydride in preparing pure nitrogen peroxide: the liquid product obtained by warming arsenious oxide with a mixture of two parts nitric and one of sulphuric acid might be freed from the small proportion of nitrous anhydride which it contained by treatment with sulphuric and a little nitric acid, and on then distilling, pure nitrogen peroxide was obtained.

Mr. WYNNE inquired whether Professor Ramsay had examined the action of nitric oxide on nitric anhydride: it had been stated that the interaction was between N_2O_3 and N_2O_5 , but nitric oxide alone should have the same effect.

Professor RAMSAY, in reply, said that the method of preparing nitrogen peroxide described by Mr. Groves gave good results, but was less economical than his own. He had not examined the action of nitric oxide on nitric anhydride.

5. "Note on the Law of the Freezing-Points of Solutions." By S. U. PICKERING.

According to views explained in a previous communication (*Proc. Chem. Soc.*, 1889), the author considers the lowering of the freezing-point of a solvent to be attributable to three actions, which he distinguishes as mechanical, physical, and chemical. He has now succeeded in reducing the values for these actions into one equation, which gives the total lowering of the freezing-point, t° , to be—

$$t^\circ = \frac{K + 167 \pm \sqrt{(K - 167)^2 - 668 \frac{Kl + H}{Ac}}}{2},$$

where l is the heat capacity of the limiting hydrate (that is, the hydrate from which no amount of cooling could make water crystallise out); H the heat absorbed in the decomposition of the hydrate (or hydrates) constituting the solution taken into the next lower one; A the maximum number of water molecules which could be crystallised out by excessive cooling; C the heat capacity of water. The author applies a small correction to Person's so-called absolute zero, -160° , based on a combination of Person's with Regnault's values for the heat capacity of ice, and gets -167° , a value which he finds to give results in his calculations of the freezing-points agreeing with those found even more closely than -160° did. K represents the "mechanical" lowering, this being equal to—

$$\frac{n167m}{300},$$

in which n is the number of foreign (fundamental) molecules (of sulphuric acid in the case taken) to 100 H_2O , and m the number of fundamental molecules constituting the active molecule of the solvent; in the case of water, m is generally 3.

In his former communication the author stated that the triple molecules of water began to simplify when sulphuric acid solutions of 30 per cent strength were reached, being resolved into simple or H_2O molecules when the

strength reached about 38 per cent. The above equation shows that this simplification must occur. As the strength of the solution increases, K becomes bigger, and a point is reached where value of—

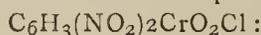
$$668 \frac{Kl+H}{Ac}$$

is bigger than $(K-167)^2$, so that the contents of the surd are negative, and there will be no freezing-point possible under these conditions. This occurs at 34 per cent: and the only way in which water could be frozen out of solutions of greater strength (as is the case) is by the reduction of the magnitude of K by the simplification of the $3H_2O$ molecules, that is, by the reduction of the value for m .

Proceeding with this reduced value for K, another point (37.95 per cent) is soon reached, where the freezing out of water would become impossible, even under these new conditions, and, as the H_2O molecules could simplify no further, it must cease absolutely: as a matter of fact it does so: the crystallisation of water ceasing at about 38.2 per cent, while that of the tetrahydrate begins.

6. "The Action of Chromium Oxylchloride on Nitrobenzene." By G. G. HENDERSON, B.Sc., M.A., and J. M. CAMPBELL, B.Sc.

These substances interact, suddenly and with great violence, even at the ordinary temperature, and no definite products are obtained. When a 50 per cent solution of chromium oxylchloride in dry chloroform is heated on the water-bath with a similar solution of nitrobenzene, hydrogen chloride is evolved and a brown powder slowly separates. After it has been washed with chloroform and dried, this powder has the composition—



it rapidly takes up moisture, and, when thrown into water, is decomposed with evolution of much heat, chromic chloride and chromic acid going into solution and nitrobenzene separating out, but the authors have failed to obtain the nitroquinone described by Etard. On using nitrobenzene containing nitrotoluene it was found, however, that a brown compound was produced which, when decomposed by water, gave nitrobenzene and, in smaller quantity, paranitrobenzoic acid; the latter substance has properties very similar to those attributed to nitroquinone, and it is suggested that Etard may have mistaken one for the other.

7. "Studies on the Constitution of the Tri-derivatives of Naphthalene. No. 1. The Constitution of Betanaphthol- and Betanaphthylaminesulphonic Acids, R and G Naphthalenemetadisulphonic Acid." By HENRY E. ARMSTRONG and W. P. WYNNE.

The study of the tri-derivatives of naphthalene is of importance from many points of view, both technical and theoretical; several are largely used in the preparation of azo-dyes, and it is necessary that their constitution should be known in order that the dependence of colour and tinctorial properties on structure may be determined; and especially is this the case, as all are not equally valuable—betanaphtholdisulphonic acid G (Gelb), like the "Bayer" modification of betanaphtholmonosulphonic acid, interacting but slowly with diazo salts; while the corresponding betanaphthylaminedisulphonic acid, like the "Badische" modification of betanaphthylaminemonosulphonic acid, is incapable of forming azo-dyes.

Moreover, having characterised the dichloronaphthalenes by converting them into sulphonic acids, the authors were anxious also to determine the exact course of the change on sulphonation, especially as isomeric changes were noticed in several instances (*Proc. Chem. Soc.*, 1889, 52, 120), it being probable that much light would thus be thrown on the laws which govern substitution in the naphthalene series; and from this same point of view the comparative study of the influence exercised by radicles, such as Cl, OH, NH_2 , on the formation of disulphonic acids appeared likely to afford results of considerable interest.

In the case of the dichloronaphthalenes, which serve as reference compounds for di-derivatives of naphthalene, the author's previous work has shown how much has to be learnt by carefully characterising the several isomerides (*Proc. Chem. Soc.*, 1888, 104); and in the case of the trichloronaphthalenes, no fewer than fourteen of which are possible, which will ultimately serve as reference compounds for tri-derivatives of naphthalene, it is still more necessary to characterise each compound, owing to the close similarity which obtains between many of the isomerides; no fewer than four, for example, melt at nearly the same temperature, about 90—92°.

The study of the betanaphtholdisulphonic acids was commenced by one of the authors in 1880 (*Chem. Soc. Journ.*, 1881, 139). Results were obtained which led to the belief that both were derivatives of the Schaefer monosulphonic acid, but at that time no methods were available by which any final determination of their constitution could be effected. Subsequently attention was directed to the corresponding amido-disulphonic acids when these became procurable. About three years ago a liberal supply of the betanaphthylaminedisulphonic acid R, in the form of acid sodium salt, was obtained from the *Actiengesellschaft für Anilinfabrikation*, through the kindness of Dr. Martius. In the spring of 1888, the authors became aware of the results since published by Duisberg and Pfitzinger (*Ber.*, 1889, 396), and arranged with Dr. Duisberg to carry on the investigation.

Constitution of the Betanaphthylaminedisulphonic Acid R.—Duisberg and Pfitzinger inferred that this acid was derived from the α -naphthalenedisulphonic acid of Ebert and Merz, as the disulphonic acid obtained from it on displacing the NH_2 group by v. Baeyer's hydrazine process gave the dihydroxynaphthalene corresponding to the α -acid on fusion with potash. Although perfectly satisfied with this proof, the authors have thought it desirable to amplify the evidence in order to meet the possible objection that isomeric change may occur during the fusion, as in the case of benzene-derivatives. They find on directly comparing the disulphonic acid with the Ebert and Merz α -acid that the two behave alike; the sulphochloride derived from the amido-acid crystallising in large prisms which gradually become opaque, fusing at 158°, and yielding the dichloronaphthalene melting at 114° on distillation with PCl_5 .

By the Sandmeyer method the amido-acid may be converted into a chlorodisulphonic acid, the chloride of which crystallises in radicle groups of spear-like needles, melting at 165°; on distillation with PCl_5 this yields a corresponding trichloronaphthalene, which crystallises from alcohol in small spherical aggregates of minute scales or flat needles, melting at 90—91°.

Taking into account the previous determination of the constitution of the Ebert and Merz α acid (*Proc. Chem. Soc.*, 1888, 48), the constitution of the amidodisulphonic acid R, and of the corresponding trichloronaphthalene is expressed by the formula:—



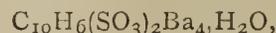
Betanaphthylamine-disulphonic acid R.



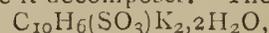
Trichloronaphthalene.
M. p. 90—91°.

Constitution of Betanaphthylaminedisulphonic Acid G.—

A quantity of this acid was first procured from the *Actiengesellschaft für Anilinfabrikation*; we have to thank the *Farbenfabriken vormals, F. Bayer and Co.*, for a subsequent larger supply. On converting it into naphthalenedisulphonic acid by the hydrazine method, a new acid was obtained. The barium salt,—

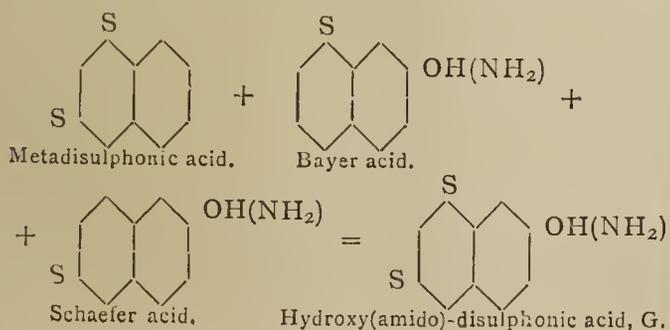


is very soluble in water, and has not been obtained in any definite crystalline form; it retains $1\frac{1}{2}H_2O$ at 270°, above which temperature it decomposes. The potassium salt,—

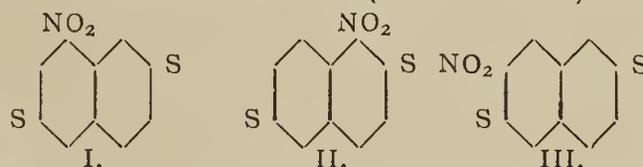


	1:4'	2:2'	2:3'	1:3'	1:3
(SO ₃ H) ₂ ..	Armstrong (<i>Chem. Soc. Journ.</i> , 1871, 173; <i>Ber.</i> , 1882, 205); Armstrong and Wynne (<i>Proc.</i> , 1886, 231; 1887, 42). Ewer and Pick, G. P. 41934.	Ebert and Merz (<i>Ber.</i> , 1876, 592).	Ebert and Merz (<i>Ber.</i> , 1876, 592).	Armstrong and Wynne (<i>Proc.</i> , 1886, 231); Armstrong (<i>Proc.</i> , 1889, 10). Ewer and Pick, G. P.	Armstrong and Wynne.
(SO ₃) ₂ Ba ..	+ 4H ₂ O, granules consisting of microscopic needles.	+ 2H ₂ O, long, broad needles.	+ H ₂ O, "crusts."	+ 4H ₂ O, granules consisting of microscopic needles.	+ 4H ₂ O, no definite form. Granular, very soluble.
(SO ₃ K) ₂ ..	+ 2H ₂ O, in prismatic needles.	+ 2H ₂ O, in needles.	Needles.	+ H ₂ O, granules, consisting of microscopic needles.	+ 2H ₂ O, small prismatic forms. Very soluble.
(SO ₃ Na) ₂ ..	+ 2H ₂ O, glistening scales.	+ 6H ₂ O, in lustrous needles.	+ H ₂ O, crystalline aggregates.	+ 7H ₂ O, long, broad needles.	Very soluble in water.
(SO ₂ Cl) ₂ ..	Needles which become opaque. M. p. = 183°.	Prisms which become opaque. M. p. = 158°.	Needles. M. p. = 216°.	Aggregates of small needles. M. p. = 127°.	Prisms or prismatic needles. M. p. = 137°.
Cl ₂	Needles. M. p. = 107°.	Scales. M. p. = 114°.	Flat needles. M. p. = 136°.	Needles. M. p. = 48°.	Needles. M. p. = 61.5°.

is very soluble, but crystallises well in small prisms. The sodium salt is very soluble, and has not been obtained in a form fit for analysis. The chloride, C₁₀H₆(SO₂Cl)₂, crystallises from benzene in prisms, from acetic acid in prismatic needles, and from petroleum spirit in small needles; it melts at 147°, and on distillation with PCl₅ yield a dichloronaphthalene melting at 61.5°, convertible by sulphonation, &c., into a sulphochloride melting at 147°. The acid is therefore the metadisulphonic acid of naphthalene. The relative position of the sulphonic radicles being thus determined, their position relatively to the β-NH₂ radicle may be inferred from the facts that the hydroxy-G-acid is obtained as direct sulphonation-product of the Bayer modification of betanaphtholsulphonic acid, and that it yields the isomeric Schaefer acid when reduced by sodium amalgam. The authors first became acquainted with the latter fact from Dr. Caro, and have verified it in the course of an experimental examination of the behaviour of substituted naphthalenesulphonic acids generally on reduction; the details of this work will be given later on, but it may be here stated that, although the sulphonic acids are usually reducible to naphthalene in the manner first pointed out by Otto in the case of naphthalene-α-sulphonic acid, the β-sulphonic derivatives are far less readily affected; the NH₂ radicle also exercises a special protecting influence in many cases. Superposing the various results, the constitution of the G-acid is shown to be as follows:—



The G-acid is convertible by Sandmeyer's method into a chlorodisulphonic acid, the chloride of which crystallises from benzene in long radiate needles, melting at 170°; this is converted by PCl₅ into a trichloronaphthalene which crystallises in very slender needles, melting at 113°, identical with that obtained by Alén (*Ber. Referate*, 1884, 437) from an α-nitro acid prepared by nitrating the β-disulphonic acid of Ebert and Merz. This result confirms the conclusion above arrived at, as of the three possible formulæ of Alén's acid (see Table above).



II. and III. are excluded by the fact that the trichloronaphthalene corresponding to III. melts at 90—91° (*vide supra*), and that corresponding to II. also at about the same temperature (*cf. Proc. Chem. Soc.*, 1889, 52).

The results now obtained show that, as in the case of the Bayer and Badische monosulphonic acids, the action of diazo-salts on the G-disulphonic acids is either retarded or prevented by the "protecting influence" exercised by an α-1'-sulphonic group.

The properties of the five known naphthalene-disulphonic acids are summarised in the appended Table.

The authors wish it to be understood that they *entirely reserve* the investigation of the metadisulphonic acid and of its derivatives; this being the third acid of the series of which they have first investigated the preparation and properties, they believe they are justified in claiming this privilege.

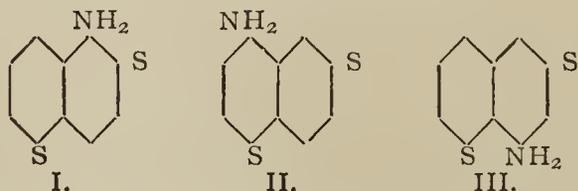
8. "Studies on the Constitution of Tri-derivatives of Naphthalene. No. 2, α-Amido 1:3'-Naphthalene-disulphonic Acid." By HENRY E. ARMSTRONG and W. P. WYNNE.

The 1:3'-naphthalene-αβ-disulphonic acid first described by the authors in 1886 (*Proc. Chem. Soc.*, 1886,

231; 1889, 10) has recently acquired considerable technical importance on account of the peculiar behaviour of the amido- and corresponding hydroxy-acid prepared from it, and as the source of valuable dye-stuffs (*cf.* Bernthsen, *Ber.*, 1889, 3327). This amido-acid has been patented by the Aëtiengesellschaft für Anilinfabrikation, in whose laboratory it was first prepared, by M. Andresen (*cf.* Schultz, *Ber.*, 1890, 77), by nitrating our acid, and reducing the nitro-derivative. We were naturally interested in determining the constitution of the amido-acid, and soon after it became known were favoured with a supply of material by the Aëtiengesellschaft für Anilinfabrikation. Technically, it has become known as α -naphthylamine- ϵ -disulphonic acid; but it appears very undesirable to perpetuate the confusion in nomenclature which reigns supreme in the case of the α -naphthylamine acids by adopting and continuing this name. We first satisfied ourselves that the amido-acid had been prepared from our $\alpha\beta$ -disulphonic acid by reducing it by the hydrazine method; the acid obtained gave a sulphochloride melting at 127° , and a dichloronaphthalene melting at 48° .

The corresponding chlorodisulphonic acid was then prepared by Sandmeyer's method; the disulphochloride of this acid crystallises from petroleum spirit in tufts of very slender needles, melting at 110° ; on distillation with PCl_5 , it is converted into a trichloronaphthalene, which appears to be dimorphous, crystallising from alcohol either in long slender needles, melting at 87° , or in large flat prisms, melting at 90° .

As the amido-acid is known to yield α -naphthylamine when deprived of its sulphonic groups, there are only three formulæ which can be assigned to it:—



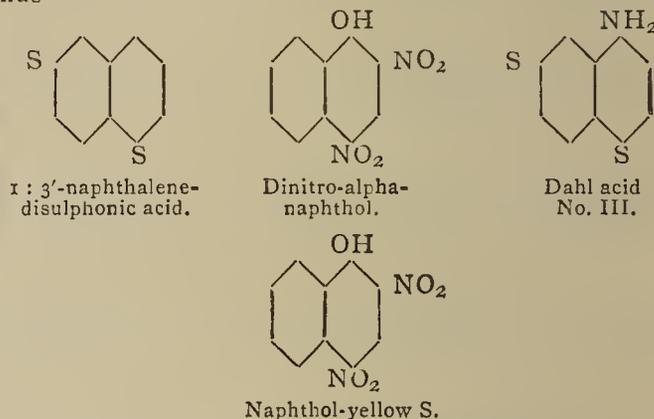
Formula I. is precluded, as the corresponding trichloronaphthalene melts at 78° (*Proc. Chem. Soc.*, 1889, 49); formula II. is likewise precluded, as the corresponding trichloronaphthalene (*vide infra*) melts at 65° and 56° ; formula III. therefore expresses the constitution of the acid. This result confirms, and is confirmed by, the conclusions arrived at by Bernthsen, who finds that the corresponding hydroxy-acid exhibits the behaviour of the 1:1'-hydroxy-sulphonic acid, readily yielding a naphthalene-sulphonelactone-sulphonic acid. Although slightly longer than the name proposed by Bernthsen, this latter appears to us to be preferable. The present tendency to construct a name on rational principles, so as to express the nature of the substance designated, and then to deprive it of all meaning by elision of the significant syllable, is most irrational; the term *sulphonelactone* is expressive, and not inelegant; sultone conveys no meaning to the uninstructed ear.

9. "Studies on the Constitution of the Tri-derivatives of Naphthalene. No. 3. Alphanaphthylaminedisulphonic Acid, Dahl, No. III. The Constitution of Naphthol-Yellow S." By HENRY E. ARMSTRONG and W. P. WYNNE.

It is well known that when alphanaphthol is sulphonated by excess of sulphuric acid, it is readily converted into acids capable of yielding naphthol-yellow S, a most valuable dye-stuff, the sulphonic acid of dinitroalphanaphthol, on treatment with nitric acid; although it is known that the yellow is a heteronuclear derivative, and that the sulphonic group is in $\alpha\beta$ -position, inasmuch as it yields 1:2:4-sulphophthalic acid on oxidation (*cf.* Grøbe and Rée, *Chem. Soc. Trans.*, 1886, 522), the position of this group has not hitherto been determined. With the object of ascertaining the constitution of the yellow, the authors have examined the alphanaphthyl-

aminedisulphonic acid No. III. prepared by sulphonating naphthionic acid with 35 per cent anhydrosulphuric acid at a temperature not exceeding 30° , described in the German patent, No. 41,957, 1886, of Dahl and Co., this acid being very readily converted into the yellow by diazotising, and then heating with nitric acid. Through the kindness of Dr. Caro, a considerable quantity of this acid was obtained from the Badische Anilin und Soda-fabrik.

When reduced by the hydrazine method, the Dahl No. III. acid is found to yield the author's 1:3'-naphthalenedisulphonic acid; the sulphochloride actually prepared from the acid, melted at 127° , and the corresponding dichloronaphthalene at 49° . Taking into account the fact that naphthol-yellow S is a heteronuclear β sulphonic derivative, this result is alone insufficient to determine the constitution of the yellow and of the amido-acid, thus—



The chlorodisulphonic acid prepared from the Dahl acid yields a sulphochloride very soluble in benzene, from which it crystallises in small prisms; it separates from petroleum spirit in rosettes of small apparently rectangular prisms, melting at 107° . The corresponding trichloronaphthalene affords a remarkable case of dimorphism; it is sparingly soluble in hot alcohol, from which it crystallises in slender needles melting at 65° ; if the melting-point be re-determined as soon as solidification has taken place, it is found to be 56° , but if determined after a longer interval 65° , as in the first instance. This trichloronaphthalene should be identical with that prepared by Widman from dichloronaphthalene- β -sulphonic chloride, which the authors have shown to be a derivative of 1:4-dichloronaphthalene (*cf.* *Proc. Chem. Soc.*, 1888, 106), but Widman's product is said to melt at 56° ; the authors find, however, on preparing it according to Widman's direction, that it also melts at 65° or 56° . By nitrating 1:3'- γ -dichloronaphthalene Clève obtained a nitrodichloronaphthalene yielding a trichloronaphthalene melting at 65° ; the author's observations show that this is in reality identical with the Widman trichloronaphthalene, and therefore that the behaviour of 1:3'-dichloronaphthalene on nitration is perfectly "normal," and strictly comparable with that of both α - and β -monochloronaphthalene.

By sulphonating 1:4-chloronaphthalenesulphonic acid in the form of potassium salt by means of the theoretical proportion of sulphuric anhydride employed as 20 per cent anhydrosulphuric acid at 100° , the authors have obtained a chlorodisulphonic acid identical with that prepared from the Dahl amido-acid; showing that the α -chloro, α -amido-, and α -hydroxy-monosulphonic compounds behave similarly on further sulphonation; but it remains to be ascertained whether the series of changes leading up to the production of the final stable compounds is identical in the several cases.

The Oxides of Manganese.—Alex. Gorgen.—The wads of psilomelanes are true acid hydrated manganites, the most characteristic samples of which have the composition $3(\text{MnO}_2)\text{RO} + 1$ to 3HO .—*Comp. Rend.*, No. 5.

NOTICES OF BOOKS.

Warren's Table and Formula Book; containing, in addition to the usual Tables, an Account of some Physical Electrical Units now in use among Scientific Men, Important Formulæ in Algebra, Mensuration, and Trigonometry, together with Valuable Information on Transactions in Exchange and Commerce. By the REV. ISAAC WARREN, M.A. London: Longmans, Green, and Co.

This collection of tables and formulæ will be exceedingly useful to students of physics, the more so as the figures given are exceptionally correct.

We notice one only typographical error, to wit, the German mark is, on p. 119, said to be " $= 100$ groschen $= 100$ pfennige," thus making the groschen and the pfennig equal to each other. It should, of course, have been said " $= 10$ groschen."

The tables of British weights and measures remind us of the number of different local standards, which even the introduction of the metric system would not do away with unless accompanied by most drastic legislation and equally drastic espionage. Thus, in this work and in actual practice in the South of England the gill is synonymous with the noggin, and is $\frac{1}{4}$ pint or 5 fluid ounces. But in the northern counties the gill $= \frac{1}{2}$ pint, or 10 fluid ounces, and is double the noggin. The difference between Irish and statute acres is duly mentioned, but it might have been useful to add the dimensions respectively of the Lancashire and the Cheshire acre, which are both larger than the Imperial standard. In some parts of Yorkshire the acre is dispensed with altogether, and land for selling or letting is stated as so many "days' work."

Many mineral-brokers have the vicious custom of expressing any fractions of a per cent of valuable matter in "eights." Thus, instead of saying that a copper ore contains 5.75 of copper, they will call it 5 $\frac{3}{4}$ ths. Here, also, belongs the custom of assigning to sodium, not its true atomic weight, but a false and arbitrary number. This custom occasionally involves analysts in unedifying disputes.

A further element of confusion is the fact that the American quart is rather smaller than the litre, whilst the British legal quart is larger.

The author remarks that though the General Medical Council directed the disuse of the drachm and the scruple in medical prescriptions, yet physicians persist in their use. It is not even certain whether these denominations are to refer to the old Troy ounce or the new Avoirdupois ounce.

If the introduction of the metric system would sweep away all the above-mentioned anomalies, it would be welcome; but if it merely co-exists with our ancient denominations, its avatar would render confusion worse confounded.

CORRESPONDENCE.

BRIN'S OXYGEN COMPANY.

To the Editor of the Chemical News.

SIR,—A good deal of unnecessary alarm has been caused by the lamentable accident which occurred rather more than a week ago at Glasgow through the bursting of a cylinder. There is no occasion either for alarm or surprise when the facts of the case are known. If we hear of a man who deliberately throws a lighted match into a barrel of gunpowder, we are neither alarmed nor surprised at the results. This is exactly what has occurred at Glasgow. The unfortunate man who lost his life charged hydrogen into a black cylinder (in direct contravention of the Company's rules), and afterwards, for

getting that he had done so, put oxygen into the same vessel; the result was an explosion, which took place at the first slight concussion which the cylinder received. A piece of the cylinder which was picked up four yards from where the accident occurred was quite hot, showing conclusively that ignition had taken place, and there could have been no spontaneous ignition if the two gases had not been present.

Every precaution is taken by the Companies to prevent the possibility of O and H getting mixed; under no circumstances will they fill hydrogen or coal-gas into a black cylinder, or oxygen into a red one; neither will they put the one gas into a cylinder which they even suspect has ever contained the other.

With a view, however, of making it absolutely impossible for two gases to be put in the same cylinder, it has been decided by this company, and also by the Scotch and Irish Oxygen Co., and the Manchester Oxygen Co., to fit all hydrogen cylinders with a left hand thread, so that they cannot be filled at the oxygen pump, and, in the same way, it will be impossible to fill oxygen cylinders at the hydrogen pump. All consumers are earnestly requested to send their hydrogen cylinders either to the Companies or to the agents through whom they obtain their supplies of gas, to have the alteration made, and the smallest possible charge will be made for taking off the present valves and fitting on new ones. After a certain limit of time, of which notice will be given, no hydrogen or coal-gas cylinders not provided with the new thread will be filled.

In some quarters, the fear has been expressed that the accident at Glasgow occurred through over-pressure; any such apprehension may be immediately dismissed from the mind; explosion from such a cause is impossible; the cylinders are tested to double the pressure at which they are ever filled, and it is impossible to exceed the standard filling pressure of 120 atmospheres. They are also re-tested periodically. For years past, the Government have been using high-pressure cylinders for ballooning purposes, similar to those in use at present; they had them in the Egyptian and Boer campaigns, and they have frequently been rolled from the top of a hill to the bottom, bounding from point to point, and in no single instance has an accident occurred or a cylinder burst.

In conclusion, I would remind you of the fact that since oxygen and hydrogen have been supplied in high-pressure cylinders—now some three or four years—only two accidents have occurred, and these at the works; whereas, when bags were in vogue, accidents, in many cases fatal, frequently took place. Only last week, in America, a lecturer on chemistry and ten or twelve of his pupils were seriously injured by the bursting of a retort in which oxygen was being made by the old-fashioned chlorate of potash process.—I am, &c.,

T. HESTER,
Secretary to Brin's Oxygen Co. (Lim.).

Brin's Oxygen Company (Lim.),
Connaught Mansions, Victoria Street,
Westminster, S.W., Feb. 7, 1890.

THE IGNITING-POINT OF SULPHUR.

To the Editor of the Chemical News.

SIR,—The letter from Mr. Blount (CHEM. NEWS, vol. lxi., p. 85) about the igniting-point of sulphur is of considerable interest to those chemists who have to do with explosives, either technically or as teachers. When one comes to think about it, a substance "should" have a fixed igniting-point. But almost all substances show great variations in this respect, and whether these are due to physical state, as with charcoal and diamond, or merely mechanical sub-division, has not been very closely enquired into.

I am certainly inclined to the belief that the igniting-point is determined solely by the physical or allotropic state of the body, in cases like carbon and silicon. In the case of substances like sulphur, which volatilise, the igniting-point must be above the boiling-point.

Experiments with iron reduced by hydrogen, and lead reduced from tartrate, are often shown as instances of the low temperature at which these substances "ignite," but do they really ignite at a lower temperature? To get lead to burn in air requires a pretty strong red heat, say, 700° C. If the lead powder from tartrate be put carefully on to the flattened bulb of an air thermometer, a steady rise of temperature will be noticed until the mass glows, by which I understand the igniting-point, similarly with iron, only the rise is more rapid; the small particles oxidise and the temperature rises locally to that of ignition.

In the case of sulphur the allotropic condition can have no, or but little, effect, for the substance, I believe, only ignites after it has attained the gaseous state. I have not attempted the matter in any strict way but for lecture purposes. As is well known, sulphur boils at 448° C., and the vapour may escape into air, as in distilling it, without ignition taking place. I have arranged a wide tube, a lamp cylinder, horizontally about half an inch above an iron plate heated by a large burner to something above the melting-point of zinc—415°; into this tube, when heated, I distil a few drops of sulphur at about the middle; it vaporises, and, of course, comes in contact with hot air at the two ends, but I have not found any time that ignition took place when the plate was just hot enough to melt zinc foil. I have not yet ventured to risk a nitrogen thermometer in the tube itself.

That sulphur ignites in air at any temperature below 300° C. I think quite out of the question. Nitre melts at 339° C., and sulphur may be put on to this, when it melts, and, of course, goes very dark in colour, and with little care, most, if not all, may be sublimed from the nitre before any chemical action takes place. Sulphur dropped on to fused potassium chlorate certainly burns at once, but the melting-point of KClO_3 may be higher than that of nitre. However this point may be determined, it will, I think, be found to be above the boiling-point.

It must also have happened to scores of people to notice that boiling sulphur can be poured through air into water, in the usual experiment of making the elastic variety, without ignition taking place. The thin stream of sulphur in this case cannot be much below the temperature of boiling (448°).

Probably the mistakes about the ignition-point of sulphur have arisen from neglect of the fact that it is one of the worst conductors of heat. When put in a flame, a piece of sulphur takes fire *rapidly*, because it becomes locally heated up to above its boiling-point; it always melts before igniting. A moderate sized sulphur flame will deposit sulphur on a cold object held in it.—I am, &c.,

W. R. HODGKINSON.

Woolwich, Feb. 15, 1890.

OCCURRENCE OF PHOSPHATES.

To the Editor of the Chemical News.

SIR,—All kinds of strange hypotheses have been advanced to account for the irregularity and fortuitous manner in which calcic phosphate occurs in various formations. Two facts can hardly fail at once to strike anyone as to these deposits:—(1) The irregularity of their occurrence. (2) Their superficial nature. I have had the good fortune to visit pretty many of these at different times, and the addition of one more to the various more or less impossible theories which have been formed as to their origin (none of these accounting for the peculiar conditions in which they are found) can hardly do any harm. I would suggest, then, that in many cases these formations may have had their origin in the constitution of

colonies of infusoria or marine insects which would have been more likely to have existed in the quiet recesses of caves and clefts of the rocks, where phosphates so often are found. We must presume that the bodies of many infusoria are largely composed of calcic or other phosphates, to judge from the wonderful manner in which their propagation is assisted by the presence of compounds rich in phosphoric acid, and we know also the manner in which they can gather and assimilate to themselves the materials necessary to their existence. Phosphates seem to be distributed, though often in small quantity, throughout the entire crust of the earth, and so they might be brought in a state of solution to the infusoria, which would thus gradually attract to themselves the phosphates they required, especially those in their more immediate neighbourhood. Fish in search of food would be attracted by the organic life of these colonies, and dying, their bones and debris and those of the predatory fishes following them would notably augment the deposits. Such a theory, if true, would, in a great measure, account for the superficial nature of most of these deposits and for their comparative purity, as well as for the poverty in phosphates often observable in the surrounding strata. It would also afford some explanation why phosphates are so often placed in holes and cavities of the rocks, instead of forming continuous veins, like other minerals, and it would afford some reason for the mixed nature of these deposits, which, so far as the more modern ones are concerned, are generally composed of pulverulent matter more or less agglomerated together, interspersed with the teeth and bones of fishes, the organised structure of which is still often apparent.—I am, &c.,

F. MAXWELL LYTE.

LARD.

To the Editor of the Chemical News.

SIR,—I have read the letter of Mr. Swindells, Ph.D., which appeared in the CHEMICAL NEWS, vol. lxi., p. 85. I know nothing about tea, therefore I am unable to speak about that subject; but having, for many years, been connected with the refining and canning of American lard, between three and four thousand tons of that commodity having annually passed under my supervision, I think you will concur with me that I ought to be able to express a pretty correct opinion as to the general purity of refined lard. Mr. Swindells says "he can believe anything of this commodity." I decline to be so credulous, or to surround any article of food with unnecessary doubt and distrust as to its purity. The public, as a rule, insist upon having pure and wholesome articles of food, and Parliament enacts laws to punish those that do not supply such. So far I am satisfied. The only difficulty which arises in my mind with respect to American lard is the soft condition in which it arrives in this country, especially in the summer. This condition is mainly owing to the small quantity of stearin found in the fat of the common hog. Ox fat, like hog's lard, is a mixture of stearin, margarin, and olein, but contains more stearin than hog's lard. The fat of oxen, since it has been used for the manufacture of oleomargarin (now so extensively used in the preparation of artificial butter), is rendered down while perfectly fresh and sweet, the residual stearin being as good for food as its other constituents. As I have intimated, steam granulated lard is a soft and sloppy article, and could not be transmitted by rail in open packages. In order to so transmit it, it has to be made more dense. Stearin is the hard constituent of all fats, and I can see no reason whatever, either on the ground of purity or economy, that ox stearin should not be mingled with lard, for they are both legitimate and wholesome articles of food; and, in my opinion, the stearin of the ox is much superior, as regards quality and freshness, to that obtained from hog's lard. I am not

singular in this opinion, as it has already been advanced by some distinguished chemists and physicists of the Victorian age. With respect to the use of cotton-seed oil as an adulterant of lard, it is well known that such a mixture must be sold as a compound. I will not enter upon its merits. No refiner dare incorporate 20 per cent of water with lard without selling it as watered lard. But the watering of lard is, I think, now almost defunct. The steam-rendered lard of the Western States arrives in Liverpool to-day as pure as ever it arrived. Of course, now and again, inferior parcels come to hand; and this must of necessity be so, seeing that the hogs are fed in some districts on corn, in other districts in forests, and in other places on distillery refuse. In the English refineries the firm and corn-fed lard is mingled with the soft and flabby article, and then cleansed and refined. The operations carried on in the refineries are on so extensive a scale, that anything savouring of "mystery" would only result in ruin and disaster to those who did the wrong.

With respect to the addition of other matter to lard, I presume Mr. Swindells alludes to stearin. Now, as stearin is a constituent of lard, and is refined with it, its use, I should say, will bring it under the 6th Section of the Sale of Food and Drugs Act, which provides that an offence shall not be deemed to be committed "Where any matter or ingredient not injurious to health has been added to the food or drug because the same is required for the production or preparation thereof as an article of commerce in a state fit for carriage or consumption, and not fraudulently to increase the bulk, weight, or measure of the food or drug or conceal the inferior quality thereof."

This section might have been specially drafted for this particular addition.—I am, &c.,

WILLIAM BROWN.

3, Hereford Road, Seaforth,
Liverpool, Feb. 18, 1890.

Action of Ethylmalonyl Chloride upon Ethylbenzene in Presence of Aluminium Chloride.—A. Béhal and V. Auger.—The product obtained is metadiethylbenzene, of the sp. gr. (at 0°) 0.8812. Its refraction index at 14° = 1.472.

No. 5, February 3, 1890.

Combinations of Gaseous Ammonia and of Hydrogen Phosphide with Silicon Dichloride and Dibromide.—M. Besson.—The author has verified the composition of the ammonium compound, $\text{Si}_2\text{Cl}_4\cdot 6\text{NH}_3$ as given by Persoz. The composition of the bromide is different, $\text{Si}_2\text{Br}_4\cdot 7\text{NH}_3$. The latter is a white amorphous solid, similar to the corresponding chloride. It is decomposed by water, and yields a strongly alkaline liquid which gives off ammonia. Hydrogen phosphide has no action upon silicon dichloride, except the latter is cooled down to -23° , when it absorbs 23 vols. of hydrogen phosphide, and at -50° to -60° , 40 vols., forming a liquid of the composition $\text{Si}_2\text{Cl}_4\cdot 2\text{PH}_3$. A crystalline compound is obtained by the joint action of pressure and refrigeration.

Part played by certain Foreign Bodies in Iron and Steels.—F. Osmond.—During the slow refrigeration of an electrolytic iron containing 0.08 per cent of carbon there ensue two liberations of heat; the one which the author calls a_3 causes the thermometer to be stationary at 855° ; the other at a_2 , less marked, presents its maximum about 730° . The bodies whose influence has been specially examined are boron, nickel, copper, silicon, arsenic, and tungsten. Boron acts in a manner analogous to carbon; a_3 is lowered in part to between 815° — 805° , and in part to 735° — 725° . In a steel free from nickel a_3 and a_2 are blended together, but a_1 (the tempering heat of steel) remains distinct. The presence of nickel brings a_3 , a_2 , and a_1 into a single point together between 660° and 640° . The action of copper on the allotropic transformation of iron is analogous to that of carbon, but less energetic. Silicon prevents the allotropic transformation. Arsenic acts similarly to silicon. Tungsten has a doubtful influence, but it lowers a_1 to 540° — 530° .

Journal für Praktische Chemie.

New Series, Vol. xl., Nos. 18 and 19.

The Oxygen Acids of Iodine.—C. W. Blomstrand.—An account of iodic acid and its double acids with other acids, such as iodosulphuric acid, molybdosulphuric acid, with its potassium, ammonium, thallium, and lead salts, iodotungstic acid, iodochromic acid, and the acid alkaline iodates.

Thermo-chemical Researches.—F. Stohmann, Cl. Kleber, and H. Langbein.—This paper is incapable of useful abstraction.

Action of Alkalies and Ammonia upon the Haloid Substitution-Products of the Quinones.—Fr. Kehrmann.—A study of the action of potassium ethylate upon chloranil; that of iodethyl upon silver chloranilate; the behaviour of iodmethyl with silver chloranilate and the conversion of the β -isomers into the α isomers.

Researches from the Laboratory of the University of Freiburg.—These comprise memoirs by Ad. Claus and C. Geissler on the dibromquinolines; by Ad. Claus and G. N. Vis on orthometadibromquinolines and certain derivatives of metabromquinoline and of anabromquinoline; and Ad. Claus and Ad. Weiter on bromised derivatives of quinoline.

Researches from the Laboratory of Prof. Alex. Saytzeff at Kasan.—Consisting of researches by Serg. Reformatzky on the synthesis of glycerins by means of hypochlorous acid.

Reply to the Answer of K. Hazura, and "Putting Matters Right."—K. Peters.—Two controversial papers, both relating to a memoir by A. Saytzeff on the oxidation of oleic acid with potassium permanganate.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 4, January 27, 1890.

The Substitution of Salts in Mixed Solutions.—A. Etard.—This paper cannot be intelligibly abstracted without the use of the accompanying diagrams.

The State of Iodine in Solution.—Henri Gautier and Georges Charpy.—The solutions of iodine are divided into two classes; the brown solutions (alcohol, ether, &c.) and the violet solutions (carbon disulphide, chloroform, benzene, &c.). The authors have treated iodine with fifteen solvents, and they arrange the colours in a series from violet to brown. The absorption-spectra of the solutions vary also in a continuous manner. In the violet solutions they show a spectrum approaching that of the vapour of iodine, but the dark band begins, not in the red, but in the yellow, and encroaches a little more upon the blue than in the vapour of iodine. In the succeeding groups the displacement of the dark band on the side of the violet is intensified. The authors conclude that the mol. of iodine which, in the brown solutions, corresponds to I_4 , is gradually split up so as to approximate to I_2 , which corresponds to iodine in the state of vapour. This hypothesis appears to be supported by the influence exerted by temperature upon the colour of the solutions.

Calorimetric State of the Sodium Phosphites and Pyrophosphites.—L. Amat.—Not capable of abstraction.

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 advertising columns.

Wool.—Could you, through the columns of the CHEMICAL NEWS, state the specific heat of wool, or mention where I could get the desired information.—ENQUIRER.

MEETINGS FOR THE WEEK.

- MONDAY, 24th.—Medical, 8.30.
Society of Arts, 8. "Stereotyping," by Thomas Bolas, F.C.S.
- TUESDAY, 25th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
Institute of Civil Engineers, 8.
Royal Medical and Chirurgical, 8.30.
- WEDNESDAY, 26th.—Society of Arts, 8. "The English in Florida," by Arthur Montefiore.
Geological, 8.
- THURSDAY, 27th.—Royal, 4.30.
Institute of Electrical Engineers, 8.
Royal Institution, 3. "The Three Stages of Shakspeare's Art," by Rev. Canon Ainger, M.A., LL.D.
Chemical, 5. "The Northern Shan States and the Burma-China Railway," by William Sherriff.
- FRIDAY, 28th.—Royal Institution, 9. "Evolution in Music," by Prof. C. Hubert H. Parry, Mus. Doc. M.A.
Quekett Club, 8. (Anniversary).
- SATURDAY, March 1st.—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.

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C. CROWTHER SMITH, Secretary.

Ogle Road, Southampton,
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A PROCESS FOR DECOMPOSING COMMERCIAL NICKEL AND ITS SALTS AND GALVANICALLY COATING OBJECTS WITH PURE NICKEL.*

I, GERHARD KRÜSS, Lecturer at the University of Munich, Doctor of Philosophy, of Munich, in the Empire of Germany, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

According to experiments, made by the inventor, metallic nickel, regardless of the known technical impurities contained therein, for instance, iron, copper, arsenic, manganese, silicium, &c., is not a chemical element, but an alloy. This alloy contains averagely about 98 per cent of a metal, similar indeed in its properties to the substance hitherto named "nickel," but finer in various respects, which metal I will designate with "Ni," and about 2 per cent of an element considerably differing from nickel in its properties and in the nature of its compounds. This element shall for the present be designated with "X."

Ni, free from X, that is to say, nickel in the new sense of the word, is produced from common nickel, nickel salts, or direct from the solutions of the raw materials obtained by concentration smelting, by proceeding according to the different nature of these elements. It is impossible to separate pure Ni by one operation from the said alloy of Ni and X, very rich in Ni, as the combinations of X, also if insoluble in the residue of their precipitant, are soluble in Ni-salts, therefore resist separation from the latter. It is therefore necessary to repeat one of the hereafter mentioned operations several times, or preferably several of these operations are successively performed to obtain pure nickel. Said operations are derived from the following peculiar properties of the compounds of the element X.

The neutral chloride, which is colourless—

(1) When treated with concentrated alkali lyes or melted with caustic alkali, is not changed into a hydroxide insoluble in water, but any hydroxide produced is wholly or partly converted into a combination of alkali soluble in water. The snow-white hydroxide precipitated by means of common alkali lyes, for instance $\frac{1}{2}$ normal solution, is, however, very little soluble in the latter, also with the addition of a large residue of the precipitant.

(2) Is but incompletely precipitated in solution through oxalic acid at a low as well as at a high temperature, more completely, however, through oxalate of ammonium even at a low temperature after short standing. A very great residue of the latter precipitant can return the precipitant into solution.

(3) Is not precipitated in solution through fixed alkali lyes or ammonia, oxalate of ammonium or oxalic acid, even at a high temperature, if the solution has been previously acidified by the addition of organic acids, for instance, acetic acid, citric acid, pyrotartaric acid, &c.; whereas the soluble double oxalates of Ni are decomposed, on heating their solution, by one of the said acids, and deposit insoluble oxalate of nickel. If the combinations of the element X are, in solution or otherwise, brought in contact with a metal which is more electro-positive than Ni, for instance, with zinc, the compounds are not reduced even by short heating.

All these properties inherent on the pure X-compounds are to a different extent or completely altered and concealed if a solution contains besides X-salts also combinations of Ni. This is the case in the nickel salt solutions of former designation. The white hydroxide of X, for instance, is not at all precipitated by ammonia, if, in a nickel salt solution of former designation, more than 70 per cent of the dissolved substance consists of Ni salt.

If the nickel raw materials obtained by concentration smelting contain mixtures, rich in X, of Ni and X, or of their salts, or solutions rich in X, of commercial nickel or commercial nickel salts, the neutral solutions, to separate the Ni from the X, are mixed with ammoniacal oxalate of ammonium, till the precipitate produced is re-dissolved. Subsequently they are allowed to stand for some time, white basic oxalate of X being thereby precipitated, and some more ammoniacal oxalate of ammonium is added. This addition is repeated until, after some longer standing, the quantity of the white precipitate ceases to increase. The blue liquid above the precipitate having been evaporated, its residue is thoroughly glowed and then mixed with such a quantity of muriatic acid as is required for solution. The solution of chloride is subsequently concentrated, and while heating it, solid hydrate of soda, up to five times the weight of the chloride, is incorporated therein, the doughy mass thereby produced being kept melting for a short time. The molten mass when cooled is broken up and brought in small pieces into ice-cold water, care being taken, if necessary by the addition of ice, to prevent the temperature of the liquid from rising above 10° C. Thereby the sodium compound of the oxide of X is dissolved, while rather pure hydroxide of Ni remains undissolved. The alkaline liquid containing X having been poured or drawn off after some standing, the hydroxide of Ni is washed by decantation and dissolved in weak mineral acids or in acetic acid. This solution is mixed with such organic acids as are also capable of preventing the aluminium from being precipitated through alkalis, for instance, with acetic acid, pyrotartaric acid, or citric acid. On adding soda lye to the liquid thus obtained, while heating, pure hydroxide of Ni, free from X, is precipitated; or pure oxalate of Ni, free from X, can be produced in boiling heat by precipitating the said solution of nickel, acidified with an organic acid, with soluble oxalates, for instance, oxalate of ammonium, all X being thus kept in solution, as by the preceding operations the greater part of X has already been eliminated from the commercial nickel or its salts.

In lieu of this, however, also the solutions of commercial nickel, of its salts, or of the nickel raw materials obtained by concentration smelting, and the nickel compounds produced by the above treatment may be decomposed into pure nickel (Ni) or its salts and the element X or its compounds respectively, by bringing the nickel compounds or solutions referred to in contact with a metal which is more electro-positive than the Ni-metal itself.

Nickel salts are in this manner more easily reducible, and, for instance, a solution of sulphate of nickel, chloride of nickel, or nitrate of nickel is soon almost completely decoloured when warming it with zinc dust or fine zinc chips, nickel metal being precipitated and zinc brought in solution as sulphate. The compounds of X are thus not reduced and remain in solution.

If the neutral or weak acid solutions of the nickel raw materials, obtained by concentration smelting, or like solutions of commercial nickel or nickel salts contain but few X-compounds, pure nickel can be obtained from them by performing once or twice one of the two last described operations.

The pure nickel obtained by the above described process is particularly adapted for galvanically coating objects. While the nickel obtained by the processes already known has a brownish yellowish hue, owing to the metal heretofore named X, inherent thereto, the colour of pure nickel (Ni), if not perfectly free from a yellowish shade, is decidedly more like silver and lighter, its application

* Complete Specification of a Patent granted to Gerhard Krüss, A.D. 1889, 25th January. No. 1418.

consequently preferable to the galvanic nickeling heretofore in use. To this end, any of the known processes may be applied by using nickel salts free from X for producing the alkaline neutral or acid nickel baths, and as nickel anodes such of nickel free from the element X, or from its oxide.

Having now particularly described and ascertained the nature of this invention, and in what manner the same is to be performed, I declare that what I claim is—

(1) The process for decomposing commercial nickel and its salts into pure nickel (Ni) or into pure nickel salts and into an element, designated with "X" in the specification, or its salts, that is to say, the process for producing such metals (Ni and X) and their compounds, substantially as described.

(2) The application of nickel, free from the element designated with X in the specification, or of the salts of such nickel for galvanically coating objects.

GERHARD KRÜSS.

Dated this 25th day of January, 1889.

A BRIEF SUMMARY ON PRACTICAL MANIPULATION.

By H. N. WARREN, Research Analyst.

(Concluded from p. 63).

Disintegration.

THE pulverisation of many substances, before operating further upon the same, not unfrequently presents one of the most irksome and troublesome undertakings that are to be met with in a laboratory, especially when adopting the general method of pestle and mortar. Quite recently small disintegrators have been supplied for practical purposes; but the present costliness of the article considerably retards their general application. In cases where it is required to reduce to powder, such as, for instance, the pulverisation of minerals, several pounds may be quickly reduced to any mesh by the application of a smooth iron plate, replacing for a pestle a large flat-headed hammer, and giving to the same a rotary motion, so as to constantly bring the same particles under its influence.

Casting and Moulding.

After the assay of a metal has been completed, it not unfrequently happens that a sample of the same is required in an elongated form in order to examine its tensile strength or other physical features. A very ready mould, and one which answers the purpose admirably on account of the non-introduction of foreign substances, may be formed by coiling round an ordinary pencil, or other convenient appendage, several thicknesses of writing-paper, closing the extremity by means of a cork, and supporting the same by immersing it to the extremity into dry sand, afterwards withdrawing the core and pouring into it the intended metal. A very perfect and uniform cast is thus obtained, which may be tested by weighting the same from about every other inch in length. By this means a very good indication will at once be formed whether any liquation has proceeded the casting, on account of the inconstancy either of the metal or alloy that has thus been treated. These paper moulds are not intended for metals above the melting-point of zinc; for copper, iron, &c., asbestos sheeting should be used in its stead.

Combustion-Tubing (how to preserve).

During a tube combustion, employing the ordinary glass tubing in general use for that purpose, direct contact of the contents will oftentimes be observed to cause, either whilst hot, or when cold, a fracture of the glass, and thus prevent further use of the same; a thin strip of asbestos placed next to the glass will, in many cases, prevent breakage, and thus preserve the same tube for

various further operations. Many combustion estimations may be accurately performed in an iron tube.

Unsuspected Impurity of Acids.

The impurity of the various commercial acids are generally well known, and the foreign substances most frequently found contaminating them are naturally sought for before employing the purer acids. As a rule, however, nitric acid, excepting small quantities of sulphates and chlorides, is usually supposed to escape contamination. I may, however, mention that I have frequently detected selenium in a so-called pure acid. As the acid was intended for parting gold, on account of the vigorous way in which selenic acid attacks that metal, it might, if it had escaped detection, cause considerable errors. It would be interesting to know to what extent of division the millionth part of a grain of gold would become if subjected to such an impurity.

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THE COLOURATION DETERMINATION OF NITRIC ACID BY MEANS OF A SULPHURIC SOLUTION OF DIPHENYL-AMINE.

By J. A. MÜLLER.

THE blue colouration first observed by W. Hofmann, which diphenylamine gives with nitric acid, and which is produced with other oxidisers, has been used for the colorimetric determination of nitrous and nitric acids. E. Kopp was the first to utilise this reaction of nitrous acid for its estimation in the sulphuric acid of commerce. R. Böttger recommends the reaction of Kopp for detecting nitrites or nitrates in potable waters. H. Settegast uses Vierordt's spectrophotometer to observe the absorbing power due to the intensity of the blue tint produced on pouring 1 c.c. of the aqueous solution of a nitrate into 9 c.c. of sulphuric acid containing one-thousandth part of diphenylamine, and makes use of it to determine the quantity of nitric acid contained in a watery solution when this quantity varies between 1 and 40 millionths of NO_3H .

More recently L. Spiegel has sought to effect the same determination by direct comparison, using standard solutions of nitric acid (in the state of potassium nitrate?). On operating as Herr Spiegel indicates in his memoir the author finds that the sensitiveness of the reaction is not satisfactory for solutions containing 0.5 grm. to 2 m.grms. N_2O_5 per litre, and that the colour only reaches its maximum intensity after about ten hours.

The author has made a number of experiments to determine the conditions which must be observed to obtain the greatest sensitiveness in the reaction. In the first place all the oxidisers which give a blue colour with a sulphuric solution of diphenylamine, care must be taken that the liquid in question contains no oxidising agents save nitric acid. The blue colour is not interfered with by a small quantity of hydrochloric acid, but it is modified, or even destroyed, by hydrobromic or hydriodic acids. Hence the colorimetric determination is not possible in presence of these latter acids.

According to Spiegel, organic matters have no influence on the intensity of the colour produced. The author has found that the addition of some drops of a solution containing 7.5 per cent of dextrine (commercial) to a liquid coloured with 0.003 m.grm. of nitric anhydride, turns the original blue tint to a green; after twenty-four hours the liquid was decolourised. The intensity of the blue colour produced on pouring an aqueous solution of nitric acid or of a nitrate into a sulphuric solution of diphenylamine varies for a given quantity of the oxidising agent with the proportion of diphenylamine and the concentration of

the sulphuric acid employed. With a very dilute acid it is not produced at all. For very dilute solutions of nitric acid or of nitrates the author has obtained good results by pouring 1 c.c. of the aqueous nitric solution into 5 c.c. of concentrated sulphuric acid containing 0.007 gm. of diphenylamine.

The following is the method of effecting a colorimetric determination:—

Into a test-tube of 15 centimetres, perfectly clean, there are poured 5 c.c. of the sulphuric solution of diphenylamine at 0.2 gm. of diphenylamine per litre of pure strong sulphuric acid and 1 c.c. of the solution of the nitrate under examination. The tube is shaken and, after a moment, the blue tint is observed; it should be very light. If not, the solution of nitrate is diluted until a new trial gives this result. With a little experience we may thus easily obtain solutions containing from 0.5 to 5 m.grms. of nitric anhydride per litre, and even form an approximate judgment of the quantities between these two limits. To determine this quantity more exactly, a number of trials were made with standard solutions of potassium nitrate contained in ten bottles, 0.5, 1, 5 m.grms. N_2O_5 (in the state of nitrate) per litre. We then, after about an hour, compare the colourations obtained with the solution under examination and those given by pure solutions of potassium nitrate. The results are not comparable except we operate as accurately as possible under the same conditions.

With solutions containing from 0.5 to 2.5 m.grms. of nitric anhydride per litre we may thus appreciate differences of colouration due to 0.5 m.grm. N_2O_5 ; at 2.5 m.grms. or at 5 or 6 m.grms. we can no longer observe differences of colour due to difference below 1 m.grm. of nitric anhydride per litre; up to 10 to 12 m.grms. of nitric anhydride per litre the blue colourations are too deep to be useful.

If, along with the nitric acid to be determined, there is a notable quantity of nitrous acid, it is oxidised with permanganate and the total nitric acid is then determined colorimetrically.

This method of determination may serve for the estimation of small quantities of nitric acid in arable soils or in drainage water, but the solution operated upon must be perfectly clear.—*Bulletin de la Société Chimique de Paris.*

THE TREATISE OF DEMOCRITUS ON THINGS NATURAL AND MYSTICAL.

Translated by ROBERT R. STEELE, F.C.S., &c.

(Continued from p. 89).

XI. O! NATURES, governors of natures! O! natures, how great, conquering natures with their changes! O! natures above Nature, delighting natures! Therefore these are great natures; no others are more excellent among tinctures than these natures; none are like, none are greater, all these take effect as solutions. You therefore, O! wise men, I plainly understand are not ignorant, but rather wonder, since ye know the power of nature. but the young men are much in error, and will not put faith in what is written, since they are ignorant of matter, not noticing that physicians where they wish to prepare a useful drug, do not set about making it inconsiderately, but first test it, whether it is warming, and how much cold, or humid, or other substance necessary, joined with it will make a medium temperament.* They, on the other hand, boldly and inconsiderately desiring to prepare that valuable medicine and ending of all diseases, do not learn that they are running into danger. As they consider that we speak in fables and not mystically, they display no diligence in inquiring into the species of

* Alluding to the four principles of nature: warm, cold, dry, and moist, by the combination of which the four elements were formed.

things. For example, if this is cleansing, but that unimportant; and if this is fitted to receive a colour, but that to prepare (for receiving it); and if this tinges the surface, or if the tincture gives off an odour from the surface, or vanishes from the interior of the metallic body; or if this resists fire, but that mixed with anything enables it to resist fire. For example, if salt cleanses the surface of *Jove** it cleanses its interior parts; and if the exterior part contracts rust after the cleansing, the interior parts do so also; and if mercury whitens and cleanses the surface of *Venus*,† it whitens also the interior; and if it leaves the exterior, it leaves the interior also. If the young men had been skilled in this kind of knowledge, applying their minds judiciously to the actions of substances, they would have suffered less loss; they know not the antipathies of nature, that one species may change ten, as a drop of oil stains much purple, and a little sulphur burns many things. Let these things be said, therefore, of medicines,‡ and of the extent to which what is written may be relied on.

XII. A GOLD VARNISH FOR SILVER.

Let us deal with liquids in their turn. Taking Pontic rhubarb, rub it up in bitter Aminean wine to the consistency of wax, and take a thin piece of *Luna* to make *Sol*, the pieces of which may be a full nail in breadth, that thou mayest use the drug again and again; place it in an empty vessel, which, luting on all sides, gently heat from beneath until the middle (of the leaf) is reached. Then place the leaf in the remainder of the drug, and complete the action with the aforesaid wine, as long as the liquid appears thick. In this, throw at once the uncooled leaf, and allow it to absorb, then take it and place it in a crucible, and thou shalt find *Sol*.

But if the rhubarb be dried with age, mix it with equal parts of celandine, preparing it, as of custom, for celandine has a relationship to rhubarb. Nature rejoices with nature.

XIII. ANOTHER GOLD VARNISH.

Take crocus of Cilicia,§ and leave it with the crocus flower, and the aforesaid juice of the vine, and thou shalt have a liquor, as is accustomed to be done. Colour silver, cut into leaves, until it seems shining to thee. But if the leaf be bronze it will be better, but first cleanse the bronze, as customary. Then taking two parts of the herb aristolochia, and double of crocus, and celandine, make it of the consistency of wax, and anointing the sheet, do as before, and wonder, since the crocus of Cilicia has the same effect as mercury, as also cassia with cinnamon. Nature conquers nature.

XIV. ANOTHER GOLD VARNISH.

Taking our lead made shining by Chian earth, and pyrites, and alum, burn with chaff, and melt into pyrites; and rub up crocus and cnicum, and the flower oecumenicus with the sharpest vinegar, and make a liquid, as of custom, and dip the lead into it, and allow it to absorb it, and thou shalt find *Sol*, but let the composition have a little unburnt sulphur; for nature conquers nature.

XV. This is the plan of Hepammenes, which he showed to the priests of Egypt, and it remains to the times of these philosophers, the matter of the *Chrysopeia*. Nor should ye wonder if one thing performs a mystery of this kind. Do ye not see that many drugs can with difficulty, even in the progress of time, heal up wounds produced by iron, but human excrement succeeds in no long interval of time; and many drugs employed for burns produce often no good, and most in no way diminish the pain, but lime alone, when rightly prepared, drives out the ailment; and if various cures are tried for ophthalmia, they generally increase it, but the plant buckthorn, used to all sickness

* Greek, copper.

† Greek, orichalium.

‡ Greek, dry pow. substances.

§ Is this the bulb, for which Cilicia was famous, or a yellow metallic compound?

of this kind, cures perfectly. Vain and unsuitable matter should therefore be despised, but things be used according to their natures. Now therefore learn from these also, that no one has ever been successful without the aforesaid natures. But if nothing can be done without these, why do we desire a forest of many things; what is our need of the concourse of many species for the work, when one surpasses all?

Let us now see the composition of the species from which silver can be made.

(To be continued).

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLET, F.R.S.,
Professor of Chemistry in the University of Virginia.
(Continued from p. 82).

General Precautions Observed in the Experiments for the Determination of the Atomic Weight.

ALL the reagents used were prepared or purified by myself, and most carefully tested for any traces of such impurities as might reasonably be suspected, and as could

FIG. 1.

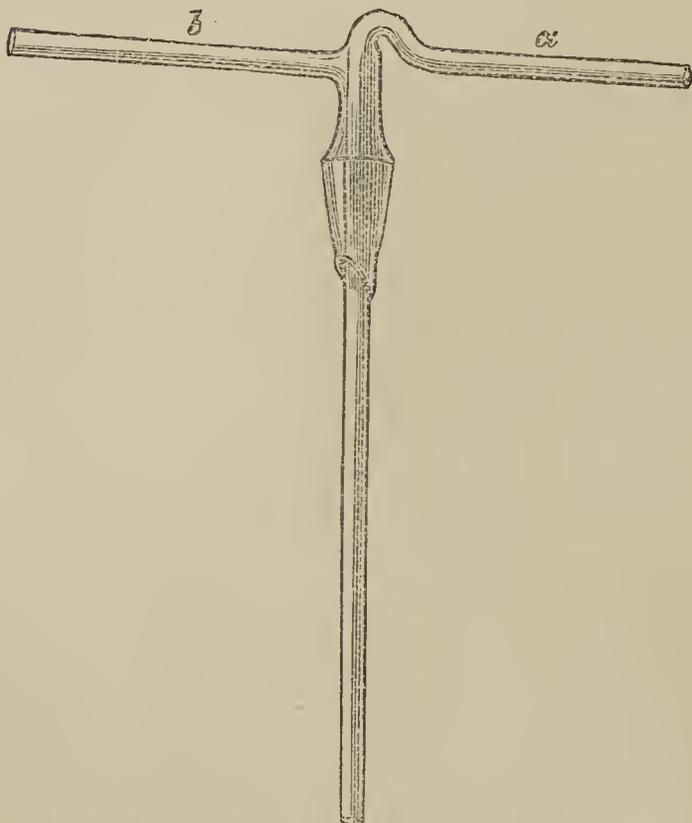
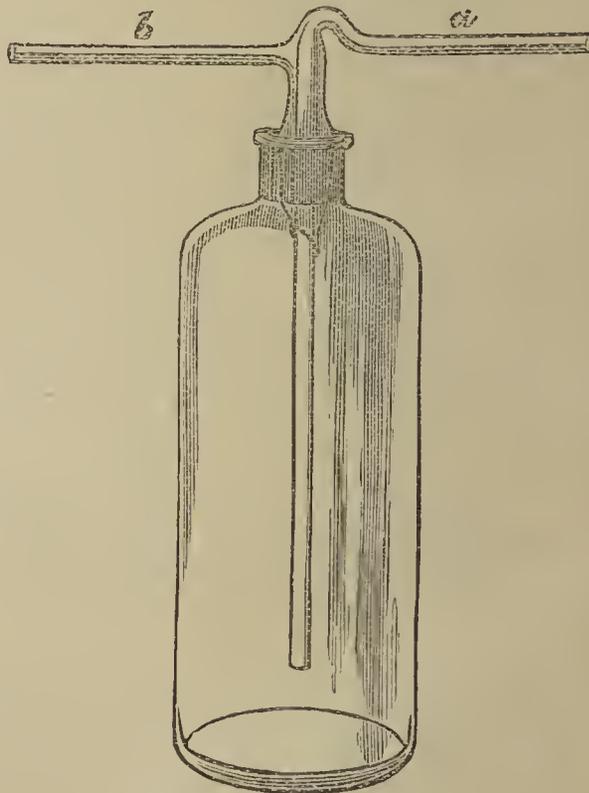


FIG. 2.



affect their application to the purpose in view. Particular care was bestowed upon the examination of the distilled water, acids, and other materials used in large quantity. To remove organic matter from the water required, it was distilled from a small amount of potassium permanganate and sulphuric acid.

Scrupulous care to exclude atmospheric dust was observed. In the evaporation of some of the gold solutions the process was carried out in a glass bottle of considerably larger capacity than the volume of liquid to be treated, furnished with a well ground glass stopper of special construction, as shown in Figs. 1 and 2, the latter representing the stopper in place. Air, purified by passing through a red-hot tube, then through a solution

of potassium permanganate and sulphuric acid, and dried by passing through concentrated sulphuric acid and over solid potash, was introduced by the tube *a*, which went down to near the level of the liquid to be evaporated, while this air, charged with vapour of water from the liquid, was withdrawn through the tube *b* by means of a water-jet pump; the bottle was moderately heated by immersion to the greater part of its height in a water-bath.

In filtering the gold solutions no paper or other organic material was used, but fine white siliceous sand, previously boiled in nitric and hydrochloric acids, washed with water, and well ignited to burn off any organic matter, was substituted, supporting it on coarser sand and larger fragments of quartz, similarly purified, and the whole arranged so as to prevent the possibility of any sand grains being mechanically carried into the filtered liquid. Vessels of hard glass and Berlin porcelain were employed. Care was taken to work in a clean laboratory atmosphere, from gases or vapours which might affect the materials dealt with.

First Series of Experiments.

A neutral solution of auric chloride was prepared by cautiously heating auric chloride, made, as suggested by Julius Thomsen, by the direct action of pure chlorine

upon finely divided metallic gold, until such an amount of chlorine had been given off that on treating the residual material with moderately warm water, metallic gold only remained undissolved, which was then filtered off. This neutral solution having been rendered uniform by agitation, two approximately equal portions of it were weighed off, using, of course, stoppered vessels to prevent evaporation during the weighing. From one of these portions the gold was thrown down in the metallic state by pure sulphurous acid with the aid of heat, carefully collected, well washed, dried, ignited in a Sprengel vacuum, and weighed. To the other portion there was added the carefully prepared solution in a minimum of nitric acid of an accurately weighed quantity of pure silver, a little more than equivalent to the chlorine present, the liquid

* A Paper read before the Royal Society, May 9, 1889.

and precipitate digested together for a considerable time with gentle warming in a stoppered glass flask, well agitated from time to time, and the precipitate (of silver chloride, containing also the gold) filtered off upon siliceous sand, and thoroughly washed, avoiding throughout the decomposing influence of light. The clear filtrate was nearly neutralised with pure sodium hydroxide (from metallic sodium), evaporated down to a small bulk, using the vessel represented in Fig. 2, and finally the remaining silver was determined (with all the needful precautions of the silver assay) by means of a weighed quantity of a weak solution of pure hydrobromic acid standardised against pure silver. This mode of determining chlorine by means of silver and hydrobromic acid was suggested to me in a letter, of the 27th January, 1887, with which I was favoured by M. Stas,* who advocates it as the most exact process available. The pure silver required was prepared in the same way as that used in my experiments on the atomic weight of aluminum,† and was heated in the Sprengel vacuum to remove all occluded gas. The hydrobromic acid was prepared as directed by Stas in his published paper—"De la Détermination du rapport proportionnel entre l'argent, les Chlorures et les Bromures."‡

In reporting the results obtained, the quantity of gold stated is that actually weighed, but the quantity of silver corresponding thereto has, for the sake of simplicity, been given as that required for an exactly equal quantity of the auric chloride solution, while, as stated above, the quantity of liquid weighed off was very nearly, but not exactly, equal to that from which the gold was thrown down, the difference being allowed for in calculation.

With this explanation the results of the first series of experiments were as follows:—

Experiment.	Character of gold used.	Gold. Grms.	Silver required to precipitate Cl. Grms.
I.	A, a	7.6075	12.4875
II.	A, b	8.4212	13.8280
III.	B	6.9407	11.3973
IV.	A, c	3.3682	5.5286
V.	C	2.8244	4.6371

In regard to conceivable sources of error connected with this method, it is to be observed that, in preparing the original auric chloride solution, if there should be any reaction between this gold salt and the water, leading to the formation of traces of hydrogen auri-chloride and precipitation of a little auric oxide or hydroxide, which might escape observation in admixture with the metallic gold left undissolved, the tendency would be to lower the atomic weight found for gold. If, by reaction between this residual metallic gold and the auric chloride solution, any traces of aurous chloride were produced and taken up by the solution of the higher chloride, the effect would be to raise the apparent value of the atomic weight.§

If, in the reaction of the silver solution upon that of auric chloride, *partial* withdrawal of chlorine should lead to the formation of any traces of aurous chloride, precipitated along with the chloride of silver, and not afterwards decomposed during the digestion of the precipitate with the remaining solution, the resulting error would also be in the direction of too high an atomic weight. The probability of the last supposition is diminished by an excess of silver for the whole amount of chlorine present having been added at once. It is not very likely that any one of

these defects actually belongs to the method and affects its results to a sensible extent. Of the three, I should be more inclined to suspect the possibility of the second than either of the two others.

Second Series of Experiments.

A neutral solution of auric bromide was prepared by a like process to that used in making the auric chloride of the first series; acting upon pure metallic gold with pure bromine (prepared with the precautions recommended by Stas), evaporating the solution to dryness, out of reach of dust, cautious heating of the residue, re-solution of auric bromide, and filtration from undissolved metallic gold.

Two nearly equal portions of the solution were accurately weighed off, and treated as described above; in one, reducing the gold to the metallic state and determining its weight; treating the other with a small excess of silver in solution as nitrate, filtering off the precipitate, concentrating the filtrate with the precautions already described, and determining in it the excess of silver by means of hydrobromic acid.

Reducing the amounts of silver actually used to the corresponding quantities for portions of auric bromide solution exactly equal to those from which in each case the gold was obtained, the results in six experiments stood as follows:—

Experiment.	Character of gold used.	Gold. Grms.	Silver required to precipitate Br. Grms.
I.	A, b	8.2345	13.5149
II.	A, c	7.6901	12.6251
III.	B	10.5233	17.2666
IV.	A, a	2.7498	4.5141
V.	C	3.5620	5.8471
VI.	A, b	3.9081	6.4129

In these experiments the sources of constant errors which suggest themselves as possible are essentially similar to those of the first series; but, if any such really exist, there is, of course the likelihood of some difference being introduced by the substitution of bromine for chlorine. Hence the desirability of multiplying experiments in this modified form.

Third Series of Experiments.

For these experiments potassium auri-bromide was prepared with great care from an excess of metallic gold treated with bromine and potassium bromide, purified in accordance with Stas's suggestions, and the double salt five times re-crystallised. The last crystallisation was conducted fractionally, in closed vessels, with special care to exclude dust, by gradual but pretty rapid cooling with agitation, and the earlier and later portions separated out were kept apart in after use.

For each atomic weight determination an unweighed quantity of this potassium auri-bromide was dissolved in water, the solution rendered uniform by agitation, and divided into two nearly equal parts, which were severally weighed with accuracy, and in one the gold reduced to metal as in the experiments of the first and second series, and in the other the total bromine precipitated by silver solution as before, the comparison being made once more between the weight of the gold and that of the silver equivalent to the bromine (in this case representing 4 atoms) existing in the double bromide.

Again stating the quantities of silver corresponding to portions of the auri-bromide solution exactly equal to those used in determining the gold, the following were the results obtained:—

Exp.	Character of gold used.	Fraction of crystallised auri-bromide used.	Gold. Grms.	Silver required to precipitate Br. Grms.
I.	A, b	First	5.7048	12.4851
II.	A, b	Second	7.9612	17.4193
III.	B	First	2.4455	5.3513
IV.	B	Second	4.1632	9.1153

* In this letter M. Stas says:—"Je me permets de vous recommander l'emploi de l'acide bromhydrique pour la précipitation de l'argent resté dans un liquide après une double décomposition opérée à l'aide d'un *chlorure* et d'un sel d'argent. On réussit à condition que l'eau mère renferme un excès d'argent dont le poids est le triple du métal qui peut rester en solution à l'état de chlorure d'argent."

† *Phil. Trans.*, 1880, p. 1020.

‡ *Mémoires de l'Acad. Royale des Sciences de Belgique*, vol. xliii., 1882.

§ These two remarks apply, of course, also to Krüss's first series of experiments.

Of the tendencies to constant error which may be imagined in connection with the experiments of the first two series, and which have been noticed above, the first may probably be considered as not applying to the method pursued in this third series, while the second and third might still be applicable. But the superior stability of the double salt constitutes an advantage in its favour, and, as it formed the chief material for the experiments of Krüss and of Thorpe and Laurie, a comparison with their results is desirable, the mode of treatment pursued by me in ascertaining the composition of the salt not having been quite the same as that used by these chemists.

Fourth Series of Experiments.

A weighed quantity of trimethyl-ammonium aurichloride $[N(CH_3)_3HAuCl_4]$ was decomposed by heating in the air, and the weight of the residual metallic gold determined. This trimethylamine salt was selected because the base is of simple and well established constitution, and may with reasonable probability be counted upon as obtainable in a state closely approaching purity, and because the gold salt is easily crystallised, possesses a considerable degree of stability, and contains approximately half its weight of gold, so as to offer the most favourable chance of determining with accuracy the ratio between the metal left behind and the sum of the remaining constituents driven off on ignition. Although its use in fixing the atomic weight of gold involves the atomic weights of three other elements—carbon, nitrogen, and chlorine—all three of these constants deserve to be ranked amongst those already known with the nearest approach to precision at present attainable.

In order to obtain pure trimethyl-ammonium chloride, the impure commercial salt, derived from the *vinasse* of beet-root sugar-making, was used, first setting free and distilling off a considerable quantity of trimethylamine and condensing at about the right temperature, and subsequently purifying the product by Hofmann's method of treatment with ethyl oxalate and renewed distillation. The purified trimethylamine was several times fractionally distilled, and the portion of correct and most constant boiling-point finally neutralised with pure hydrochloric acid. The concentrated solution of trimethylammonium chloride was now precipitated by a strong solution of auric chloride, the mother-liquor decanted off, and the gold re-dissolved in hot water, and re-crystallised several times. The bright yellow crystalline powder was dried, first over sulphuric acid, and afterwards over phosphorus pentoxide, until it ceased to lose weight; towards the end of the drying the temperature of the vessel was raised to about $50^\circ C$. Preliminary experiments seemed to indicate the probable existence of this salt crystallised with a single molecule of water, but most of that prepared contained no constituent water, and it appeared easy to attain complete drying without any decomposition of the salt itself. Throughout its treatment the salt, which was not in any high degree hygroscopic, was well guarded from dust and from any possible decomposing effect of light.

The portion of the salt to be used in each experiment was contained in a small glass-stoppered weighing flask, which was removed just before it was needed from the phosphorus pentoxide desiccator, the stopper having been inserted; the flask was weighed, the greater part of its contents transferred quickly to a weighed porcelain crucible, the stopper at once replaced, and, the flask being again weighed, the quantity of gold salt taken from it was found by difference.

In order to avoid mechanical loss by splattering on igniting the crucible and its contents, the auri-chloride lying together at the bottom of the crucible was covered by a layer, nearly a centimetre deep, of clean, carefully purified, and just previously well-ignited siliceous sand, the weight of this sand being known by taking it from a weighing flask in which it had been cooled over phosphorus pentoxide, and noting the loss of weight of this flask. In applying heat to the crucible and its contents it was found necessary to heat gently for a long time, raising the temperature slowly, in order to prevent extensive charring at the bottom. Then, before the temperature had become too high, but after a considerable part of the volatile matter had been driven off, the sand was carefully stirred in with the remaining material so as to produce pretty uniform mixture, in order that the gold might not undergo partial welding together at a higher temperature, which might have led to wrapping up particles of carbon and their protection from combustion. In this operation a very small porcelain stirrer was used, as a platinum wire would have welded on and taken up some of the metallic gold; the weight of this stirrer was determined in advance, and checked after use. Finally, the contents of the crucible were submitted to very careful and prolonged heating to moderate redness, with free access of air and occasional cautious stirring, so as to burn away every trace of carbon. After cooling in a desiccator, the crucible and its remaining contents were weighed, giving the weight of the residual gold by subtraction of the weights of the crucible itself and the siliceous sand. As an additional safeguard against any particles of carbon left unburned escaping detection, the gold was afterwards dissolved out with aqua regia, and the white sand carefully looked over with a lens.

The results of five experiments thus conducted were as in Table below.

In these experiments the most probable source of error may be fairly taken as arising from the presence of traces of methyl-ammonium or dimethyl-ammonium aurichloride with the trimethyl-ammonium salt. I know of no direct evidence that any such impurity was present, and the absence of any such evidence in the results from the earlier as compared with the later crops of crystals rather tells against the supposition of its presence, but one cannot feel certain of its entire absence. If present, its effect would be to raise the atomic weight obtained for gold. It is also conceivable that there may have occurred volatilisation of gold to a minute extent as auric chloride, in accordance with the observation of Krüss that this salt may be sublimed in small quantity at moderate temperatures in a stream of chlorine; but, there being no such stream of chlorine in these experiments, and, on the contrary, the decomposing action of the hydrogen of the trimethylamine salt, this does not seem likely; the effect would, of course, be to raise the atomic weight obtained for gold. Another possible cause of error might consist in imperfect drying of the gold salt used, but the constancy of weight attained on drying renders it unlikely that any other than extremely minute error should come of this, though not altogether excluding the possibility of its occurrence; its tendency would, of course, be to lower the atomic weight obtained. Any trouble from hygroscopic moisture on the surface of the porcelain crucible and sand was, I think, satisfactorily guarded against by the use of a corresponding tare crucible, and by more than one weighing after a near approach to the true figures had been obtained, the crucibles having meanwhile been restored to the desiccator

Experiment.	Character of gold used.	Character of gold salt used.	Salt ignited. Grms.	Residual gold. Grms.	Loss by ignition. Grms.
I.	A, b	Earlier crop of crystals	14.9072	-7.3754	=7.5318
II.	A, b	Middle „ „	15.5263	-7.6831	=7.8432
III.	A, b	Last „ „	10.4523	-5.1712	=5.2811
IV.	C	Middle „ „	6.5912	-3.2603	=3.3309
V.	C	Last „ „	5.5744	-2.7579	=2.8165

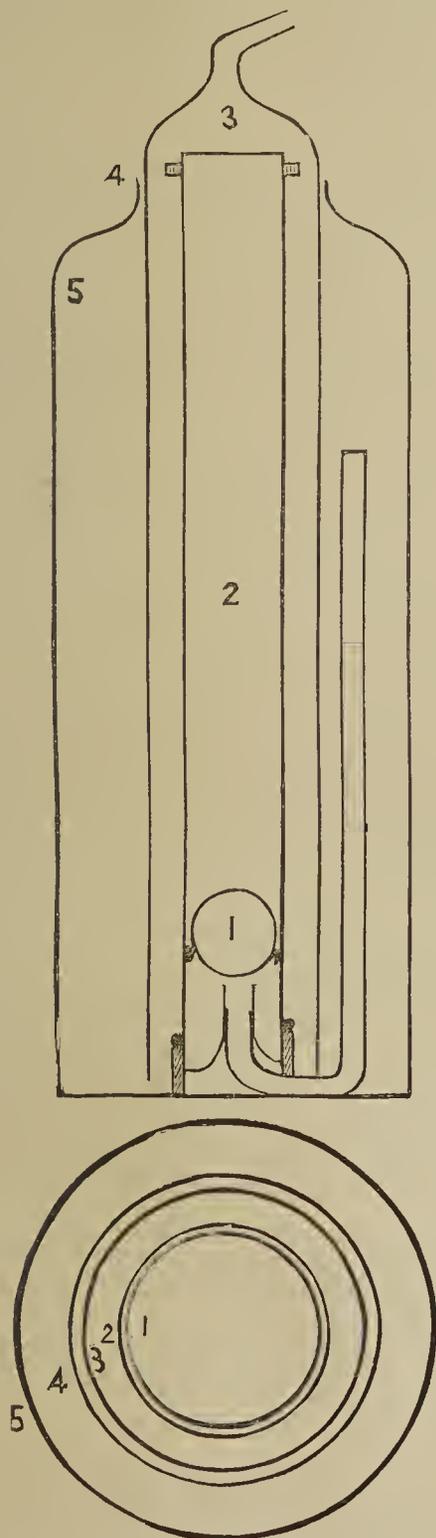
and kept therein for some time. The precautions taken seemed to afford sufficient protection against any merely mechanical loss during the ignition.

(To be continued).

SULPHURETTED HYDROGEN GENERATOR.

By W. OAKES KIBBLE.

I HEREWITH enclose a sketch of my improved H_2S generator. The advantages claimed are as follows:—1. Simplicity—hence cost small. 2. Sulphide is effectively prevented from entering main body of acid, thus saving



1, Glass Ball.

waste and smell. 3. Very easily re-charged and cleaned. 4. Store of gas is always ready. 5. When not in use automatically the action ceases. 6. A continuous supply

at a moderate pressure—4 inches in water in smallest to 8 or 12 inches in larger. 7. If any part broken, can be renewed at a proportional cost. 8. The acid being used from the top, the specifically heavier spent acid does not interfere with working of apparatus even after standing for days. 9. No direct escape of gas. 10. Compactness.

Parts and Functions of Apparatus.—Inner tube with studs holding glass ball (loosely fitting); this supports sulphide of iron. The bottom is closed and a tube sealed in, thus forming an effectual trap for the small particles of sulphide. An outer tube drawn out for attachment of rubber tube and tap or pinch-cock. A glass tube (thin) from the trap into which it fits, reaching three-fourths of the way upon the outside. A rubber collar at the bottom and band at the top of inner tube to prevent jarring. An ordinary broad necked reagent bottle to hold acid. A rubber ring is fitted three-fourths of the way round in the neck to prevent outer cylinder from rising.

To use, fill jar three-fourths full of acid (dilute), then put in inner tube filled with sulphide, and slip outer tube over it; shut tap or close pinch-cock. The acid which has entered immediately acts on the sulphide, generating H_2S , which fills the tubes, leaving the sulphide practically dry, any pieces of sulphide falling past 1 being dissolved. As the gas is used acid re-enters and generates fresh supply.

It will shortly be obtainable in sizes from 10 in. high 3 in. diameter to 20 in. high and 7—8 in. diameter, the capacity of the smallest being about 1 litre and the largest about 10 litres.

Finsbury Technical College,
Leonard Street, City Road.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, February 6th, 1890.

SIR,—We submit herewith 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 seven London Water Companies taking their supply from the Thames and Lea.

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

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

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

The whole of the 189 samples examined were found to be clear, bright, and well filtered.

During the first month of the new year the quality of the water supplied to the Metropolis has not shown any retrogression, but has continued to be of the same high character (exceptionally high for the period of the year) as recorded in our previous monthly report. Taking the estimations of organic matter present, of oxygen required for its oxidation, and of degree of colour tint, while one

item has shown a slight increase, and another a slight decrease, the variation in each case is within very narrow limits. As regards the water furnished by the Companies taking their supply from the Thames, the maximum amount of organic carbon found in any single sample examined was 0.146 part in 100,000 parts of the water, as against a maximum of 0.153 part, and a mean of 0.143 part in the previous month's entire supply.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Annual General Meeting, February 21st, 1890.

Prof. G. CAREY FOSTER, F.R.S., Past President,
in the Chair.

MR. S. EVERSLED was elected a member of the Society.

The following communications were read:—

"On a Carbon Deposit in a Blake Telephone Transmitter." By F. B. HAWES.

The author exhibited photographs of the interior portions of the transmitter on which the deposit had taken place. These portions consist of a metal diaphragm, a highly polished carbon button, and a platinum contact piece carried by a German silver spring placed between them. The diaphragm presented a mottled appearance, due to the deposit, but the part which had been behind the German silver spring seemed comparatively clean. The deposits on the carbon button and German silver spring were much less dense than that on the exposed parts of the diaphragm, and the space near the point of contact between the platinum and carbon was free from deposit. The deposit was fairly adherent, considerable rubbing being necessary to remove it, and, on examination under the microscope, particles of copper and metallic crystals could be seen. The author believes the deposit due to some kind of bombardment of carbon particles, but was unable to say why it should occur, or why the varnished diaphragm should receive the greater deposit, although it was further from the carbon than the German silver spring.

Mr. C. V. BOYS said the photographs reminded him of a phenomenon he observed some time ago on a glass sheet against which one terminal of a dry pile had been resting for some weeks. Just as on the carbon button, the glass near the point of contact was clean, and has a comet-shaped deposit formed around it. He could offer no explanation of the appearance.

"The Geometrical Construction of Direct Reading Scales for Reflecting Galvanometers." By Mr. A. P. TROTTER.

In a recent paper "On Galvanometers," by Prof. W. E. AYRTON, F.R.S., T. MATHER, and Dr. W. E. SUMPNER, read before the Society, the opinion was expressed that proportionality of scale reading to current was very desirable, and the present paper shows how to bend a scale of equal divisions so as to give the required proportionality. Suppose the currents required to produce several deflections have been experimentally determined. A full size plan of the scale is then drawn, and radial lines from the points on the scale at which the observations were taken are drawn towards the centre of the mirror. Let these radii be numbered 0, 1, 2, 3, &c., commencing from zero-azimuth. According to the procedure recommended, distances proportional to the

several current strengths are marked off along the edge of a strip of paper, a few inches being left over at each end. Call the marks *a, b, c, d, &c.*, *a* being the zero point. Two points on the radii 0, 1, and equidistant from the mirror, are now found such that the distance between them is equal to that between *a* and *b* on the strip, and the points marked by fine needles stuck in the board. The zero end of the strip is now fixed, so that the marks *a* and *b* lie against the needles, and the strip is swept round until the mark *c* coincides with the radius 2, where also a needle is placed. Repeating the process gives a series of points which, on being joined, form part of a polygon. A line can then be drawn between the inscribed and circumscribing curves, which has the same length as the sum of the straight lines; and this is the curve to which the original scale may be bent, so as to give proportional readings. Diagrams showing such curves constructed from the calibrations of instruments given in the paper above referred to, accompany the paper.

The author showed that a family of curves may be drawn, each of which satisfies the required condition. Of the two limiting curves, one is tangential to the usual scale line at zero azimuth, and the other passes through the vertical axis of the mirror. The flattest of the various curves is generally the most convenient.

Mr. J. SWINBURNE asked whether good definitions could be obtained when such curved scale not equidistant from the mirror were used, and also whether it was not easier to divide a flat scale unequally, so that the readings are proportional to the current.

Mr. TROTTER, in reply, said Dr. Sumpner thought there would be no difficulty as regards definition with the flat curves shown. He (Mr. Trotter) also added that a curved scale might be advantageous in reading the deflections from one side of a table, as the more distant part of the scale could be more nearly perpendicular to the line of sight. For such an arrangement, however, a parallel beam of light would be required.

"A Parallel Motion suitable for Recording Instruments." By Mr. A. P. TROTTER.

This is a modification of Watts's parallel motion, in which the two fixed centres are on the same side of the line described by the "parallel point." The arrangement consists of two vibrating arms, one of which is twice the length of the other, and whose outer ends are jointed respectively to the middle and end of a short lever; the free end of the latter describes an approximate straight line. The motion was arrived at by considering the curve traced out by a point on the radius of a circle, such that its distance from the circumference, measured towards the centre, is equal to the radial intercept between the circle and a tangent line. The equation to the curve is $r = 2 - \sec \theta$ (conchoid of Nicomedes), and the radius of the osculating circle at the point where the intercept is zero is given as half that of the initial circle. This osculating circle, the author finds, practically coincides with the curve over a considerable angle (40°), and therefore may replace this part of the curve; hence the motion.

The author thinks the motion will be useful for recording barometers, ammeters, and voltmeters, as it is more compact than that of Watt, and needs no fixed point beyond the straight path.

Owing to the absence of Prof. S. P. THOMPSON his paper "On Bertrand's Refractometer" was not read.

Detection of Free Chlorine in Hydrochloric Acid.—G. A. Le Roy.—The author recommends the use of metallic copper or phosphorus, and also diphenylamine or phenylamine. The acid containing infinitely small traces of chlorine, if treated in a test-tube with a few particles of chlorine, takes immediately a blue colour.—*Bull. de la Soc. Chim. de Paris*, Vol. ii., No. 11.

NOTICES OF BOOKS.

A Dictionary of Applied Chemistry. By T. E. THORPE, B.Sc. (Vict.), Ph.D., F.R.S., Treas.C.S., Professor of Chemistry in the Normal School of Science and Royal School of Mines, South Kensington. Assisted by eminent Contributors. In Three Volumes. Vol. I. London: Longmans, Green, and Co.

THIS work, as we learn from the preface, is intended to be complementary to the new edition of "Watts's Dictionary of Chemistry." Many of the articles inserted—we may, perhaps, most prominently signalise those on the coal-tar colours and their raw materials—are of remarkable excellence. Others, again, not less ably written, may be regarded as of questionable relevance. We should certainly be slow to undervalue a study of the "rare earths." But until they can be procured in much greater quantity than at present, a consideration of the "Cerium Metals and Earths" can have little interest for the technical chemist.

The elaborate article on the balance is also of doubtful relevance. Indispensable as this appliance is to every chemist, its construction does not depend on chemical principles, and hence the carefully written and freely illustrated description here to be found seems out of place.

Of remarkable value are the sections on indicators, in connection with alkalimetry and acidimetry, and accompanied by a tabular view of the conditions under which each gives trustworthy results. It will scarcely be believed that no longer than thirty-five years ago the indicator used by a commercial analyst whose valuations of soda-ash were greatly admired by brokers, was his tongue!

The article on albumen does not omit the important caution that, in the manufacture of blood-albumen, all agitation must be avoided. If the climate were colder the best place in the world for the manufacture of blood-albumen would be Fray Bentos, where the blood might be conveyed directly from the slaughter-houses to the works.

Under "Alcoholometry" we find no condemnation of the "proof spirit" still absurdly used in Britain as a standard both for fiscal and commercial purposes.

Alizarin forms the subject of an excellent chapter, in which are given representations of the absorption and spectra of alizarin and purpurin. This is an example which ought to be followed.

Aluminium and its numerous compounds are very fully and ably described. By an oversight the manufacture of alum from the aluminous shales of Whitby is represented as being still carried on.

The remark is made that if all the ammonia possible were recovered and collected from the beet-sugar works in Germany, it would amount to 15,000 tons of sulphate yearly. But this manufacture cannot be very lucrative in the long run, as the beet-root fields have to be supplied with combined nitrogen either in the form of ammonium sulphate or sodium nitrate. The case of using wool as source of potash is very similar.

The chapter on the azines and their derivative colours, on the azo-colours, benzene and its homologues, bromine, cellulose, cements, chlorine, and the cyanides, as also that on bleaching, are fully on a level with the present state of knowledge, and will be found trustworthy. Dyeing scarcely receives full justice; calico-printing is omitted, but it will probably be noticed subsequently under "Tissue-printing."

There is a copious table of the reactions of the most important colours when fixed upon the fibre.

Lovibond's tintometer is described and figured, as well as other appliances and processes for colorimetric investigations.

It is scarcely necessary to say that Dr. Thorpe's work

will be universally appreciated by technical and manufacturing chemists.

*On the Present Position of the Question on the Sources of the Nitrogen of Vegetation; with some New Results, and Preliminary Notice of New Lines of Investigation.** By Sir J. B. LAWES, Bart., LL.D., F.R.S., and Professor J. H. GILBERT, LL.D., F.R.S. London: Published for the Royal Society by Trübner and Co.

THE question of the supply of nitrogen to vegetation is one of the utmost importance, not merely from a theoretical but from a practical point of view. Put in a slightly different form it means, Are we, as far as the nitrogenous constituents of our frames are concerned, living on the earth's income, or, as in the case of coal, on its capital? Do plants depend for their growth on the combined nitrogen present in the soil and the sub-soil, supplied by manures and by the decomposing remnants of defunct organisms, or brought down by the rain in the form of ammonia or of nitric acid? Or are they able to fix in their tissues, directly or indirectly, any portion of the unlimited store of free nitrogen existing in the atmosphere? Such fixation might conceivably take place in various manners; by the direct action of the plant, by the mediation of fungi or microbia, by some reaction of constituents of the soil, by the silent electrical discharge, &c.

The subject has latterly received much careful experimental study at the hands of M. Berthelot, Dehérain, Joule, Dr. B. E. Dietzell, Prof. B. Frank, Prof. Hellriegel and Dr. Wilfarth, Prof. Emil von Wolff, Prof. W. O. Atwater and M. Boussingault, and of the authors themselves. The results cannot be pronounced decisive. Few authorities now, indeed, admit the direct condensation of free nitrogen. But certain observations, if they do not formally prove an indirect fixation do not so far give any decisive evidence to the contrary.

M. Berthelot thinks it proved by his experiments that vegetable soils, at least under the influence of the silent discharge, fix free nitrogen. The combination of nitrogen in the atmosphere itself is of course admitted, but its available limit in Europe has been approximately ascertained.

M. Dehérain has sought, during a period of ten years, to determine the loss or gain in the field under the influence of different manures, different crops, and different modes of cultivation. He records, in some cases, a loss of nitrogen, and in others a gain, but our authors, whilst fully admitting the accuracy of his analyses, entertain doubts concerning his method of sampling.

M. Joulie concludes that the fixation of free nitrogen is due to the action of microbia. Sir J. B. Lawes and Dr. Gilbert hold that such gains as M. Joulie finds within a lapse of fourteen months do not take place in ordinary agricultural practice.

Dr. Dietzell, in his cultivation experiments, finds, in every case but one with pears, and in every case with clover, a loss, not a gain, of nitrogen. Dr. Frank, like Dietzell, operated with soils exceptionally rich in nitrogen.

Prof. Hellriegel and Dr. Wilfarth conclude that the *Papilionaceæ* are less dependent than the *Graminæ* upon the soil as the source of their nitrogenous food. They accept Berthelot's view that the nodules on the roots of the *Papilionaceæ* swarm with microbia, which have the power of bringing free nitrogen into organic combination. Further confirmation, however, is necessary. In sterilised soils papilionaceous plants were as little capable of flourishing (in the absence of mineral manures) as vegetables belonging to other families.

Prof. E. von Wolff also finds a gain of nitrogen in experiments with the *Papilionaceæ*, but he admits that the amounts of absorption found in his experiments cannot be expected in agricultural practice, where the soil is

* *Philosophical Transactions of the Royal Society of London*, vol. clxxx. (1889) B, pp. 1-107.

not kept so porous. He ascribes the gain of nitrogen to the absorption of combined nitrogen from the air by the soils, as well as to the fixation of free nitrogen within the soil owing to the effects of porous and alkaline matter, rather than to the influence of microbia. He does not, at the same time, see his way to explain why other plants should not benefit by such absorption and fixation as well as the *Papilionaceæ*.

Prof. W. O. Attwater concludes that plants themselves are the agents in the fixation of nitrogen, as in his experiments the agency of electricity and of micro-organisms did not exist.

M. Boussingault has latterly re-examined the question, as in his former experiments the action of electricity and of micro-organisms was excluded. He writes to the authors that "If there is in physiology a fact perfectly demonstrated, it is the non-assimilability of free nitrogen of plants, even those of an inferior order, such as mycodermis and fungi."

In summarising the evidence on the question, the authors consider it decided that, since experimentation in the open air, instead of in closed vessels, has become more general, the evidence which is supposed to show the fixation of free nitrogen has become more plentiful. But the methods of explaining the facts are so conflicting that it is right to suspend judgment.

Underlying many of the experiments recently made is the assumption that there must exist some source of compensation for the nitrogen lost by the soil in the removal of crops. These losses seem to have been exaggerated. For Great Britain the average loss of nitrogen is probably under 20 lbs. per acre. A loss of nitrogen from the plants themselves is not proven, and the authors do not believe that it takes place. Sir J. B. Lawes and Dr. Gilbert think that the fungi are nourished chiefly by organic nitrogen, and that on their decay it becomes available for higher vegetation. Whether or not the microbia affect the combination of free nitrogen within the soil, they seem, at any rate, to bring the inert nitrogenous matter in the soil and subsoil into a condition assimilable by crops.

CORRESPONDENCE.

THE IGNITING-POINT OF SULPHUR.

To the Editor of the Chemical News.

SIR,—I must first express my sense of obligation to Professor Hodgkinson for his authoritative correction of the current mis-statements of the igniting-point of sulphur. Before writing my former note I had experimented on the subject, but being unable to quote the temperature observed, owing to its being above the range of the mercurial thermometer, I made no mention of my results. A brief account of the simple method used may be of some slight interest. The determination of the igniting-point of sulphur seems at first blush absurdly easy, and one naturally begins (particularly if one be impressed with a belief in its taking place at a comparatively low temperature) by heating some of the element in a small capsule standing on a hot plate and containing the bulb of a thermometer. One then notices that the sulphur volatilises freely much below its boiling-point, and, on continuing to heat, finds that it takes fire about 270° C. Careful observation at the moment of ignition clearly shows that the flame does not start at the surface of the fused sulphur, but proceeds from its vapour, which has flowed out of the capsule on to the hot plate, the temperature of which is, of course, considerably higher than that of the sulphur itself. It is to a failure to perceive this fact, that the statement usually adopted is due, some early experimenters having doubtless fallen into the error, and industrious copyists having perpetuated it.

Recognising the necessity of preventing the sulphur vapour from coming into contact with any object at a higher temperature than the sulphur from which it was derived, I placed my capsule in the centre of a hot plate one foot square, and surrounded it by a second plate parallel to the first, on which it was supported by little bits of tile, and having a central hole to accommodate the capsule, the fitting of the two being made good by judicious packing with slag wool. On heating the lower plate the temperature of the sulphur rose above the boiling-point of mercury without it showing the slightest tendency to catch fire, and ultimately it boiled before doing so. The large volume of vapour then arising sufficed to evade the barriers between it and the burner below, and transmitted the flame to the sulphur; but it was proved beyond question that, so far from sulphur igniting at a low temperature, it refuses to do so at all as long as it remains liquid, and the only fact that needs ascertainment is the temperature of ignition of *gaseous sulphur*.—I am, &c.,

BERTRAM BLOUNT.

Laboratory, Broadway,
Westminster, S.W.
Feb. 22, 1890.

ULTRA CREPIDAM?

To the Editor of the Chemical News.

SIR,—From a merely scientific point of view it would greatly interest me, and doubtless not a few of your readers, to see what comments your correspondents may have to offer on the following analysis of a water—which analysis was last week received and acted upon by the Local Board of a small country town:—

"I hereby certify that I have analysed the water from a well at The following is a detailed result:—Physical examination: Clear, colourless, pleasant taste, and no smell. Microscopic: Nil. Chemical: Total solids, 7.9 grains per gallon; chlorine, 6 grains per gallon; ammonia free, 0.03 parts per million; ammonia albumenoid, 0.08 parts per million. Considering the amount of chlorine I must condemn this water as absolutely unfit for use; it presents clear and unmistakable signs of constant sewage pollution.—(Signed) ———, M.B.

P.S.—I may state that, except under exceptional circumstances, 1.5 grains per gallon of chlorine would render a water unfit for use."

I enclose my card and am, &c.,

R. R.

Feb. 21, 1890.

DETERMINATION OF OXIDE OF IRON AND ALUMINA IN PHOSPHATES.

To the Editor of the Chemical News.

SIR,—May we, through your columns, draw the attention of those of your readers interested in this question to a method for the determination of oxide of iron and alumina in phosphates, published in the *Zeitschrift f. Angew. Chem.*, 1889, 636—638, a reprint of which we received last November through the courtesy of the author—Mr. E. Glaser.

Mr. Glaser in his method avoids the use of acetate of ammonia or acetic acid, and therefore, on the one hand, any error from the solubility of phosphate of iron and alumina in free acetic acid, even when highly dilute; and, on the other hand, the difficulty of obtaining the phosphate of iron and alumina free from phosphate of lime. His process is to precipitate lime and magnesia as sulphates by addition of first excess of sulphuric acid and afterwards alcohol to render the removal of these bases as sulphates complete.

The alcoholic solution, after separation of the insoluble

sulphates by filtration, will then contain the whole of the oxide of iron and alumina, and also the phosphoric acid, with the excess of sulphuric acid, and the muriatic acid employed in dissolving the phosphate in the first instance. The alcohol is evaporated, and on the addition of a solution of ammonia in excess (the excess to be afterwards removed by boiling), the oxide of iron and alumina are precipitated and subsequently weighed as phosphates. The phosphoric acid in the weighed precipitate is determined, and the remainder will be the oxide of iron and alumina sought for.

For details of this "alcohol process" we refer your readers to Mr. Glaser's paper.

The correct determination of oxide of iron and alumina in the phosphates met with in commerce is, at the present time, a question of considerable importance to importers of mineral sulphate and manufacturers of superphosphate, and it is at the request of one of these that we trespass on your kindness in asking you to insert this letter,—We are, &c.,

E. F. TESCHEMACHER and J. DENHAM SMITH.

Highbury, London,
Feb. 21, 1890.

LARD.

To the Editor of the Chemical News.

SIR,—Just a few more words upon this subject. I quite expected a defender of the above would put in an appearance. If your correspondent, Mr. Brown, will look at my first letter, he will see that I say "Its common adulterant is cotton-seed oil, but we may look for many other foreign bodies and find them." I was not referring to stearin. I had in my mind such matters as starch, lime, suet, and others than cotton-seed oil, say, sesame, &c., oils. I say these substances have been, and still are, found in lard. It is all very well to talk of what the public expect; it is rather what they get. I am quite aware that the law says the public shall have wholesome articles of food, but the getting of them is another thing. Of course, when pretty well the whole of the hog is rendered down you may look for a "sloppy" article, termed lard; consequently "other matter" is mixed with it in order to get something like solidity. I object to this being called refined lard, or refined leaf lard—it is more like doctored dripping. What I term lard is that made from the flare or fat about the kidneys of the hog. It is no use to say dare not do so-and-so, that is all rhodomontade; such sophistication is done; and I again say something is wrong. I am quite content, after nearly thirty years' knowledge of the way articles of food have been, and still are, manipulated and adulterated, to know this. I shall be told next that there is no butter (not margarine) in the market which does not contain from 15 to 25 per cent of water; I say it is to be found. I have had my say, and will take leave of the subject.—I am, &c.,

JOHN H. SWINDELLS, Ph.D., D.Sc.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Bulletin de la Société Chimique de Paris.
Series 3, Vol. ii., No. 11.

New Researches on the Constitution of the Nitro-camphor- β and of the Chloronitrocamphor- α .—P. Cazeneuve.

On New Bases derived from Camphor: the Camphamine.—P. Cazeneuve.—The author heats 5 grms. of

normal monochlorocamphor- α with 20 grms. of saturated aqueous ammonia for twenty-four hours to 180° in a sealed tube. He obtains a blackish residue. From the solution of this matter after purification he obtains a body which crystallises in small needles radiating out from a centre. It melts at 180°, and is insoluble in water, but soluble in alcohol, ether, chloroform, and ligroine. This body is evidently of a basic nature, and its saline solutions give precipitates with all the general precipitants for alkaloids.

Monochlorocamphor obtained by Hypochlorous Acid; a New Monobromocamphor obtained by Hypobromous Acid; Constitution of the Mono-substituted Derivatives of Camphor.—P. Cazeneuve.—These papers have been, in substance, noticed already.

Influence of Certain Groups on the Valence of Oxhydryl and Carboxyl in the Aromatic Series.—P. Alexeyeff and E. Werner.—A thermo-chemical paper, not suitable for abstraction.

A New Hydrated Potassium Bisulphate.—J. B. Senderens.—The author ascribes to this compound the formula $S_2O_6 \cdot HO, KO + 11H_2O$. It melts at 30° and loses all its water of crystallisation at 100°, and is partially dehydrated even at a lower temperature.

Solubility of Saline Mixtures.—A. Etard.—The author explains his views by means of a diagram.

Chemical Studies published at the Session of the Hungarian Society of the Natural Sciences on October 12, 1889.—L. Ilosvay de N. Ilosva.—There is no ozone in oxygen prepared with strong sulphuric acid and potassium permanganate. The author further examines the formation of nitrous acid in certain special cases of active combustion, and the formation of cyanogen in the inverse case. He next examines the union of nitrogen and oxygen by means of platinum. Nitrogen combines with oxygen, even on the slow oxidation of iron reduced by hydrogen.

Action of Heat upon Chloralammonia.—A. Béhal and M. Choay.—On heating chloralammonia it is decomposed into chloroform and formiamide.

An Acid Cerium Sulphate.—G. Wyrouboff.—The question of the atomicity and the atomic weight of cerium and the metals of its group is far from being solved. M. Mendeleeff proposes to change the formulæ of the two cerium oxides from CeO and Ce_3O_4 to Ce_2O_3 and CeO_2 . The atomic weight which, according to the recent researches of Buhig is 94.4, becomes thus 141.6. This view is confirmed by the determination of the specific heat, which Hillebrand found = 0.4479 between 0° and 100°, giving an atomic weight of 4.22 with $Ce = 94.4$, or of 6.34 with $Ce = 141.6$. The author holds that both physical and chemical properties contradict the hypothesis of Mendeleeff and support the older view.

Zeitschrift für Physikalische Chemie.
Vol. iii., Part 4.

Magnitudes of the Affinities of Organic Acids and their Relations to their Composition and Constitution.—W. Ostwald.—A continuation.

Determination of the Specific Gravity of Salts Soluble in Water.—J. W. Retgers.—The discrepancies in the published specific gravities of such salts are traced to the want of homogeneity of the salts in question and the imperfection of the method employed. To obtain perfectly homogeneous crystals of a salt, the author puts them in methylene iodide and dilutes the liquid gradually with benzene, stirring diligently. The crystals which sink first are selected. Being the heaviest, they may be considered the purest, being free from inclosed particles of mother-liquor and air. The sp. gr. of these selected crystals are then determined in Thoulet's liquid—a solution of potassium-mercury iodide in water,

Diffusion in Agar Jelly.—Felix Voigtländer.—Diffusion in agar galler from watery solutions is not disturbed by the process of imbibition. The validity of Fick's law for dilute solutions might be demonstrated at some length. The rate of diffusion of a substance in different concentrations of the agar jelly is alike. The constants of diffusion observed in the jelly are equal to those found for water, a larger and smaller. With a rise of temperature the constant does not augment, but the quantity of salt introduced increases in a linear proportion.

Reversible Transformation of Cupri-bipotassium Chloride.—W. Meyerhoffer.—This paper requires the accompanying plate and two woodcuts.

Relation of Pyrrol and its Derivatives to the Law of Raoult.—Gaetano Magnanini.—This memoir cannot be reproduced with the two accompanying illustrations.

Cryoscopic Behaviour of Solutions of Iodoform in Benzene and Glacial Acetic Acid.—Nik. von Klobulow.—The non-existence of the anomaly of iodoform mentioned by Raoult may be demonstrated with certainty.

Drop-Electrodes.—W. Ostwald.—A critique on the "Studies on the Chemical Theory of the Galvanic Element," published by F. Exner and J. Tuma in the *Berichte* of the Vienna Academy.

MEETINGS FOR THE WEEK.

- MONDAY, 3rd.—Medical, 8 30.
— Society of Arts, 8. "Stereotyping," by Thomas Bolas, F.C.S.
— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 4th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
WEDNESDAY, 5th.—Society of Arts, 8. "Recent Progress in British Watch- and Clock-making," by Julian Tripplin.
— Geological, 8.
THURSDAY, 6th.—Royal, 4.30
— Royal Institution, 3. "The Early Developments of the Forms of Instrumental Music" (with Musical Illustrations), by Frederick Niecks.
— Royal Society Club, 6.30.
FRIDAY, 7th.—Royal Institution, 9. "Electrical Relations of the Brain and Spinal Cord," by Francis Gotch, Hon. M.A.Oxon., B.A., B.Sc.
— Geologists' Association, 8.
— Physical, 7. "On Bertrand's Refractometer," by Prof. S. P. Thompson.
SATURDAY, 8th.—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.
— Society of Arts, 3. "The Atmosphere," by Prof. Vivian Lewes.

ASSAY BALANCE (Second-hand, equal to New), with 10-inch Beam, to carry 500 grains in each Pan, turn with 1-1000th of a grain, agate knife-edges and planes, glass case, with adjusting screws, £8 10s., has cost £14 14s.—Apply to O. WOLTERS, 55, Upper Marylebone St., London, W.

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Specifications for the contracts can be seen at my Office, or will be sent on application.

Rail and Water Communication direct to the Works.

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February 25, 1890.

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The Contractor must agree to remove the same whenever required, and not to allow an accumulation of more than 10,000 gallons of either Tar or Liquor. Tank trucks and barges can be loaded at the Company's wharf.

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Tenders to be delivered to the undersigned not later than 10 o'clock in the morning of the 5th March, 1890. The Directors do not pledge themselves to accept the highest or any Tender.

C. CROWTHER SMITH, Secretary.

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February 12, 1890.

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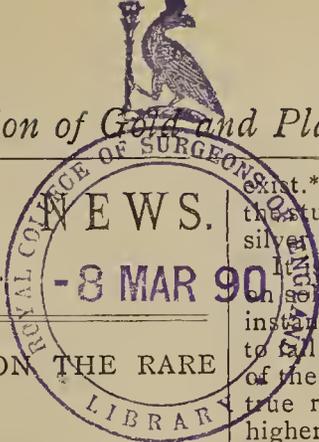
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THE CHEMICAL NEWS.

VOL. LXI. No. 1580.



M. LECOQ DE BOISBAUDRAN ON THE RARE EARTHS.

M. DE BOISBAUDRAN has contributed to the *Bulletin de la Société Chimique de Paris* a comment on my Presidential Address delivered before the Chemical Society in March, 1889. I must confess myself no little disappointed with my distinguished friend's reply. Considering the length of time at his disposal I had hoped, in the interests of truth, that M. de Boisbaudran would have been able to advance some novel and decisive facts—"instantiæ crucis," as Bacon called them—in support of his views. Such, however, does not appear to be the case. The memoir contains very little beyond a re-assertion of the statements which I considered in my Address.

I must point out as incorrect the following assertion:—"As this *savant* (*i.e.*, myself) publishes sometimes in scientific journals which everybody is not obliged to read." The number of journals in which I publish my results is small: the *Transactions and Proceedings of the Royal Society*, the *Journal of the Chemical Society*, and the *CHEMICAL NEWS*. To these alone anyone who wishes to ascertain what are my opinions may refer.

The fluorescence method M. de Boisbaudran admits to be very delicate for the detection of slight traces, but he considers, curiously enough, that it becomes less sensitive when applied to "larger quantities of the same active matters." Too high sensitiveness is not often urged as an objection against any reagent, especially when the question is the recognition of substances which may occur only in infinitesimal traces.

The answer to the question why I did not try to eliminate manganese from my calcium sulphate prepared from Iceland spar is not hard to find: there was none to eliminate.

My learned friend does not appear to have thrown any new light on the yttrium question, nor does he succeed, to my thinking, in justifying his use of the term "yttria."

I will not, however, abandon the hope that M. de Boisbaudran and myself, in continuing our labours, may ultimately arrive at an agreement, based on truth, more complete than either of us has hitherto attained.

W. C.

THE LIQUATION OF GOLD AND PLATINUM ALLOYS.*

By EDWARD MATTHEY, F.S.A., F.C.S.,
Associate Royal School of Mines.

It is a well-known fact that when molten alloys of certain metals are cooled, some of the constituents separate and become concentrated either in the centre or in the external portions of the solidified mass; to this segregation the name of liquation is given. It is specially noticeable in the case of silver-copper alloys, and its importance is now being widely recognised in almost all branches of metallurgy.

In the case of gold, however, the phenomenon of liquation does not appear to have been much observed. Gold alloys, to the value of many millions sterling, pass annually from hand to hand upon the results of assays cut from the external portions of ingots, which assays cannot, of course, be trustworthy if the centre of the bars differs in composition from the external portions. Peligot has recently endeavoured to obtain evidence of liquation in gold-copper alloys, and has concluded that it does not

exist.* Roberts-Austen,† who has devoted much time to the study of liquation, has also satisfied himself that gold-silver alloys do not re-arrange themselves on cooling.‡ It is, of course, well known that gold does not retain on solidifying certain metals of the platinum group; for instance, iridium, when associated with it, always tends to fall through the fluid metal, and is found at the bottom of the solidified mass, but this is probably not a case of true rejection of a metal by liquation, but is due to the higher specific gravity of the iridium, coupled with the fact that the usual heat at which gold is melted is not sufficiently high to bring about a true alloy. It appeared to me that alloys of gold and platinum would well repay examination. They have been generally considered to be uniform in composition, but certain results which I obtained in the course of their treatment led me to suspect that they would give interesting results, and the following experiments were therefore undertaken.

The metal platinum frequently occurs in the gold and silver bullion which has to be treated by the ordinary methods of refining, and its presence occasions no small amount of trouble to the refiner.

It is well known that there are two methods of refining, both of which involve alloying one part of gold with (about) three parts by weight of silver, and treating the mass directly—

- (a). With nitric acid.
- (b). With sulphuric acid.

The final result from either method, if properly conducted, is fine gold and fine silver—that is to say, if the alloy so treated is composed of gold and silver only (a little copper present making no difference).

In the case of platinum being present in the gold or the silver, if it is refined by the nitric acid process, the platinum, when existing in small proportions, is eliminated with the silver, becoming dissolved up with it, leaving the gold free, and the platinum so dissolved can afterwards be readily separated from the silver, but upon the large scale refining by means of nitric acid is far too costly; practically, therefore, this has to be replaced by the sulphuric acid process.

In an alloy of gold and silver, containing a small proportion of platinum, nearly all the silver is dissolved by the sulphuric acid, leaving the platinum associated with the gold.

In order to simplify matters for further treatment, this partially refined gold holding the platinum is melted and assayed, to determine the amount of platinum and gold it contains; it is the platinum-gold alloys so obtained that I desire to bring under notice.

It has been found in practice that the ordinary method of assaying a small portion cut from one end of a bar or ingot of such metal does *not* indicate the actual percentage of gold and of platinum existing in the entire mass, and it is therefore evident that the platinum has been re-distributed by liquation during the cooling and solidification of the mass.

Having been struck by the experiments made by Professor Roberts-Austen, as detailed in the paper to which reference has already been made, I cast some gold containing platinum into a special iron mould 3 inches in diameter, and cut the spheres of metal so obtained in two halves. I may mention that I had to cast these spheres many times over in order to obtain a solid casting, so great was the shrinkage.

Portions were then carefully taken from each of the points marked on the diagrams A, B, and C given herewith, and the results of the assays of the metal taken at each point of the hemispheres are indicated on the diagrams.

- A. Composed of about 880 gold to 050 platina.
- B. Composed of about 700 gold to 120 platina.

In the one case the maximum difference between the

* *Bulletin Société d'Encouragement*, 1889, p. 481.

† *Roy. Soc. Proc.*, vol. xxiii., 1874, p. 481.

‡ "Nineteenth Annual Report of the Mint," 1888, p. 35.

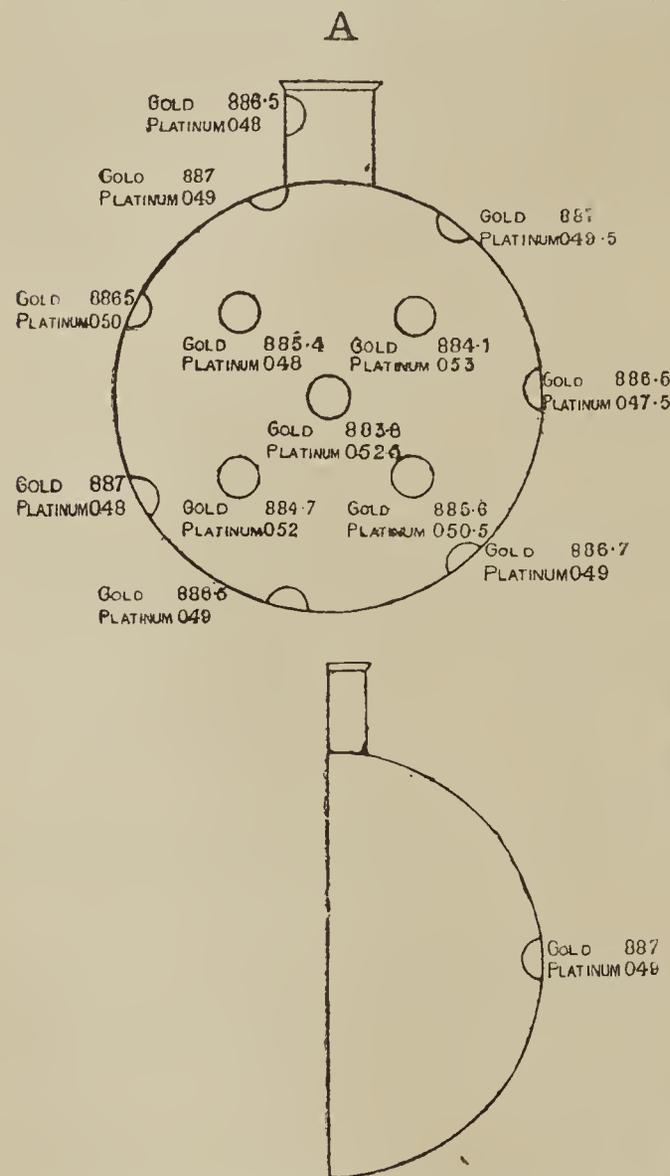
* A Paper read before the Royal Society, February 13, 1890.

gold percentage is a variation of 032, viz., 887 on the outside against 883.8 at the centre of the alloy; and in the platinum 007.5 on the outside against 052.5 at the centre, an extreme variation of 005 is shown.

In the other case the maximum difference between the gold percentage is a variation of 041, viz., 732.4 on the outside against 694.1 at the centre of the alloy; and in the platinum 122 on the outside against 166 at the centre, an extreme variation of 044.

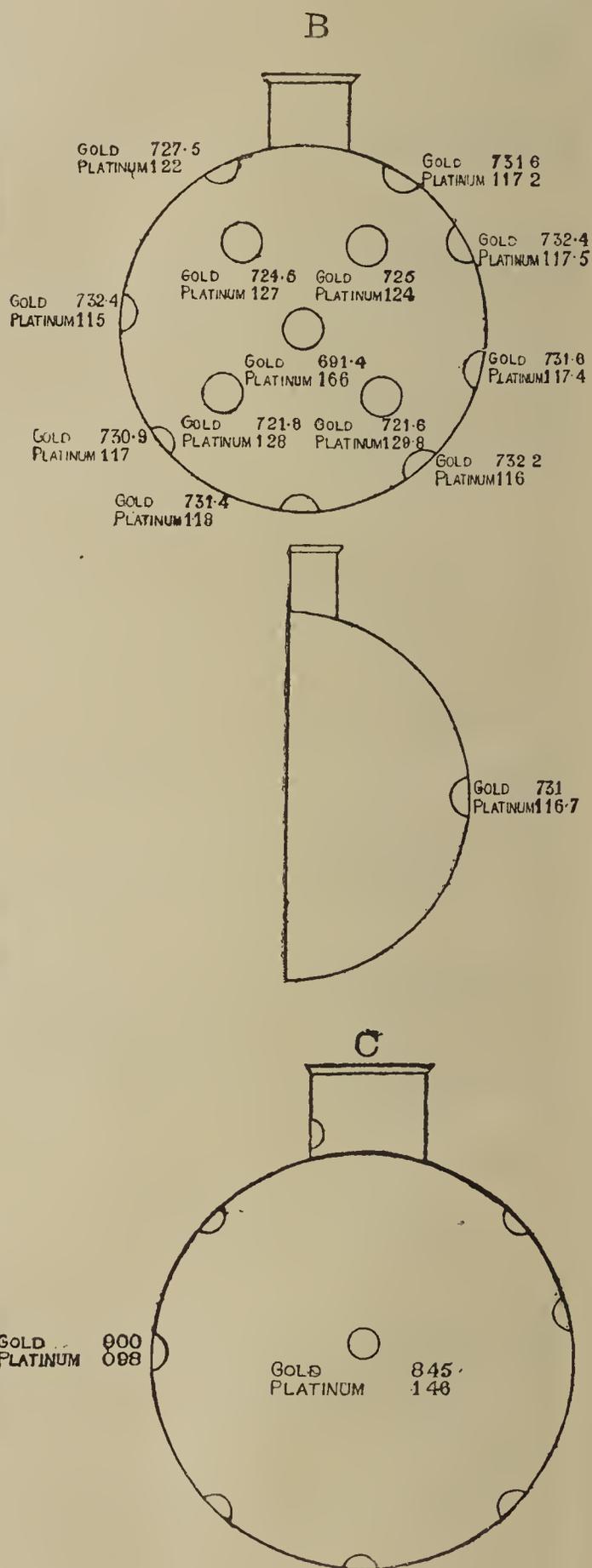
Thus showing indisputably that the platinum in cooling liquates from the gold and becomes concentrated towards the centre of the alloy.

In support of these experimental results I give the actual figures obtained from six platinum gold ingots,



taken at different times and of different qualities, as they occurred in the course of refining commercially. Each of these bars, after melting and assaying, was separately heated with a view to extract the amount of gold contained. It will be at once seen that the higher percentage of gold indicated by the assay of a portion cut from one end of the ingot is not borne out by the actual amount of fine gold obtained by refining, which, of course, truly represents the proportion of gold existing in each bar.

No.	Weight in troy ounces.	Platinum by assay.	Gold by assay.	Percentage of gold by the fine gold actually obtained.
42	728.5	0.111	0.825	0.812
67	355.0	0.120	0.660	0.630
109	589.5	0.120	0.800	0.780
126	435.0	0.045	0.850	0.845
149	480.5	0.086	0.842	0.830
188	473.0	0.110	0.830	0.821



These results prove that the percentage of gold in the outer portion of ingots of platinum gold alloy does not represent the true percentage of gold in the alloy, and that liquation does take place to an extent which, independently of its scientific and metallurgical interest,

has, I believe, been by many overlooked up to the present time in commercial transactions with such metal.

The results given were observed in platinum gold alloyed with silver, with copper, and with both silver and copper; but in order to prove whether or not such alloy had any tendency to carry the platinum to the centre of the mass, I melted 900 parts of fine gold with 100 parts of pure platinum, and, after repeated meltings, cast this alloy into the same mould used for the experiments recorded above. The result was, as in the previous cases, liquation of the platinum towards the centre of the sphere, the gold and platinum in 1000 parts being as 900 to 100 on the exterior, against 845 and 146 at the centre of the mass (see diagram C).

THE TREATISE OF DEMOCRITUS
ON THINGS NATURAL AND MYSTICAL.

Translated by ROBERT R. STEELE, F.C.S., &c.

(Continued from p. 102).

THE BOOK OF SILVER.

XVI. THE SURFACE OF A COPPER ALLOY IS WHITENED
BY AN ARSENICAL COMPOUND.

Fix quicksilver from arsenic, or sandarach, or that thou knowest, as of custom, and mix *Venus* with iron treated with sulphur, and it will be whitened; but whitened magnesia is also excellent, and *sublimed* arsenic, and calcined *cadmia*, unfired sandarach, whitened pyrites, and ceruse roasted with sulphur. Thou dissolvest iron by throwing into magnesia, or the half of sulphur, or a little of loadstone, since that has affinity with iron. Nature rejoices with nature.

XVII. A COMPOSITION FOR AMALGAMATING THE
SURFACE OF ALLOYS.

Taking the aforesaid vapour,* heat it with castor or radish oil, mixing with a little alum; then taking tin, purge it with sulphur, as of custom, or *marchasite*, or what is known to thee, and throw it into the vapour, mixing the whole. Roast, covered with coals, and thou shalt see this medicine formed, like to white lead, which whitens all (metallic) bodies,† but by anointing. Mix with it Chian earth, or Asterites, or Aphroselinum, or that thou knowest, since Aphroselinum associated with mercury whitens all (metallic) bodies. Nature conquers nature.

XVIII. THE SAME APPLIED TO ORICHALIUM ALLOY.

Take white magnesia; thou shalt whiten it with brine and alum, in sea-water, or citron juice, or with the smoke of sulphur; for the fume of sulphur, when it is white, whitens all things. But others say that the fume of cobathia whitens it. Mix with it, after whitening, equal parts of lye, that it may become white enough. Taking of whitish bronze, of orichalium, I say, 4 ounces, place it in a crucible, placing under it little by little 1 ounce of previously purged tin, agitating until the substances unite; it will be frangible. Throw on, therefore, the half of white medicine, and it will be the *chief*; for whitened magnesia does not render bodies fragile, or allow the blackness of bronze to come forth. Nature restrains nature.

XIX. A WHITE ALLOY OF LEAD IS MODIFIED BY
ARSENICAL COMPOUNDS.

Take the white sulphur, which will flourish whitest; but thou shalt whiten it, dissolving with urine in the sun, or alum and sea-water. Dissolve it with sandarach, or the urine of a young girl, for six days, until the medicine

nearly approaches the likeness of marble; when it becomes so, it will be wonderful, for it whitens *Venus*, softens iron, takes away the creaking of tin, renders lead white, and makes *substances infrangible*, and tinctures permanent. For sulphur mixed with sulphur makes *divine* substances, since they have close relationship with each other; for natures rejoice with natures.

XX. A WHITE ALLOY OF LEAD USED TO WHITEN
THE SURFACE OF METALS.

Foin whitened litharge with sulphur, or *cadmia*, or arsenic, or pyrites, or oxymel, lest it flow widely (be too fluid). Therefore roast it with glowing embers, furnishing the vessel with a lute. Let it be combined with roasted lime, and absorb vinegar for three days, that it may have greater power of cleansing. Apply it therefore (to the metal), when it is whiter than ceruse. Very often it will be yellow, if much fire be put under it; but if it becomes yellow it will not be of use to thee at present, for the intention is to whiten bodies with it. Heat it moderately, therefore, and mix it with every body which thou desirest to whiten. If litharge be *whitened*, it will be lead no longer, but it easily becomes (whitened). The nature of lead is quickly changed into many forms; for natures conquer natures.

XXI. A SILVER VARNISH FOR METALS.

Taking the crocus of Cilicia, put it into sea-water, or brine, and make a liquor in which immerse heated leaves of bronze or iron, until they are whitened to thy satisfaction. Then take a half of the medicine, rub it up with sandarach and white arsenic, or unburnt sulphur, or that thou knowest, to the consistency of wax; anoint the leaf and place it in an empty closed vessel, as of custom, and put it in a vessel where shavings are being burnt the whole day. Then, taking it away, place it in a pure liquid, and the bronze will be very white; then set to work like a craftsman; for the crocus of Cilicia whitens with sea-water, and tinges metals a yellow colour with wine. Nature rejoices with nature.

XXII. ANOTHER VARNISH.

Take white litharge, and rub it up with laurel shoots, and cimolia, and honey, and white sandarach, and let it have the consistency of scrapings (viscid). Anoint (the leaf of the metal) with half of the medicine, and warm from below, as of custom. Immerse it in the remainder of the medicine, dissolving with the water of the ash of white wood; for *dissolved mixtures* work well without fire. Such solutions with liquors are able to resist fire; for nature conquers nature.

XXIII. A METAL IS SILVERED BY A MERCURY
COMPOUND.

Taking the prescribed vapour, rub it up with alum and misy, washing with vinegar, add to it also a little white *cadmia*, or magnesia or unslaked lime, that it may become a (metallic) body from another (metallic) body. Mix with the whitest honey, and make a liquid, in which immerse ignited whatever thou will, and leave it in it, the operation takes place. But let the composition have a little native sulphur, that the medicine may pervade and penetrate. Nature conquers nature.

XXIV. ANOTHER TINCTURE BY AMALGAMATION.

Take 1 ounce of arsenic, and half an ounce of nitre, and 2 ounces of the cortex of the tender little leaves of *Persea*, and half (an ounce) of salt, and 1 ounce of mulberry juice, and equal parts of scissile, rub with vinegar, or urine, or of *unslaked lime of urine*, until a liquid is formed. Immerse in this *glowing leaves of Venus* growing black, and thou takest away the blackness. Nature conquers nature.

Thou hast all things which are required for gold and silver, nothing is left out, nothing is wanting, except the

* Probably sublimed mercury.

† The body of a substance is its metallic state.

elevation of the vapour and of water.* But these I have omitted of purpose, seeing that I have dealt with them freely in my other writings. In this writing, farewell.

(To be continued).

OPENING UP SULPHIDES SUCH AS BOURNONITE, PROUSTITE, &c., IN A CURRENT OF AIR CHARGED WITH BROMINE.

By P. JANNASCH.

THE unpleasantness of working in a current of chlorine in the determination of sulphides induced the author to submit the action of bromine upon these minerals to a careful examination. It appeared that the diluted vapour of bromine decomposes such minerals as completely as does chlorine, if not as energetically. The process is as follows:—Air passes out of a gas-holder through a Drechsel drying cylinder charged with concentrated sulphuric acid, then through another such cylinder containing 50 c.m. (? c.c.) of bromine; then traverses a tube of potash glass 20 c.m. in length, in which the boat with the substance is heated, and ultimately enters the usual receivers filled with a mixture of equal volumes of dilute hydrochloric acid (1 : 4) and a 10 per cent solution of tartaric acid.

In the first experiments the author made he used, for conveying the bromine, a Kipp carbonic acid apparatus. Subsequently he found the use of an air-gas holder more convenient, as the reaction proceeds more readily in a current of air. An unexpected difficulty was at first occasioned by the decomposition of the sulphur bromide which remained in the receiver as a liquid. On standing or heating in a beaker, abundance of sulphur was deposited, which required to be oxidised by a further treatment with bromine. The author did not succeed in effecting a decomposition of the sulphur bromide into sulphuric and hydrobromic acid by the addition of chlorine-water or potassium chlorate. Finally he succeeded by adding to the liquid from the receiver, in a capacious beaker, an excess of bromine, and heating it on the water-bath whilst stirring diligently. In a short time all the sulphur bromide is dissolved and the excess of bromine sufficiently driven off, whereupon the sulphuric acid is precipitated at a boiling heat with barium chloride. Next the antimony and arsenic are separated in the usual manner after the removal of the barium chloride. The portion not volatile in the current of bromine, consisting of lead, copper, and silver bromides, &c., is heated in a beaker on the water-bath with dilute nitric acid for about an hour, when lead, copper, &c., pass into solution. That this may be effected rapidly and completely, the decomposition of the original sulphide in the current of bromine is so regulated that the heat is never sufficient to melt the bromides formed. The product of the reaction is quickly dissolved away from the porcelain boat on treatment with nitric acid. If silver bromide is simultaneously present the material is carefully crushed in the liquid with a glass rod. When the nitric acid has acted long enough the insoluble matters (silver bromide, gangue, &c.) are filtered off, the acid solution is evaporated to dryness, and lead, copper, and nickel are separated as usual. The mixture of silver bromide and gangue is further digested with a dilute solution of potassium cyanide (2–4 grms. of a pure preparation), when all the silver bromide is easily and completely dissolved and separated by filtration. The filtrate is precipitated by an excess of nitric acid in a porcelain capsule, the solution is dried along with the precipitate in order to destroy small quantities of silver

cyanide if formed, the residue is afresh heated with water, some nitric acid, and bromine-water, and filtered off to be weighed.

As compared with the chlorine method, the bromine process presents decided advantages. In the first place, we have to dispose of a current of gas, the regulation of which is perfectly at command, and which does not suddenly fail in the midst of operation, a difficulty which often occurs in using an apparatus charged with blocks of chloride of lime. It is also not necessary either to arrange a special apparatus for evolving chlorine with manganese and hydrochloric acid or on every new analysis to undertake the tedious arrangement of a Winkler apparatus. A cylinder filled with bromine can always be kept at hand. The consumption of bromine is so trifling and the whole process so little offensive that there is no necessity to work under a draught-hood. It is very important that, under the conditions given, iron and zinc bromides are practically non-volatile.

The following two analyses may show the accuracy of the process.

1. Crystals of Bournonite from Neudorf in the Harz.

Pb	40.20
Cu	12.55
Sb	26.35
S	19.90
Gangue	0.50
	99.50

2. A Massive Crystalline Specimen of Pyrargyrite from Chanarcillo in Chile.

Ag	58.42
Sb	21.10
Fe	1.33
S	18.20
Quartz	0.78
	99.83

The bromine, before use, must be tested for a possible impurity of sulphuric acid. If argentiferous sulphides are in question the bromide must be free from chlorine, so that the silver may be weighed as bromide. For this purpose a portion of the reagent is shaken up with powdered potassium bromide, let stand for some time, and the necessary quantity is filtered through slag-wool.—*Journal für Praktische Chemie.*

A NEW METHOD FOR THE ANALYSIS OF PYRITES.

By P. JANNASCH.

IN executing the analysis of sulphides, previously recorded, the author made the observation that on very gently heating the substance, the portion carried away in the current of bromine contained no iron, or only traces, on account of the very slight volatility of the ferric bromide formed. This observation led to the idea of attempting to open up pyrites by heating them in fine powder in a current of bromine, thus effecting a simple and expeditious separation of the iron from the sulphur. In fact, bromine acted at once upon the material placed in a porcelain boat, and heated in a tube of potash-glass, with formation of chloride of sulphur. But at the end of the experiment the fixed residue was only in part soluble in hot hydrochloric acid, whilst another part, judging from its appearance, had remained undecomposed. A series of quantitative determinations of the sulphuric acid really formed gave an approximate result of 26 per cent of sulphur as having been liberated. Hence the pyrites had given up to the bromine only one atom of sulphur,

* This seems to point to a work on distillation, which was practised in the first centuries of our era.

leaving iron monosulphide, which, on further treatment with strong nitric acid, readily dissolved as ferric sulphate. Better results were obtained by using vapours of bromine and nitric acid conjointly for opening up the pyrites. To effect this behind the boat with the powdered pyrites there was placed another, half-filled with fuming nitric acid, and the nitric fumes are mixed with the bromine vapours by a proper management of the heat. In this manner the pyrites, very finely powdered, was completely opened up, but not without the use of a strong ignition, whereby much of the iron was volatilised. This circumstance induced the author to dispense with bromine, and work merely in a current of air containing nitric vapours. The apparatus used was arranged as follows:—

Air passes from a gas-holder through strong sulphuric acid and through a Drechsel flask containing about 50 c.c. of strong fuming nitric acid. It passes then through a tube of potash-glass laid in a short combustion furnace, and containing the boat filled with finely pulverised pyrites, and opens into a tubulated receiver charged with 100 c.c. bromine-water, to which is further attached a Peligot tube containing 40 c.c. bromine-water, and lastly a cylinder with distilled water. To begin the decomposition, a current of air (150 to 200 bubbles per minute) is passed through the apparatus, and the substance is then heated, beginning at the back. The free anterior end of the tube is heated in order to drive the sulphuric acid into the absorption vessels as fast as it is formed.

The whole course of the reaction extends to about three-quarters of an hour, and it is then let cool in a slow current of air after removing the flask containing nitric acid. If it is too strongly heated, a sublimation of sulphur ensues, which is to be avoided as far as possible.

Finally, the tube must be strongly ignited after covering the furnace with tiles, though not so strongly as to soften

drawn out with a wire hook when the tube is cold, laid in an inverted position in a flat porcelain or platinum capsule, and heated with strong hydrochloric acid on the water-bath, when the ferric oxide is quickly dissolved. The boat is then removed, cleansed with hot water and the feather of a pen, and removed; the iron solution is evaporated almost to dryness and the insoluble portion (silica, silicates, &c.) is determined. A repeated examination showed the perfect absence of sulphuric acid, and the portion of the ore insoluble in hydrochloric acid is also free from traces of undecomposed pyrites.

A continued use of this method will doubtless lead to simplifications. It will probably be found useful, when the samples contain ingredients which interfere with the use of direct solvents.—*Journal für Praktische Chemie.*

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLET, F.R.S.,

Professor of Chemistry in the University of Virginia.

(Continued from p. 105).

Fifth Series of Experiments.

In these experiments an attempt was made to determine the ratio between the weights of metallic gold and metallic silver deposited by the passage of one and the same electric current successively through solutions of the two metals. The simplicity and accuracy with which the direct weighings may be made seemed to present decided advantage, but various difficulties were encountered, and, after the expenditure of a very large amount of time and labour upon the method, it cannot be said, on the whole, to have satisfied me with its results.

Fig. 3.

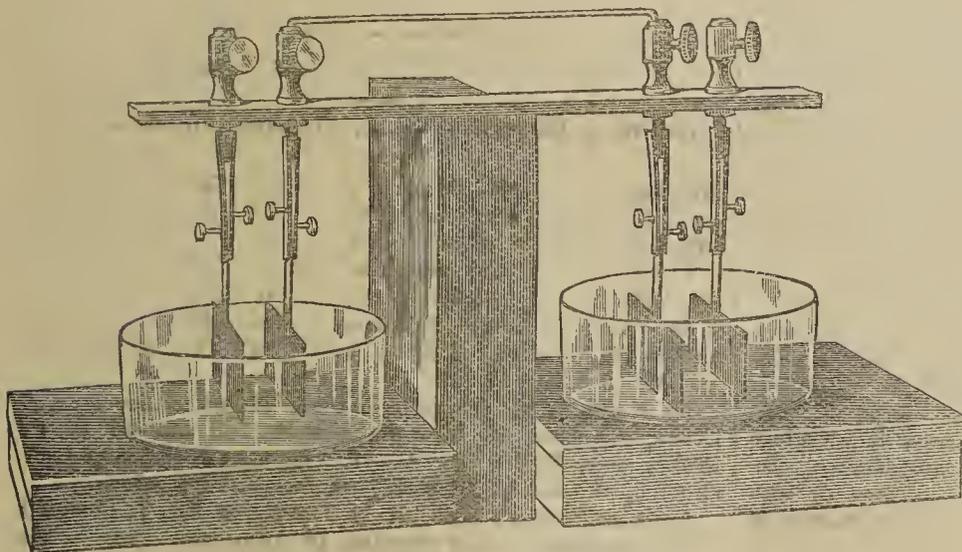
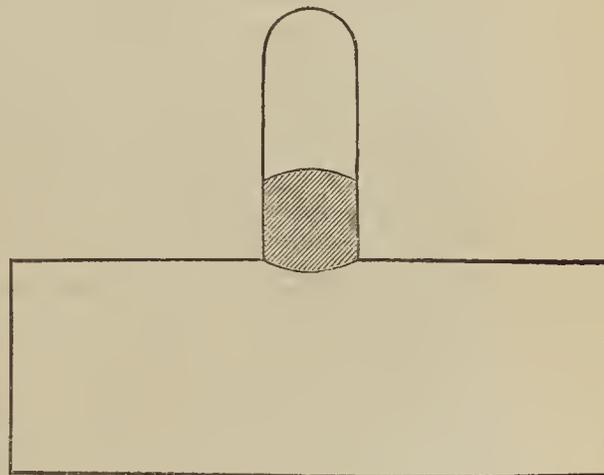


Fig. 4.



the glass tube and cause the boat to adhere. After complete decomposition the contents of the receivers are rinsed into a beaker, the excess of bromine is evaporated off, 1 c.c. of strong hydrochloric acid is added to the liquid, and the sulphuric acid is precipitated at a boiling heat with barium chloride, avoiding any considerable excess.

The precipitate, before being washed on the filter, must be very carefully purified by repeated decantation with boiling water containing hydrochloric acid, in order to remove any barium nitrate which has been carried down. A final treatment of the ignited barium sulphate with dilute hydrochloric acid and a re-weighing is recommended. If the presence of barium sulphate is to be absolutely avoided, the solution, before the addition of barium chloride, should be evaporated down in a roomy porcelain capsule. The boat with the ferric oxide is

While taking due note of the recent literature on the subject of the quantitative electro-deposition of metals from their solutions, especially the reports of work by A. Classen,† Lord Rayleigh and Mrs. Sidgwick,‡ Dr. Gore,§ Thos. Gray,|| and W. N. Shaw,¶ the author of the present paper made for himself a somewhat extended preliminary examination of the effects of varying conditions on such depositions, so far at least as seemed to be required for his immediate purpose.

The general arrangement of apparatus adopted consisted of a horizontal strip, 4 m.m. thick, of vulcanite, or

* A Paper read before the Royal Society, May 9, 1889.

† A. Classen, "Quantitative Chemische Analyse durch Electrolyse," 2te Aufl., Berlin, 1886.

‡ *Phil. Trans.*, 1884, p. 411.

§ *Nature*, March 16, 1882; Feb. 1 and Feb. 15, 1883.

|| *Phil. Mag.*, Nov., 1886, p. 389; and March, 1888, p. 179.

¶ *Phil. Mag.*, Feb., 1887, p. 138.

hard vulcanised india-rubber, about 26 c.m. long by 3 c.m. wide, near each end of which and in the middle of the width were two small holes, through which passed short bits of brass rod, each having attached to it above a binding screw, and below a forceps-like clip, which could be opened by pressure on two little outside studs, but closed firmly, on release of this pressure, by the elasticity of the metal. In these clips were supported the plates of metal to be immersed in the electrolysed solutions, and to serve as anode and cathode terminals respectively, there being two pairs of such plates, one pair near each end of the vulcanite strip, with four corresponding binding screws. The electric current passed from the first binding screw through one of two metallic solutions—as, for instance, that containing gold—between the first pair of plates, consisting of the same metal as that in this solution, then from the second binding screw to the third (at the other end of the vulcanite strip) by a stout copper wire above, and then through the second of the two solutions—as, for instance, that of silver—between the second pair of plates, consisting again of the same metal as that in the solution in which they were immersed, thus reaching the fourth and last binding screw, the first and last binding screws being, of course, connected by wires with the terminals of the galvanic cells used to develop the current. Fig. 3 shows the disposition in question. The source of the electric current was for the most part galvanic cells of the Meidinger pattern, but in some of the experiments small Daniell cells, and also a Clamond thermo-electric battery, were used. The lower parts of the clips were heavily electroplated with the same metal as that in the solution to which they respectively belonged, in order to avoid any risk of contamination of the solution, in case there should be splattering or accidental immersion, even for a moment, of any part of the clip.

It was decided to place the plates vertically in the liquids, but to make the vertical height small in proportion to width, so as to preserve as far as possible a uniform condition of the solution in depth. The form adopted for the plates was that of Fig. 4, the shaded part of the surface being coated with hard paraffin, with a view to preventing the strip by which the anode plate was suspended from its clip being cut across by solvent action at the surface of the liquid. This coating of paraffin was put on after the plates were first weighed, and carefully removed before the second weighing. The four plates for each experiment were of equal size as to length and breadth; in most of the experiments the immersed surface (of one side) measured about 25 square c.m., though in some cases plates of double this size were used. The thickness was the same for plates of the same metal, but those of the different metals to be compared were made to differ in thickness to such an extent as to allow for the different rate of solution to be expected of the anode plate. I was indebted to the kindness of Mr. Eckfeldt, of the Philadelphia Mint, for having plates of "proof" gold and silver specially rolled for me, with all necessary precautions as to perfect cleanliness of the rolls, &c., so as to obtain the determinate thicknesses desired.*

By heating in a Sprengel vacuum I found traces of oxygen in the rolled silver plates, and extremely minute

* Mr. Eckfeldt informed me that his method of preparing the proof silver used for these plates was as follows:—"Nitrate of silver from the gold assay parting is, after careful filtering, precipitated with hydrochloric acid, and the chloride of silver, after a thorough washing with pure water, is dried and reduced in the melting pot with pure carbonates of soda and potash and carbon in the shape of wheat flour, the melting being done in a clay crucible. The resulting silver bar is then dissolved in dilute nitric acid, and after standing some time filtered, precipitated, and reduced as before; then re-melted with the addition of pure nitrate of potash and borax. This generally gives a bar somewhat brittle (crystalline in fracture). It is then re-melted, and stirred with a pine stick, and chloride of ammonium added; when the chloride has disappeared the metal is poured. I find this method more satisfactory than any other I have tried."

traces of gas, apparently also oxygen, were likewise obtained from the gold plates, before either had been used.

The middle of the vulcanite strip was supported at a suitable height, so as to allow of equal immersion of the two pairs of plates in their respective solutions, which were contained in small vessels of good hard glass, free from lead. Care was taken to keep the vulcanite strip dry, so that there should be no practical defect of insulation between the two plates of each pair; the necessity for this precaution having been shown in some of the very early preliminary experiments with copper plates, using a wooden supporting strip; some puzzling results being traced back to a little accidental moistening with sulphate of copper solution of the part of the strip between one pair of plates, while those of the other pair were well insulated as to the strip from which they hung.

In all the experiments the two pairs of plates, previously ignited in the Sprengel vacuum, cooled, and weighed, were placed in position in the clips, the distance between the parallel surfaces of the plates of each pair being the same, and in most of the experiments measuring about 2.5 c.m., and connection was made with the terminals of the galvanic cell or cells used before immersion of the plates in the metallic solutions. All four plates were immersed at the same moment, and at the end of the experiment were in like manner lifted out of the solutions at the same moment, before the current had been broken. They were immediately introduced into one after another of several portions of distilled water, before removal from the clips, thorough washing, heating in the Sprengel vacuum, and final weighing.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 20th, 1890.

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

MESSRS. Frank H. Mason, A. H. McConnell, Edward Russell, John Wade, and S. Russell Wells, were formally admitted Fellows of the Society.

It was announced that the following changes in the Council list were proposed by the Council:—

As *Vice-Presidents*—Professors Crum Brown, F.R.S., and W. N. Hartley, F.R.S.; *vice* Prof. McLeod, F.R.S., and Mr. Ludwig Mond.

As *Members of Council*—Messrs. Henry Bassett, C. F. Cross, Professor R. Meldola, F.R.S., and Mr. M. M. P. Muir; *vice* Professors A. H. Church, F.R.S., and F. Clowes, Mr. C. W. Heaton, and Dr. H. F. Morley.

Messrs. Bernard Dyer, R. H. Davies, and R. J. Friswell were appointed by the meeting to audit the Treasurer's accounts.

Certificates were read for the first time in favour of Messrs. William Frederick Laycock, Ph.D., 2, Park Street, Dewsbury; Arthur Sheridan Lea, Caius College, Cambridge; George Müller, 125, Mercer Street, Jersey City, N. Jersey, U.S.A.; E. H. Neville, M.A., Sidney College, Cambridge; Ernest George Scott, Mayer Hall, near Birkenhead; Willie Brewin Shuttlewood, Hong Kong; Frederick Richard M. Stone, 64, Thomas Street' Merthyr.

The following papers were read:—

10. "The Behaviour of the more Stable Oxides at High Temperatures." By G. H. BAILEY, D.Sc., Ph.D., and W. B. HOPKINS.

The authors chiefly devote attention in this notice to oxide of copper. Previous experimenters had obtained cuprous oxide by heating the oxide to redness. From the

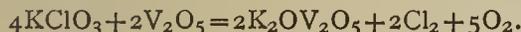
results obtained by the authors, it appears that at higher temperatures oxygen is given off, and that an oxide having the composition Cu_3O is formed. This is insoluble in mineral acids and even in boiling aqua regia; it can, however, be changed into a soluble form by fusion with caustic potash, from which it separates on treatment with water. The oxides of lead and tin seem to behave like that of copper at high temperatures.

II. "The Influence of Different Oxides on the Decomposition of Potassium Chlorate." By G. J. FOWLER, M.Sc., and J. GRANT.

The object of the experiments has been to systematically examine the influence of the chief metallic oxides and certain unstable salts on the decomposition of potassium chlorate. Upwards of a hundred experiments have been made, the most significant of which are recorded in the paper. In each case, the temperature at which oxygen is evolved, the amount of chlorine given off, and the composition of the residue after heating have been determined. The variation of the results according to the acid or basic character of the oxide added, its physical condition, and the relative masses of the oxide and chlorate has been recorded.

The results obtained may be summarised as follows:—

(1). Acid oxides, such as V_2O_5 , WO_3 , and U_3O_8 , cause the evolution of oxygen at a reduced temperature, a metavanadate, tungstate, or uranate being formed. Chlorine is evolved in these cases in large quantity, but the whole of the oxygen of the chlorate is not evolved, as the compound of K_2O with the oxide is not decomposed either by heat or by chlorine:—



(2). Alumina probably acts similarly but less energetically, the attraction between the K_2O and Al_2O_3 not being so great.

(3). In the case of chromium sesquioxide, the oxygen is evolved at a reduced temperature, accompanied by chlorine. The decomposition may be supposed to be brought about by the affinity of the Cr_2O_3 for O, and the affinity of the CrO_3 thus formed for K_2O ; but all the oxygen of the chlorate is not evolved, since—



(4). In the case of the sesquioxides of iron, cobalt, and nickel, cupric oxide, and manganese dioxide, oxygen is evolved at a comparatively low temperature accompanied by only a little chlorine; the oxide is left but little altered at the end of the experiment.

Accepting McLeod's theory of the action of manganese dioxide (*Chem. Soc. Trans.*, 1889, 184), which is fully in harmony with the results of the experiments under consideration, it would seem that manganese dioxide first acts by reason of its affinity for oxygen and the affinity of the higher oxide thus formed for K_2O . The permanganate first formed, however, is unstable (here there is a difference between the oxides of this class and those of the preceding), and is resolved into $\text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$. The K_2MnO_4 is decomposed by chlorine into KCl and MnO_2 , which is thus regenerated. The addition of sodium carbonate retards the evolution of oxygen, probably because the manganate is thereby rendered more stable. The action of the other oxides (*cf.* Spring and Prost) of this class can, it is believed, be explained in a similar manner to that of manganese dioxide.

(5). The monoxides of barium, calcium, and lead cause no evolution of oxygen when heated with chlorate, but the latter breaks up below its normal temperature of decomposition, potassium chloride, and a peroxide being formed. Here the affinity of the oxide for oxygen induces change.

(6). On the other hand, potassium chlorate may act as a reducing agent in the presence of such oxides as silver oxide and the peroxides of barium and lead, a perchlorate being formed. No oxygen is evolved. Here the change is brought about by the affinity of the chlorate for oxygen.

In the case of the oxides of calcium, barium, and lead, the extent to which the chlorate is oxidised evidently depends on the relative masses of the interacting substances.

(7). Water of hydration appears to diminish the activity of an oxide, owing doubtless to the absorption of heat necessary for its conversion into steam.

(8). The physical condition of the oxide is of influence. Copper oxide prepared in the dry way is almost inactive.

(9). Certain substances, although apparently they undergo no chemical change, assist the decomposition, *e.g.*, powdered glass, sand, and kaolin.

(10). Oxides such as those of zinc and magnesium are inactive.

DISCUSSION.

Dr. HODGKINSON said that he had noticed that all the chlorine was expelled from potassium chlorate by heating it with either uranic or tungstic or vanadic oxide—was this because these oxides expel the chlorine from chlorides? In the case of stannic oxide, everything depended on the state of the oxide: the native form had no action, but metastannic acid expelled chlorine.

Professor McLEOD thought that the decomposition of potassium chlorate was promoted in some cases by a mere action of presence similar to that which charcoal exercises on the boiling of water: for instance, platinum black appeared to act in this way, and probably basic oxides exercised a similar influence.

Professor RAMSAY expressed the opinion that in some cases the oxides were converted into corresponding chlorates: that copper oxide, for instance, became converted into copper chlorate, which was thereupon resolved into copper oxide and an unstable oxide of chlorine; it was desirable from this point of view to study the behaviour of various chlorates.

Professor THORPE said that much had already been done in the direction suggested by Professor Ramsay; but difficulty arose as many chlorates were hydrated salts which decomposed during dehydration. After calling attention to Teed's and Frankland and Dingwall's experiments, he said there was no evidence that when, for example, manganese dioxide was used manganese chlorate was formed. Mr. Eccles had several years ago made experiments in his laboratory to test this point, and had found that no alkali was formed when manganese dioxide was used, as must have been the case if any chlorate of the oxide were produced. The non-production of perchlorate was the most remarkable feature of the change in presence of manganese dioxide (*cf.* *Chem. Soc. Journ.*, 1876, 856).

In reply to a remark by Professor Ramsay, Professor McLEOD said that the formation of permanganate accounted for the fact that no alkali was obtained, although chlorine was given off.

12. "The Interaction of Hypochlorites and Ammonium Salts. Ammonium Hypochlorite." By C. F. CROSS and E. J. BEVAN.

No mention is made of ammonium hypochlorite in the later text-books and dictionaries; in the last edition of "Gmelin" (vol. ii., 479), however, there is a short paragraph headed "Ammonium Hypochlorite?" in which its probable existence is spoken of on the authority of Schönbein. This chemist observed that a pungent odour is developed when ammonia is added to chlorine-water, and that the liquid exhibits bleaching powers and the property of decomposing hydrogen peroxide with liberation of oxygen; hence it was supposed that the destructive action of chlorine on ammonia is preceded by the formation of ammonium hypochlorite.

The authors have recently had occasion to study the subject more closely. On treating a dilute solution of bleaching powder with the equivalent quantity of an ammonium salt, no sensible loss of "available chlorine" takes place provided interaction occur at a low temperature (10°). The pungent odour already mentioned as noticed

by Schönbein suggested that the resulting compound was volatile, and, therefore, in order to obtain evidence as to its composition, a current of air was passed through the solution and subsequently through water and through a solution of potassium iodide acidified with normal acid; eventually the liberated iodine was titrated with thio-sulphate and the excess of acid was determined in the same solution by means of normal alkali. The iodine liberated was taken as equivalent to the chlorine, and the amount of acid saturated as equivalent to ammonia; the results obtained were—

(1). Cl=0.0365	NH ₄ =0.0090	2.06 : 1
(2). Cl=0.0316	NH ₄ =0.0081	1.98 : 1

These correspond with the formula NH₄OCl, in which the ratio of oxidising chlorine to ammonia is that of 2Cl : NH₄. Further evidence as to the composition of the compound was obtained by extracting the aqueous solution with ether, and after diluting the extract with alcohol, adding potassium iodide and the necessary quantity of thio-sulphate: the resulting mixture was neutral. The compound was also volatilised by means of a current of air, which was then washed and passed into a solution of sodium sulphite; the oxidation of the sulphite was the only change observed, the solution remaining neutral, whereas had no ammonia been present it would necessarily have become acid.

The evidence of the formation and existence of ammonium hypochlorite in solution would seem, therefore, to be complete; the isolation of such a compound, however, is necessarily attended with considerable difficulty, and all attempts in this direction have hitherto failed to give a result.

At ordinary temperatures solutions prepared as described containing from 1 to 2 grms. Cl per 100 lose oxidising chlorine comparatively rapidly; thus one containing 1.6 grms. per 100 immediately after preparation contained after filtering and standing two hours 0.12 gm.; after forty-eight hours 0.06, and after seventy-two hours 0.04.

The ammonia product presents curious anomalies in oxidising properties in comparison with other hypochlorites; thus it is without action on many colouring matters, *e.g.*, those of vegetable fibres; a solution tinged with a drop of a solution of indigo sulphonate retains its colour for some hours, although it at once liberates iodine from potassium iodide; and it does not peroxidise hydrated lead oxide, nor does it oxidise potassium ferrocyanide in presence of acetic acid. But it oxidises sulphites and arsenites, and its effect on aniline salts is identical with that of ordinary hypochlorites.

The compound is easily formed by the electrolysis of ammonium chloride solutions.

DISCUSSION.

Professor RAMSAY said that a few months ago he also had attempted to prepare ammonium hypochlorite, and had found that on adding ammonia to hypochlorous acid nitrogen was not given off. It was to be noted that the formula of ammonium hypochlorite was equivalent to that of hydroxylamine hydrochloride.

In answer to Professor Dunstan, Mr. CROSS said that the addition of acid did not alter the properties of the liquid as an oxidising agent.

Dr. ARMSTRONG suggested that probably the authors were dealing with a chlorinated derivative of ammonia, *e.g.*, NH₂Cl: Gattermann's experiments show that such compounds are more stable than is usually supposed.

13. "The Action of Phosphoric Anhydride on Stearic Acid." By F. STANLEY KIPPING, Ph.D., D.Sc., Heriot Watt college.

It is stated in both editions of "Beilstein" that when stearic acid is heated with phosphoric anhydride it yields a compound of the formula C₁₈H₃₄O, melting at 54—56°, insoluble in potash. As the formation of a compound so

related to the acid in this manner appeared remarkable, being, I believe, without a parallel, I have re-examined the subject, and am led to give a brief account of my results in order to reserve the study of this and similar changes.

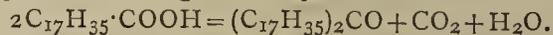
If stearic acid be heated at about 200° in an oil-bath, and about an equal weight of phosphoric anhydride be added in small portions at a time, the whole being well stirred, a considerable quantity of gas is evolved and a black, tarry mass is obtained. The mixture is allowed to cool, then stirred with water, and the whole boiled for some time with a large excess of moderately concentrated potash in order to remove the phosphoric acid. A dark brown, almost black oil collects on the surface, and, on cooling, solidifies to a soft waxy cake; this product is separated from the alkaline solution, washed with water, transferred to a flask, and repeatedly extracted with boiling dilute alcohol. The alcoholic extracts deposit, on cooling, a yellowish flocculent substance, and there remains in the flask a dark brown waxy mass which is very sparingly soluble in dilute alcohol; this residue is being investigated.

The compound which separates from the alcoholic solution can be obtained in a colourless condition by repeatedly re-crystallising it from alcohol and ether. It crystallises in colourless waxy microscopic plates, and is only sparingly soluble in cold ether and alcohol, but much more readily in the warm solvents and in benzene; it seems to be insoluble in hot potash or in ammonia. When heated slowly in a capillary tube it begins to soften at 73° and melts completely at 75—76°, or about 3° higher than stearic acid. On combustion, 0.1420 gm. gave 0.4316 gm. CO₂ and 0.1771 gm. H₂O.

C ₁₈ H ₃₄ O.	C ₁₈ H ₃₆ O ₂ .	C ₃₅ H ₇₀ O.	Found.
C=81.20	76.27	83.00	82.88 per cent
H=12.78	12.68	13.83	13.85 "
O=6.02	11.05	3.17	3.27 "

The results show clearly that the compound is not simply unchanged stearic acid, a fact which is further proved by the higher melting-point, and that it has not the composition C₁₈H₃₄O is apparent from the high percentage of hydrogen which it contains. The results of the analysis agree very closely with the formula C₃₅H₇₀O, and the experiment described below confirms this conclusion.

It seems, then, that when stearic acid is heated with phosphoric anhydride, under the conditions described above, one of the products is stearone, and that action takes place according to the equation:—



Quantitative experiments have not yet been made, but the yield appears to be as good, or better, than that obtained in preparing stearone by the distillation of salts of stearic acid.

Stearone has been previously prepared by Heintz (*Fahresb.*, 1855, 515, 516) by distilling stearic acid alone or with lime; Heintz gives 87.8° as the melting-point, whereas the compound obtained as described above melts at 75—76°. The cause of this difference has not yet been ascertained, but it is probably due to the presence of impurities too small in quantity to have any effect on the analysis. The stearic acid employed melted at about 62°; the experiments will be repeated with the pure acid.

Stearonehydroxime (C₁₇H₃₅)₂C:N·ON. A small quantity of the colourless crystalline compound (m. p. 75—76°) was dissolved in warm alcohol and boiled for about three hours with excess of hydroxylamine and a large excess of potash. On cooling the solution and adding water, a colourless flocculent substance was precipitated; the solution was filtered, the precipitate washed repeatedly, first with dilute hydrochloric acid and then with water, and dried on a porous plate. 0.2514 gm. gave 6.6 c.c. of nitrogen at 755 m.m. and 40°, or 2.67 per cent; the theoretical percentage corresponding to the

formula $C_{35}H_{71}NO$ is 3.07 per cent. This hydroxime is a colourless, seemingly amorphous compound readily soluble in benzene and warm alcohol, but insoluble in acids and in alkalis. When heated very slowly in a capillary tube, it begins to soften at about 53° , and melts completely at $58-59^{\circ}$. It separates from alcohol as a powder which, when examined under the microscope, appears to be perfectly homogeneous.

14. "Semithiocarbazides." By AUGUSTUS E. DIXON, M.D.

Orthotolylphenylsemithiocarbazide (from *o*-tolylthiocarbamide and phenylhydrazine) forms vitreous prisms melting at $162-163^{\circ}$. It is nearly insoluble in water; soluble in alcohol, ether, and chloroform.

Phenylorthotolylsemithiocarbazide (from phenylthiocarbimide and *o*-tolylhydrazine) is isomeric with the preceding. It forms long, pearly-white prisms melting at $145-146^{\circ}$; it is nearly insoluble in water, but dissolves freely in alcohol, ether, and chloroform.

Methylphenylsemithiocarbazide forms delicate, silky needles melting between 88° and 89° . It is somewhat soluble in hot water; very soluble in alcohol and in chloroform.

Ethylorthotolylsemithiocarbazide crystallises from alcohol, in which it is rather freely soluble, in fine white needles possessing a faint pink tinge. It melts at $129-130^{\circ}$; is insoluble in cold water, but dissolves freely in ether and chloroform.

Allylphenylsemithiocarbazide separates from benzene in tangled masses of silvery-white flexible needles, which become highly electrical on friction; it melts at $118-119^{\circ}$ to a bluish green liquid. It is soluble in ordinary solvents, but is precipitated from solution in benzene by light petroleum.

These compounds all give with concentrated sulphuric acid solutions varying in colour from greenish-blue to deep azure. They are desulphurised, either with great difficulty, or not at all, by boiling alkaline lead tartrate; but readily yield their sulphur to ammoniacal silver nitrate. With $CuSO_4$ or Fe_2Cl_6 they afford strongly marked colour changes.

The connection between the solubility and fusibility of the several compounds is traced, and it is shown that, as a rule, Carnelley's principle holds good that the greater the solubility the lower is the melting-point; the author also suggests an application of Carnelley's principle to connect the melting-points with the molecular structure.

15. "Note on the Production of Ozone by Flames." By J. TUDOR CUNDALL, B.Sc., University College, Cardiff.

It is stated by L. Ilosva de N. Ilosva (*Ber. Referate*, 1889, 791 *et seq*) that when the products of combustion of various kinds of flames are collected, they do not exhibit the smell and taste of ozone. This is confirmed by the results of some unpublished experiments made by the author in a similar manner in 1886.

Recently, however, the author has found that the air aspirated through a tube (3 m.m. in bore) whose mouth is fixed about 5 m.m. above the tube, and 5 m.m. away from the flame, of a Bunsen burner, both tastes and smells strongly of ozone. Similar results were obtained both from luminous and hydrogen flames.

It was not found possible to confirm this fact by any other test for ozone, owing to the impossibility of finding any which was sufficiently sensitive which was not common to it and dilute nitrogen oxides. At first sight it seemed that Houzeau's papers (impregnated with red litmus and potassium iodide) would give the necessary distinction, as an acid gas could not be expected to give an alkaline product. Ilosva states, however, that nitrogen oxides turn these papers blue, and the author has confirmed this result.

Papers impregnated with thallium hydroxide were employed with negative results, but, on testing them in a stream of ozonised oxygen from a Siemens tube, they were found to be far from sensitive. The same applies

to an acidified solution of sulphanic acid and α -naphthylamine, which certainly gives a yellow colour with a fair amount of ozone, but this colour is completely masked by the rose-red produced by small traces of nitrogen oxides which may be present simultaneously.

The gas aspirated in this way both from coal-gas and hydrogen flames gave definite indications with mercury of the peculiar behaviour of ozone, but the quantity present was not sufficient to make the mercury adhere completely to its containing flask.

In conclusion, the author agrees with Ilosva in so far that he regards the smell and taste of ozone as the only tests for it that are at all reliable when it is present only in traces, but differs from him as regards its formation in flames; although nitrogen oxides are undoubtedly formed in flames, yet at the same time ozone can be detected by aspirating the air surrounding the flame in such a manner as to get a minimum of the products of combustion, and at as low a temperature as possible.

Anniversary Meeting.

The anniversary meeting will be held at *Four o'clock in the Afternoon* of Thursday, March 27.

It is arranged that, in the evening of the same day, the Fellows and their friends will dine together at the Whitehall Rooms, Hôtel Métropole (entrance in Whitehall Place). Dinner will be on the table at seven for half-past seven o'clock. Fellows intending to be present are particularly requested to give notice by means of a post-card which they will receive for the purpose not later than Saturday, March 22. Price of dinner, including wine, one guinea.

It is proposed to hold a special meeting of the Society on Thursday, May 8, for the exhibition of new interesting apparatus or specimens. Fellows who desire to exhibit objects are requested to communicate with the Secretaries.

At the Meeting on March 20 Professor Judd, F.R.S., will deliver a lecture on "The Evidence afforded by Petrographical Research of the Occurrence of Chemical Change under Great Pressures."

CORRESPONDENCE.

LARD.

To the Editor of the Chemical News.

SIR,—When I replied to the letter of Mr. John H. Swindells, Ph.D., I did not do so in the spirit of rhodomontade, which characterised his remarks on the above subject. I simply stated facts, being surprised that anyone should express such incredulity about the purity of an article of food which, from pretty long experience, I was certain was, *as a rule*, sold in sweet, fresh, and pure condition. Dr. Swindells says he was not referring to the use of stearin, the only matter which I think could "not be considered an adulteration." Anyone would know that starch, lime, and cotton, or sesame oils, when added to lard, are adulterants. Starch and water, tradition says, were, before the advent of Food and Drug Acts, added in considerable quantity to lard. But I will not dwell upon the past; I shall confine myself to my own experience. In the first place, the addition of stearin to lard is a necessity, and, being so, it is only folly to prejudice its use by calling it "doctored dripping." During the last fifteen years I have examined almost every registered brand of lard made in England, but I have never found a trace of starch or lime in one. I have found cotton-seed oil in lard sold as compounds, I have found 20 per cent of water in lard sold as "prime watered lard," I have found from 2 to 5 per cent of water occasionally in some samples, and I have found infinitesimal particles of bi-

stearate of soda, the result, not of adulteration, but of careless refining. I have also found samples rancid from age or causes beyond my knowledge. On the whole, however, the lard which I have examined has been, *as a rule*, pure, sweet, and wholesome, showing that the refiners of England endeavour to supply a good article.

If only the kidney-fat of the hog is to be called lard, Dr. Swindells is certainly right when he says "something must be wrong." But this is only an Utopian idea, as from time immemorial the whole of the fat enveloped by the adipose tissue of the hog has been, when rendered down, called lard, and sold as such in all the markets of the world. Had mankind to depend for their supply of lard solely upon what is derived from the kidney-fat of the hog, the majority of the human race would, I think, have little chance of procuring it. In conclusion, I beg to thank you for the space you have allowed me to pass my opinion on this subject.—I am, &c.,

WILLIAM BROWN.

3, Hereford Road, Seaforth,
Liverpool, March 5, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 6, February 10, 1890.

Bodies which Present a Tension of Dissociation Equal to the Vapour-Tension of their Saturated Solutions.—H. Lescœur.—The class of saline hydrates presents numerous examples of this class of bodies. This feature is by no means an anomaly, but belongs to all saline hydrates during a longer or shorter period of their definite existence.

Action of Fluorine on the Different Forms of Carbon.—H. Moissan.—Fluorine, unlike chlorine, is able to combine directly with carbon. If dry, cold lampblack, not ignited and freed from carbides by treatment with petroleum and boiling alcohol, is placed in a current of pure fluorine, there is an immediate combination accompanied with incandescence. Charcoal of light woods, under the same conditions, may also take fire spontaneously. If the density of the charcoal is greater, and if it is free from dust, its temperature must be raised to 50° or 100° before incandescence takes place. Ferruginous graphite from cast-iron requires to be raised to a heat below dull redness before it can combine with fluorine. The graphite of Ceylon, purified with melting potassa, takes fire only at a rather higher temperature. Retort-coke does not combine until raised to redness. The diamond, kept at a red heat in the flame of a Bunsen burner, suffers no change of weight in a current of fluorine. If fluorine is passed over carbon which is readily attackable without raising the temperature too high, there is produced a gaseous mixture consisting chiefly of carbon tetrafluoride, a colourless gas which liquefies at 10° under a pressure of five atmospheres. If fluorine is passed over an excess of charcoal heated to redness there is formed another gaseous body which liquefies at 10° under a pressure of nineteen to twenty atmospheres. The two fluorides give a very extended spectrum of lines and bands, in which the rays of fluorine are very distinct.

A General Method of Preparing Carbon Fluorides.—C. Chabrié.—The author heats in a tube of Bohemian glass, sealed at the lamp, 5 grms. silver fluoride with 1.55 grms. carbon chloride (CCl₄) to 220° for two hours.

The Blue Flame of Common Salt and the Spectral Reaction of Copper Chloride.—G. Salet.—The spec-

trum of the flame of salt thrown on a coal fire has been described by Mr. A. P. Smith in the CHEMICAL NEWS (1879, p. 141). Its bands are due to copper chloride. Copper may be detected as follows in the ash of the coke or the coal employed. The metals present are dissolved in the ordinary manner and the copper is precipitated on a steel needle. This needle, if placed in the outer flame of a Bunsen burner, does not colour the flame, but if a little hydrochloric acid is volatilised in it there is at once seen a fine blue colouration, giving the spectrum of copper chloride. To chlorinise a flame, as it is often needful in spectrum analysis, the most convenient way is to introduce into it a bundle of some thirty very fine platinum wires moistened with hydrochloric acid.

The Electric Resistance of Iron and its Alloys at High Temperatures.—H. Le Chatelier.—The author's results are given in the form of a diagram.

Thermo-Chemical Researches on Silk.—Leo Vignon.—The absorbent power of silk is shown in the calorimeter by distinctly appreciable liberations of heat. These liberations represent the sum of the chemical and physical work effected by the contact of the silk with the reagents.

Determination of Potassa and Humus in Soils.—J. Raulin.—This paper will be inserted in full.

Colouring-Matter of the Diaptomes.—R. Blanchard.—The Copepods of the genus *Diaptomus* are represented in the lakes of the high Alpine tablelands by the species *D. bacillifer* and *D. denticornis*. They vary in colour from carmine-red to white, colourless, or even to a pale greenish blue. Their pigment is a carotene, an additional substance common to animals and plants. This proves that the animal organism is able to produce hydrocarbides, bodies hitherto unknown in healthy animals, though very common among plants. This is a new example of the existence of carotene independently of chlorophyll.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. ii., No. 12.

Easy Processes for Distinguishing Phosphorus Oxychloride and Trichloride.—G. Denigès.—A very small quantity of zinc powder is put in a very dry glass tube and a few drops of the liquid in question is poured upon it. The trichloride is without sensible action, whilst, with the oxychloride, there is immediately a brisk reaction. The grey zinc-powder turns to a dirty green, then to a yellow. If water is added, with agitation, the zinc dissolves in the case of the trichloride, forming a liquid almost colourless. With the oxychloride the oxide P₄O remains unchanged and the colour of the liquid is darkened.

Synthesis of Certain Seleniuretted Compounds in the Aromatic Series.—C. Chabrié.—The author has studied the reaction of selenium tetrachloride alone upon benzene; the same reaction in presence of aluminium chloride; the behaviour of selenium with organo-metallic compounds; the formation of phenyl selenide; the reaction of oxidisers upon phenyl selenide; the action of selenious anhydride and of selenious acid upon benzene; the synthesis of oxygenous selenium compounds; the action of bromine-water upon diphenyl-selenine; the action of selenious anhydride upon the amines; the formation of melted selenious anhydride; the reduction of selenious acid by alcoholic fermentation. In order to determine selenium the author attacks the products at 220—240° in a sealed tube with forty times their weight of pure nitric acid. He then dilutes with water, neutralises with potassa, and, after evaporation and the addition of a large quantity of hydrochloric acid, precipitates the selenium with sodium bisulphite.

The Vapour-Density of Selenium Chlorides.—C. Chabrié.—The experimental densities are 7.69 and 8.123, the theoretic value being 7.95.

MISCELLANEOUS.

The Mining and Metallurgical Exhibition.—On July 2 there will open, at the Crystal Palace, an Exhibition of novel and important kind. Mining and metallurgy rank among our most important and most progressive industries, and an exhibition dealing exclusively with their leading features will present a very high interest. Among the regulations for exhibitors we notice as especially important that nothing of an explosive, inflammable, or dangerous character will be admitted, and that the articles displayed will be at the exhibitor's own risk in all respects. It is not the intention of the Executive Council to issue awards and medals indiscriminately, though they "will initiate special competitions of mining and allied machinery, and make special awards in these and other cases, as may be decided upon by any jurors who may be appointed." This passage of the prospectus is scarcely as definite as we should wish to see. Probably the entire absence of awards and medals would have been a better policy. A series of popular and technical lectures will be delivered on the subjects of the Exhibition and a mining congress is also announced. An important feature is that one-half the certified surplus will be distributed among the exhibitors in proportion to the space which they have paid for and occupied. The other half will be disposed of by the Council "either in founding a scholarship at the Royal School of Mines, or in helping some other institution connected with mining and metallurgy. Applications for space must be sent in to 18, Finch Lane, not later than March 15. The articles admissible will fall within the following range:—Machinery in motion and at rest; gold-mining; silver-mining; diamond-mining; iron stone and ore mining, with the manufacture of iron and steel; lead mining and manufacture with the production of white-lead; tin-mining and smelting, with the manufacture of tin plate; copper-mining, smelting, and refining; coal-mining, with coke, coal-gas, and utilisation of the by-products; the petroleum and asphalt industries; mining for precious stones; the salt industry; mining for antimony, mercury, arsenic, manganese, cobalt, platinum, bismuth, uranium, &c., ochres, sulphur, and other minerals; manufacture and uses of alloys; nitrates and phosphates; assaying and chemistry of mining and metallurgy, quarrying, cements, clays, concretes; electricity applied in mining and metallurgy; explosives (*shown in model only*) used in mining; scientific instruments used in mining; collections of minerals; mining and metallurgical literature; tools and appliances; ambulance practice and condition of working miners. A guarantee fund has been subscribed to the amount of £2410 6s. The sum total of all calls made upon the guarantors will be repaid to them out of the first funds available after payment of expenses. The project seems a departure from the common run of exhibitions; it merits and will, we trust, command success.

Royal Institution of Great Britain.—The following are the arrangements for the Lectures after Easter:—

The Hon. George C. Brodrick, D.C.L., Warden of Merton College, Oxford, three Lectures on "The Place of Oxford University in English History"; on Tuesdays, April 15, 22, 29.

Louis Fagan, Assistant Keeper of Prints and Drawings, British Museum, three Lectures on "The Art of Engraving": (1) Line Engraving; (2) Wood Engraving; (3) Mezzotint Engraving; on Tuesdays, May 6, 13, 20.

Andrew Lang, three Lectures on "The Natural History of Society"; on Tuesdays, May 27, June 3, 10.

C. V. Boys, A.R.S.M., F.R.S., Assistant Professor of Physics, Normal School of Science, South Kensington, three Lectures on "The Heat of the Moon and Stars" (the Tyndall Lectures); on Thursdays, April 17, 24, May 1.

Professor Dewar, M.A., F.R.S., Fullerian Professor of Chemistry, R.I., Jacksonian Professor of Natural Ex-

perimental Philosophy, Cambridge, six Lectures on "Flame and Explosives"; on Thursdays, May 8, 15, 22, 29, June 5, 12.

Captain W. de W. Abney, R.E., C.B., F.R.S., three Lectures on "Colour and its Chemical Action"; on Saturdays, April 19, 26, May 3.

Charles Waldstein, Litt.D., Ph.D., three Lectures on "Excavating in Greece"; on Saturdays, May 10, 17, 24.

The Rev. S. Baring-Gould, M.A., three Lectures on "The Ballad Music of the West of England" (with Musical Illustrations); on Saturdays, May 31, June 7, 14.

New Process for Titrating Alcohol with Chromic Acid.—R. Bourcart.—In the author's process the diluted alcohol is heated with dilute solutions of potassium bichromate and sulphuric acid and gradually oxidised, first to aldehyd and then to acetic acid. The conversion is quantitative. As it is easily seen, $\frac{2}{3}$ mol. of bichromate are required for the oxidation of 1 mol. alcohol. The author operates in tubes sealed at both ends, or in a tube sealed at one end and closed at the other with a caoutchouc stopper, the end of which is secured in any convenient manner. After being heated for two to three hours in a boiling water-bath the tube is let cool. The liquid is then mixed with a sufficiency of potassium iodide, so that the iodine set free may re-dissolve, and titrated with hyposulphite until the colour passes from a dirty yellow to a yellowish green. Starch-paste is then added, and the titration is continued until the dark violet colour disappears. The liquid does not become colourless, as it is coloured a turquoise blue by chrome-alum, which, however, does not interfere with the sharpness of the reaction. The author uses a solution of bichromate containing exactly 5 grms. per litre (in some cases, also, a 1 per cent solution), a sulphuric acid of 25 vol. per cent (in some cases 10 per cent), a 10 per cent potassium iodide solution, and a 2 per cent solution of starch which has been boiled and filtered. The solutions of alcohol taken for examination are of about 0.5 per cent. To 10 c.c. of such dilute alcohol there are used about 50 c.c. of the 0.5 per cent solution of bichromate and 10 c.c. of the 25 per cent sulphuric acid.—*Bull. Soc. Ind. de Mulhouse and Chemiker Zeitung.*

Determination of Silicon in Crude Iron and in Spiegeleisen.—M. Clerc.—The author places in a flask holding from 350 to 400 c.c. 4 grms. of the metal as finely pulverised as possible, along with 15—20 c.c. of water, 8—10 c.c. of pure bromine, and 75 c.c. of pure hydrochloric acid, and heat to about 100° on the sand-bath. The silicon is oxidised and the iron and manganese pass into solution. If the heating is continued until the volume of the liquid is reduced to 40—50 c.c., the process is completed. The liquid is diluted with 200—300 c.c. hot water, filtered, and the insoluble residue is incinerated, when the silica is obtained white and pure. The error does not exceed 0.001—0.002 per cent.—*Soc. de l'Ind. Minerale and Chemiker Zeitung.*

NOTES AND QUERIES.

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

Laboratory and Lecture Room Fittings.—Will any reader of the CHEM. NEWS recommend a firm to carry out above-mentioned work? Good work at a fair price required.—BALBUS.

Analysis of Manufactured Rubber.—In what way or process can I determine the composition of manufactured rubber, so that I might know what quantity of the different compositions are used?—ANALYST.

Fire-damp Indicator.—Could any of your readers inform me whether there is an effective instrument for indicating explosive gas in coal mines, and if it is in general use in dangerous pits?—A. L. C.

ERRATUM.—Page 109, column 1, line 17 from top, for "sulphate" read "phosphate."

MEETINGS FOR THE WEEK.

- MONDAY, 10th.—Medical, 8.30.
 TUESDAY, 11th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
 — Society of Arts, 8. "The Claims of the British School of Painting to a Thorough Representation in the National Gallery," by James Orrock, R.I.
 — Institute of Civil Engineers, 8.
 — Photographic, 8.
 — Royal Medical and Chirurgical, 8.30.
 WEDNESDAY, 12th.—Society of Arts, 8. "The Chemin de fer Glissant, or Sliding Railway," by Sir Douglas Galton, K.C.B., D.C.L., F.R.S.
 — Geological, 8.
 — Microscopical, 8.
 — Pharmaceutical, 8.
 THURSDAY, 13th.—Royal, 4.30.
 — Royal Institution, 3. "The Early Developments of the Forms of Instrumental Music" (with Musical Illustrations), by Frederick Niecks.
 — Mathematical, 8.
 — Institute of Electrical Engineers, 8.
 — Society of Arts, 5. "Agriculture and the State in India," by W. R. Robertson.
 FRIDAY, 14th.—Royal Institution, 9. "The Glow of Phosphorus," by Prof. T. E. Thorpe, Ph.D., F.R.S.
 — Astronomical, 8.
 — Quekett Club, 8.
 SATURDAY, 15th.—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.
 — Society of Arts, 3. "The Atmosphere," by Prof. Vivian Lewes.

TO CORRESPONDENTS.

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THE CHEMICAL NEWS.

Vol. LXI. No. 1581.

THE SYSTEM OF "SEALED PAPERS."

IN reply to the strictures on this practice urged by Mr. Crookes in his Presidential Address before the Chemical Society in March, 1889, M. Lecoq de Boisbaudran utters a vehement protest. The distinguished French chemist is in error if he supposes that he was here personally or specially alluded to. A Presidential Address before the Chemical Society consists of two portions, having, in reality, no connection beyond their being delivered on the same occasion. In the former of these portions the practice of "sealed papers" was made the subject of condemnatory mention. But this has not the least reference to the second, or scientific portion of the Address, in which are discussed the views of M. de Boisbaudran on the rare earths.

No one can deny that "sealed papers" do lend themselves to dishonourable, if not formally dishonest, practices; and, as the German proverb says, "opportunity makes thieves." The *savant* who deposits half a dozen sealed papers with some learned society calls for one of them only to be opened. What was in the others the world never learns. Why are they not also opened and read, unless they contain something which the author desires to conceal, *i.e.*, some different and contrary solution of the question concerned? If the suppressed papers are merely steps leading up to the conclusion ultimately adopted, we fail to see the motive for withholding them from ultimate inspection. The advantage gained by the dishonest person whom Mr. Crookes supposes is distinctly that of priority—and in many cases that is everything. That the person injured—the true discoverer—"cannot have gathered his ideas from the contents of the sealed paper" is perfectly true and very unimportant. No one says he has!

M. de Boisbaudran's objections to the publication of preliminary papers, as customary in England and Germany, are not valid. The subjects which a chemist thus appropriates for his further study are not "vast questions," but are generally well defined in their scope, as anyone may see who will look over the "preliminary notices" published in various scientific journals. Nor will they be found to be "hazardous hypotheses." By speaking of some imaginary "conscientious experimentalist," whose "useful researches" are thus interfered with, M. de Boisbaudran evidently insinuates that the authors of such notices are not conscientious, but "dishonest, or simply superficial," and that they "effect no real work." But the writers thus disparaged are not like the dealers in "sealed papers," working under a cloak. Their memoirs come at once under the notice of their colleagues, and if they are found to be dishonest or superficial, or if they are not worked to some definite conclusion, they speedily find their own level.

It must not be supposed that the objection to "sealed papers" is a peculiarity of Mr. Crookes. When attempts have been made to introduce this system into England they have been condemned by the general sense of the Royal and the Chemical Society.

THE MANGANESE WATERS OF EXCELSIOR SPRINGS.

By W. P. MASON.

A CONSIDERABLE amount of a manganese salt in spring water is so unusual an occurrence that the following analysis may prove of interest:—

Excelsior Springs is a small town about thirty miles north-east of Kansas City, Mo., and has grown up on account of the increasing fame of its chalybeate waters, the curative powers of which are recognised throughout a large section of the western country.

Manganese is reported (usually as carbonate) in some sixty-two springs in the United States, but in nearly half of these it exists in traces only, and in the great bulk of the remainder the amount present is but small. In seven instances the manganese equals or exceeds the amount present in the Excelsior water, but in all but two of these seven (and these doubtful) the element is present as sulphate or chloride, while the Excelsior water contains it as carbonate only. Occurring, as it does, associated with ferrous carbonate, it readily places the water in a favourable light to medical practitioners for use in anæmia and kindred troubles, inasmuch as combinations of manganese and iron are so much more effective than the iron preparations alone. The fact of the manganese being in the readily-assimilated carbonate form, gives advantage over the more astringent sulphate and chloride.

MnCO ₃	9.41	parts per million.
Al ₂ O ₃	2.10	" "
SiO ₂	12.00	" "
K ₂ SO ₄	4.86	" "
NaCl	17.60	" "
FeCO ₃	23.43	" "
CaCO ₃	362.75	" "
MgCO ₃	54.70	" "
KCl	2.80	" "
NaHCO ₃	9.35	" "
		492.00	" "

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 Troy, N. Y.

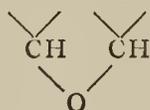
THE CONSTITUTION OF CELLULOSE.

By C. F. CROSS and E. J. BEVAN.

IN recent communications (CHEMICAL NEWS, lx., 163, and *Your. Chem. Soc.*, lvii., 1) we have recorded certain observations on the ethereal derivatives of cellulose—acetates and benzoates—the study of which was undertaken with the view to throw light on the constitutional problem, which for this, as for perhaps the greater number of the carbohydrates, remains unsolved. In preparing the benzoates we start from the hydrates precipitated from the solution of cellulose (cotton) in ZnCl₂.Aq, which we find to be soluble, under certain conditions, in solutions of the alkaline hydrates. The general behaviour of these hydrates is suggestive of the forms of cellulose found in the growing parts of plants. Certain of these we have found to yield furfural on hydrolysis (H₂SO₄.Aq), and we therefore, assuming a similar behaviour in this respect also, investigated the conditions under which the typical cellulose could be made to yield this aldehyd in such quantity as to establish between them an essential relationship. On heating purified cotton with zinc chloride solution (50 per cent) and raising the temperature gradually to 120—135°, furfural is formed, and distils with the water in such quantity that a drop of the distillate strikes a deep crimson with aniline acetate.

While we are pursuing the investigation so as to determine the quantity formed, and the maximum yield under the most favourable conditions, it may not be out of place to call attention to the bearing of the result upon the problem in question. Assuming a unit group of C₆, which appears to be justified by Franchimont's researches, the presence in this of three alcoholic OH groups is established by the formation of a triacetate and trinitrate, under what we may regard as normal conditions of such transformations. In acetylising cellulose in presence of zinc chloride, an acetate is obtained which, from our

analyses and determinations of yield, appeared to be a pentacetate. The formation of such a derivative indicates either the existence of additional OH groups, or the hydrolysis of aldehydic groups, condensed to build up the complex anhydride which cellulose probably is, with conversion of the resulting pairs of OH-groups into the corresponding OAc. In the absence of direct evidence of the presence of aldehyd or ketone oxygen we have inclined to the former view (*Journ. Chem. Soc.*, lvii., 4), but it would now appear, from the formation of furfural under the conditions above named, that the latter is the more probable explanation, indicating, as it does, the existence of aldehydic oxygen in the cellulose molecule. And further, the remaining O atom of the C₆ unit would also be accounted for as existing in a—



group. To such a view the lines of evidence appear to us to be converging, and at least there is sufficient ground for adopting it as a working hypothesis. On this view the higher acetate is derived, not from the original cellulose, but from a hydrate of lower molecular weight.

In studying the condensation of the carbohydrates, Tollens usually employs sulphuric acid. Our experiments tend to show that zinc chloride is to be preferred, as oxidation is excluded, and the action can be pushed to a higher temperature without complicating the results. We find also that the ligno-celluloses readily yield to this reagent, giving derivatives (hydrates) soluble in alkaline solutions, to some extent also in water, *i.e.*, on diluting the solution in ZnCl₂Aq and filtering off the precipitated hydrate, the solutions contain dissolved carbohydrates, which, on concentrating, are resolved with formation of furfural. It is probable that the ligno-celluloses could be made to yield a much larger proportion of wood-gum (holzgummi) and xylose by previous treatment with this reagent than by direct treatment with the ordinary hydrolytic reagents.

In the light of these results the so-called wood-gum is seen to be more closely related to the typical cellulose than has been supposed.

ON OPENING UP PYRITES IN A CURRENT OF OXYGEN.

By P. JANNASCH.

THE author communicates a simplification of the process for opening up pyrites in the dry way, resulting from experiments on its behaviour with oxygen at a red heat. If pulverised pyrites are heated in a glass tube in a current of oxygen, there soon sets in vivid incandescence, accompanied with a shower of sparks, and extends quickly through the entire mass. There appears an odour of sulphurous acid, there follow vapours of sulphur trioxide, and drops of sulphuric acid condense on the cold parts of the tube; if the heat is applied too suddenly sulphur sublimes. The decomposition is perfect, since the residue of dark red ferric oxide dissolves, excepting the small quantities of quartz and gangue present. This fact rendered it possible to improve the author's proposed method for opening up pyrites in a current of air and nitric acid. He uses in the ignition of pyrites the apparatus described in his former paper, with the modification that the air-holder is filled with oxygen and the bottle with nitric acid is omitted. The flexible caoutchouc tube connecting the drying-cylinder with the combustion-tube can be closed by a pinch-cock.

Above all things, the heating of the porcelain boat containing the substance has to be very carefully regulated at the commencement. The author begins with the hindmost flame, which must not be more than an inch in

height, and waits until the boat begins to glow before extending the ignition as the reaction proceeds. With care any spirting of the substance or sublimation of sulphur can easily be avoided. The current of oxygen must not be too rapid, about 200 bubbles per minute. If too large a quantity of sulphuric acid vapour appears in the first receiver, the current of oxygen must be arrested momentarily by closing the pinch-cock. After a full half-hour has expired, the tube is strongly ignited for about a quarter of an hour in order to ensure the decomposition of all the material and to expel all the sulphuric acid; the tube is then allowed to cool a little in the current of oxygen, the boat is drawn out of the tube (which is still hot), and the current of oxygen is broken off. The sulphurous acid formed is substantially oxidised to sulphuric acid by the bromine in the first two receivers. The liquid in the receivers is poured into a beaker, mixed with a few c.c. of strong hydrochloric acid, the bulk of the bromine present is removed by evaporation, and the sulphuric acid is precipitated with barium chloride. By this method it is possible to determine the sulphur in pyrites with the needful accuracy in the space of four to six hours.—*Journal fur Praktische Chemie.*

SEPARATION OF ZINC FROM NICKEL.

By H. ALT and J. SCHULZE.

In a solution of zinc and nickel containing a sufficiency of succinic acid, a current of sulphuretted hydrogen precipitates all the zinc as a perfectly white zinc sulphide, whilst the nickel remains in solution. The liquid may be either hot or cold, and an excess of the precipitant is not objectionable. The succinic solution must be free from salts, as otherwise nickel sulphide may be simultaneously precipitated.

The authors give an especial description of the analysis of nickel silver. The alloy is dissolved in nitric acid, which is almost entirely driven off by heat, the stannic acid is filtered off, and the copper is precipitated with sulphuretted hydrogen. The filtrate is evaporated down to a small volume, the sulphuretted hydrogen being expelled. Potassa-lye is then added almost to neutrality, and the liquid is precipitated with 10 to 20 drops of a 10 per cent solution of sodium acetate. The precipitate of basic iron acetate is filtered off, any excess of acetic acid is expelled by boiling the filtrate with an addition of a mineral acid, and the bases are precipitated with sodium carbonate at a boiling heat. The zinc and nickel carbonates are filtered off, washed, and dissolved in succinic acid, filtered if needful, the liquid made up to a known volume, and an aliquot part of the liquid is taken for further treatment. The authors take from 1.5 to 2 grms. of the alloy, make up the solution to 500 c.c., and take 100 c.c. for further treatment. There are added 5 grms. succinic acid, the liquid is slightly diluted with water, heated almost to a boil, and treated with a current of sulphuretted hydrogen until it smells strongly of the gas. It is then let stand for twenty-four hours, filtered, the white zinc sulphide is washed, and determined as such.

The filtrate is mixed with a little hydrochloric acid (to prevent any deposition of nickel sulphide on heating in consequence of the great dilution of the succinic acid), and the hydrosulphuric acid is expelled by evaporation. The liquid is then treated at a boiling heat with potassa-lye, when nickelous oxide is precipitated quantitatively even in presence of much succinic acid.—*Berichte der D. Chem. Gesellschaft and Chemiker Zeitung.*

Molecular Weights of Metals.—W. Ramsay.—The author gives the molecular weight of lithium as 7.03 by experiment and 7.02 by calculation; that of sodium, 12.1 and 11.52; cadmium, 102.9, 112.0; thallium, 181.0 and 204.0, &c.—*Ztschr. f. Physik. Chem.*, Vol. iii., Part 4.

THE TREATISE OF DEMOCRITUS
ON THINGS NATURAL AND MYSTICAL.

Translated by ROBERT R. STEELE, F.C.S., &c.

(Concluded from p. 114).

GLOSSARY AND REMARKS.

(The references are to Pliny's "Natural History.")

- Alum.* (35, 15). Was generally an astringent salt of Fe or Al. Alum from Melos was a true alum and is still obtained there.
- Androdamas.* (36, 20; 37, 54). Arsenical pyrites; from its silvery lustre used with silver.
- Antimony.* (33, 33, 34). Is invariably the sulphide. The metal was obtained by the ancients, but confused with lead.
- Aphroselinum.* Selenite, sulphate of lime, &c.
- Aristolochia.* (25, 8). Birth-wort.
- Arsenic.* (34, 28). Orpiment, As_2S_3 .
- Asterites.* Identical with androdamas.
- Auriconchylum.* Gold in powder, coquille d'or.
- Bronze* is here used for a metal of which copper is the principal constituent.
- Cadmia.* (34, 1). Generally calamine; sometimes the "furnace calamine," ZnO , containing Cu, Pb, Sb, and As. (A passage in Strabo, liii., p. 419, Ed. 1587, fo., shows metallic zinc to have been worked in his time, and called false silver).
- Ceruse.* (34, 18). White-lead.
- Chalcanth.* (34, 12). Copperas, $FeSO_4$, of course containing copper. From the vitreous crystals are derived the words "vitriol," &c.
- Chalcites.* (34, 12). Copper pyrites, $CuFeS_2$.
- Chian Earth.* (35, 16). A white substance like fuller's earth.
- Chrysitis.* (33, 6; 35). A mixture of silver and lead, which becomes yellow on heating. Davy thought it massicot, yellow oxide of lead.
- Chrysocolla.* (33, 5). Malachite; or a solder for gold, 9, 29. The name means "gold glue." It did not contain borax.
- Cimolia.* (35, 17). Cimolite, a fuller's earth.
- Cinnabar.* (33, 17). Minium, Pb_3O_4 , was sometimes spoken of under this name.
- Claudianum* was a metal, named from its manufacturer. An alloy of Sn and Pb, with Cu, Zn, &c.
- Cnicus.* (21, 15). *Carthamus tinctoria*, the safflower; still used as a tinctorial agent.
- Cobathia.* Arsenical fumes of furnaces (in which cobalt was first found).
- Cyanus.* (37, 9). Blue carbonate of copper, Azurite.
- Electrum.* (23, 4). An alloy of gold with more than 20 per cent silver, amber coloured.
- Ecumenicus flower.* Herb basil?
- Flower of Copper.* (34, 11). Small black scales of oxide of copper, which separate on cooling.
- Zove.* Tin.
- Luna.* Silver.
- Magnesia.* (36, 16). Any white body, steatite; as in XVI., an amalgam; an ore of iron. Workmen in mines now are accustomed to call any white ore unknown to them magnesia.
- Misy.* (34, 12). Roman vitriol, a mixture of $CuSO_4$, with basic sulphate of iron; oxidised copper pyrites.
- Molybdochalium.* An alloy of Cu and Pb.
- Nitre.* (31, 10). A white salt. Pliny's description answers to sal ammoniac, may be Na_2CO_3 , KNO_3 , Na_2SO_4 , &c., &c.
- Orichalium.* (33). Yellow copper ore, mountain brass; or white copper, an alloy of Cu and As.
- Oxymel.* (23, 2). Vinegar and honey.
- Persea.* (13, 9). Balanites $\mathcal{A}g$. Berthelot translates it peach.
- Lead.* (34, 16). *White*, is Sn; *Black*, is Pb.

Pyrites. (36, 19). *White*, arsenical pyrites. *Yellow*, iron pyrites.

Sal Cappadocia. A variety of sal gemma.

Sandarach. (34, 18). As_2S_2 (realgar) or HgS.

Scissile. Alum schist; any ore distinguished by a laminated structure, saline efflorescence, and styptic properties; yellow ochre colour.

Sol. Gold.

Sory. (34, 12). Basic sulphate of iron, brown from exposure, containing $CuSO_4$.

Silver Spume. (33, 6). Argentiferous litharge.

Venus. Copper.

The gold and silver varnishes still used to brighten the colour of gold and silver alloys are nearly identical with those given in this work.

THE IGNITING-POINT OF SULPHUR.

By J. RUTHERFORD HILL.

THIS note is the result of some experiments suggested by a letter in the CHEM. NEWS (vol. lxi., p. 95). Mr. Bertram Blount there states that in the course of a recent conversation a remark was made to the effect that sulphur ignites at a temperature not far above its melting-point ($107^\circ C.$). On referring to published authorities, Mr. Blount was apparently puzzled by the very discordant statements on the subject, which ranged from $115^\circ C.$ to $293^\circ C.$ He makes an appeal to any one who has determined the igniting-point of sulphur to publish the result and indicate the method employed. What follows is intended as a reply to his appeal.

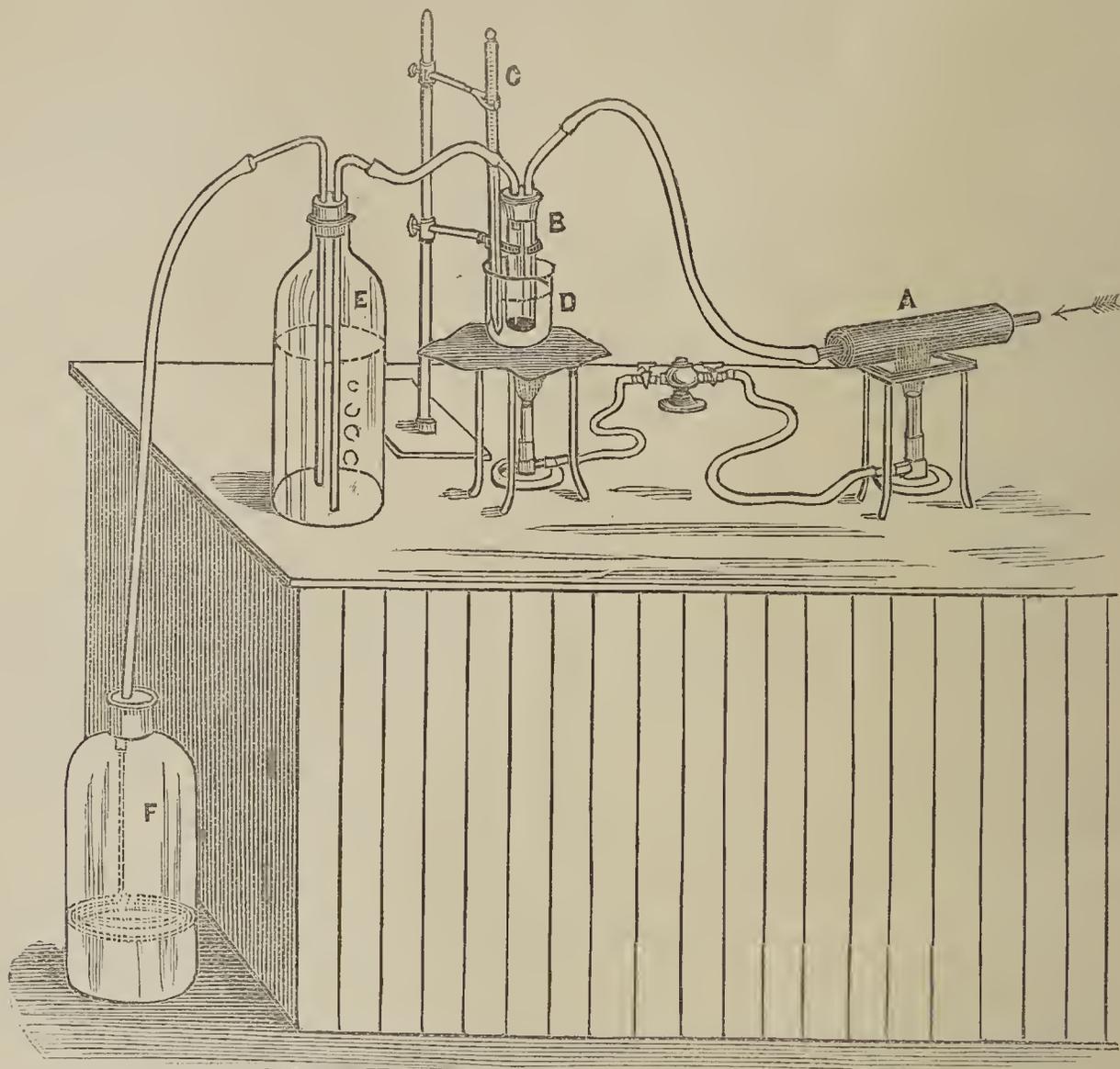
It will be convenient to state here the published igniting-points of sulphur quoted by Mr. Blount as follows:—Tidy, $115^\circ C.$ to $120^\circ C.$; Dumas, $150^\circ C.$; Pelouze et Fremy, $150^\circ C.$; Miller, $235^\circ C.$ to $260^\circ C.$; Watta, $250^\circ C.$; Dalton, $260^\circ C.$; Thomson, $293^\circ C.$

After some little planning and experiment the following method was adopted as being the least open to objection:—A test tube, B, size $5 \times \frac{5}{8}$ inches, is fitted accurately with a cork perforated for two glass tubes. The inlet tube, A, passes to about 1 inch from the bottom of the test-tube, so as to carry the air down to the surface of the sulphur. The outlet tube, A', stops at the entrance to the test-tube; the outlet tube is connected with the aspirator, E, which is emptied by a syphon tube into the receiver, F, and thus draws a current of fresh air through the whole apparatus in the direction indicated by the arrow.

To prevent cooling of the test-tube the fresh air is heated by covering a portion of A with wire gauze and keeping it nearly red hot by a Bunsen flame. By this means it was found that when the current was passing freely the air entered the test-tube at a temperature of about $60^\circ C.$, and when made to pass slowly the temperature was considerably higher.

A portion of the sulphur to be tested was placed in the test-tube, B. The test-tube is immersed, along with a thermometer, c, in a bath of strong sulphuric acid boiling at $332^\circ C.$ contained in the beaker, D, which is heated by a Bunsen flame. When the thermometer indicates a temperature of about $120^\circ C.$, the test-tube, B, is lowered into the bath, and the air current started by lowering the receiver, F, beneath the level of the aspirator, E.

As the temperature rises, vapour of sulphur, mixed with air, fills the test-tube and passes over into the aspirator. There would be risk that when the flashing-point is reached the mass of vapour in the aspirator might also be fired and cause damage. This risk is avoided by causing the outlet tube, A', to pass down to the bottom of the column of water in E and below the level of the syphon tube. By this means direct communication between the vapour in B and that in E is cut off.



When the thermometer reached 255°C. , the vapour of sulphur burst into flame; this occurred several times on repeating the experiment; on one occasion it inflamed at 253°C. , and once or twice at slightly higher temperatures. On pinching the india-rubber syphon tube with the hand, the air current is stopped, the test-tube fills with sulphur vapour, and the flame is instantly extinguished. On removing the pressure from the syphon tube, fresh air immediately enters the test-tube and the sulphur vapour instantly rekindles. This takes place with great sharpness, and the operation can be repeated with great ease and rapidity. By removing the Bunsen flame from the bath, *D*, the temperature rapidly falls, and the sulphur flame can be extinguished and re-kindled at every degree. This continues till the thermometer falls to 248°C. , but below that temperature the vapour will not re-ignite. The experiment was repeated eight or nine times with the same result. On one occasion the thermometer was read 246°C. when the flash last appeared, but this was possibly a mistake in observation.

An experiment was now made to ascertain if the sulphur inside the tube was at the same temperature as that indicated by the thermometer in the sulphuric acid bath outside. A thermometer was placed in a test-tube containing sulphur. This test-tube was placed in the sulphuric acid bath. On applying heat it was found that while the temperature was rising, the sulphur inside the test-tube was always at few degrees lower temperature than the sulphuric acid outside. On withdrawing the heat and allowing the temperature to fall, however, it was found that both thermometers speedily indicated the same temperature, and continued to fall at the same rate.

This would indicate that the point at which the sulphur flame was first seen (255°C.) was probably not the real temperature inside the tube, and also that the point at which the flame ceased while the thermometer was falling (248°C.) was the real temperature inside the tube. To test this point the sulphuric acid bath was raised once to 261°C. and at another time to 271°C. , and on both occasions the flame disappeared on allowing the temperature to fall to 248°C.

Mr. D. B. Dott has kindly tested my thermometer by a comparison with a standard instrument, and the foregoing temperatures have been corrected accordingly.

From these results it would appear that the igniting-point of sulphur in air is 248°C. , and that the temperature stated by Watts (250°C.) is most nearly correct. It may be noted that the sulphur used was sublimed sulphur of ascertained purity and free from moisture.

Pharmaceutical Society of Great Britain,
36, York Place, Edinburgh.
February 19, 1890.

On the Dioxyphosphinic and Oxyphosphinous Acids.—J. Ville.—The aldehyds unite with hypophosphorous acid to form two new classes of acids:—(1) Trivalent and monobasic acids, the dioxyphosphinic acids, formed by the direct union of the elements of 2 mols. of aldehyd and 1 mol. of hypophosphorous acid; (2) divalent and monobasic acids, resulting from the direct combination of hypophosphorous acid and aldehyd, mol. to mol.—*Comptes Rendus*, Vol. cx., No. 7.

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLET, F.R.S.,
Professor of Chemistry in the University of Virginia.

(Continued from p. 116).

A PRELIMINARY course of experiments was carried out with plates of pure electrotype copper (both pairs) in solutions of cupric sulphate, in order to test the effects, if any, of the following differences in the conditions of the two electrolysis cells compared.

1. *Effect of Difference in the Degree of Concentration of the two Solutions.*—The solution in one of the two vessels in which the plates were immersed being made to contain but one-tenth the proportion of cupric sulphate existing in the other, acidification and all other conditions being the same for both, only a very minute difference was found between the quantities of copper deposited in the same time on the two cathode plates, and the difference was not invariably in the same direction. The tendency, however, seemed on the whole to be toward a slightly larger amount thrown down from the stronger than from the weaker solution. In every case there was decidedly more copper dissolved from the anode than was deposited on the cathode plate.

2. *Effect of Difference in Acidity of two Solutions, otherwise of the same Strength.*—With the same proportion of cupric sulphate in both solutions, one was made to contain but one-tenth as much free sulphuric acid as the other; all other conditions remained the same for both. As before, the difference of result was insignificant, and somewhat variable in direction, with an apparent tendency towards a very slightly greater deposit on the cathode plate in the less acid as compared with the more acid solution. As before, there was in every case a distinctly greater loss of copper from the anode than gain on the cathode plate, especially in the more acid solution.

3. *Effect of Difference in Temperature of the two Solutions.*—The proportion of cupric sulphate and of free acid being the same for both solutions, and all other conditions the same, one of the two, however, being maintained at 72°, 47°, or 37° C., while the other was at 2° C., thus establishing a difference in temperature of 70°, 45°, or 35° respectively, there was distinctly in every instance rather more copper thrown down on the cathode plate in the colder than in the warmer solution. The loss of weight of the anode plate was always greater than the gain at the cathode, and the difference in this respect was greater in the warmer than in the colder solution.

4. *Effect of Difference in the Size of the Plates.*—All other conditions being the same in both the electrolysis cells, the plates in one were made to present but one-fourth the surface of those in the other, so that the "current density" was proportionally increased in the former. Under these circumstances there was a constant, though but small difference in the amount of copper deposited on the two cathodes, the quantity being greater on the cathode plate with the smaller surface. The tendency seemed to be towards a greater excess of metal removed from the anode over that deposited on the cathode plate in the case of the larger plates, as compared with the smaller.

5. *Effect of Difference in the Distance between the Plates.*—The plates of both pairs being equal in size, and all other conditions being uniform, the plates in one of the two electrolysis cells were placed at a distance apart only one-fifth that intervening between those of the other pair. It was not clear that any constant difference of result could be detected, but the tendency seemed to be rather toward a very slightly greater deposit on the cathode plate in the case in which the plates were farther apart as compared with that in which they were nearer

together. There was no recognisable difference in the proportion of metal dissolved off from the anode plate.

Similar experiments were made with two pairs of plates of pure silver, thus checking the results obtained with copper, and contrasting the behaviour of one at least of the less chemically alterable metals with that of the more easily alterable copper. It was intended to make a set of similar experiments also with gold plates only, but the available supply of pure gold in the form of rolled plates was not sufficient for the numerous experiments required. The silver solution used was one of potassium argento-cyanide, and the substitute for the free sulphuric acid of the copper experiments was an excess of potassium cyanide. The results obtained were essentially similar to those of the copper experiments, the effect of difference in temperature between the two solutions being, however, less decided, and the slight effect of difference in the size of the plates ("density of current") less constant and distinct.

In all the preceding experiments it was found that the most constant results under otherwise similar conditions were obtained by using feeble currents rather than those of greater strength, especially in the case of the silver solutions. There seemed, however, to be a limit to this. On the whole, the most satisfactory results were obtained (both in these preliminary experiments, and in those aiming at the atomic weight determination) with currents not exceeding $\frac{1}{100}$ th of an ampère per square c.m. of surface of (one side of) the opposed plates, and in some cases a current but one-fifth of this maximum was used.

Having in view the indications afforded by the preliminary experiments, it was determined to use tolerably strong solutions of the metals to be deposited with not more than a moderate excess of free acid, or, in the case of the double cyanide solutions, excess of potassium cyanide, to maintain the same temperature in both the electrolysis cells, and to have their temperature as low as possible (about 2° C.), and to have the plates of the two metals to be compared equal in size, and at equal distances apart, using a weak electric current, and keeping watch over its strength by means of an ordinary hydrogen voltameter in the circuit.

In the actual experiments on the deposition of gold as compared with silver it was originally proposed to use a solution of potassium auri-cyanide against one of potassium argento-cyanide, with the expectation that 3 atoms of silver would be thrown down for 1 atom of gold. But the first attempts made showed clearly that this reaction could not be obtained. The comparison as to gain in weight of the gold and silver cathode plates gave results leading to an atomic weight for gold impossibly high if the silver deposited were taken to represent 3 atoms, and much too low if it were taken to represent but 1 atom. Hence it appeared that the potassium auri-cyanide had been partially, but not completely, reduced to auro-cyanide by the action of the current, and an intermediate result obtained as to the equivalent quantity of silver between that due to the one or the other gold salt if exclusively present.

A change was therefore made to the auro-cyanide in the preparation of the solution to be electrolysed. A pure form of potassium cyanide was prepared with the aid of alcohol, and carefully tested as to the absence of any metal capable of deposition from the watery solution on electrolysis. Auric chloride was precipitated by ammonia the fulminating gold, after washing, dissolved in a strong solution of this potassium cyanide by the aid of heat, and the auro-cyanide crystallised out by cooling. The crystals were washed, re-dissolved in water, aurous cyanide separated from the solution by evaporation with hydrochloric acid, and the crystalline powder after cautious washing again dissolved in potassium cyanide solution, using for the purpose the barely necessary amount of the solvent liquid, but afterwards adding a further quantity, so as to have potassium cyanide in excess. Potassium argento-cyanide was prepared by precipitation of a solu-

* A Paper read before the Royal Society, May 9, 1889.

tion of pure silver in nitric acid with the purified potassium cyanide, washing the precipitate, and re-solution with the aid of the necessary quantity of potassium cyanide, of which finally a moderate excess was added.

The solutions of the gold and silver salts were made of equivalent strength, for the most part at the rate of 7 grms. of metallic gold for each 100 c.c. of solution, and an approximately corresponding amount of silver, taken atom for atom. Both solutions received the same excess of potassium cyanide, generally equal to one-half of that already present in the double salt, but in some of the experiments it was found necessary to add yet more during the electrolysis in order to preserve the purely metallic character of the surface of the plates. As an additional security against the admixture of auri-cyanide with the auro-cyanide of the gold solution, it was subjected for some time to electrolysis with unweighed gold plates immersed, these being reversed two or three times in position, just before the introduction of the weighed plates for a quantitative experiment. A number of attempts were made to substitute for the solution of potassium auro-cyanide one of sodium auro-thiosulphate, of potassium or sodium auri-chloride, and of simple auric chloride, in the last two cases employing at the same time a solution of silver nitrate, but these efforts led to no success.

In many of the experiments made with the double cyanide solutions the cathode plates, both of gold and silver, after removal from the electrolysis cells and thorough washing, were found to curl up on being heated, the deposit, which in these cases was rather hard and brittle, swelling up in a remarkable way, with formation and bursting of little blebs, or minute bubbles of the metallic surface, and parting off to some extent of the deposit from the original plate underneath. When the heating was carried out in the Sprengel vacuum small but quite appreciable amounts of hydrogen were found to be given off, having been occluded in the metal deposited. It seemed necessary to throw aside the results in all cases in which this condition of the deposit was well marked. Other experiments were vitiated by the gold deposit not being thoroughly compact, and still others by the surface not being clearly metallic, aurous cyanide making its appearance from the solution. It was hoped that in the experiments, free from apparent defect, any irregular behaviour of the gold solution at first might be got rid of by continued electrolysis, with reversal of the anode and cathode plates when necessary, until the ratio of gold to silver deposited should become constant; but confidence in this was greatly shaken when an instance occurred, followed afterwards by others, of sudden change in this ratio, attended with much less loss from the anode gold plate than the gain of the opposed cathode plate, pointing to the deposition of gold from the auro-cyanide with simultaneous formation of auri-cyanide in the solution.*

Altogether but five experiments were made in this way, yielding results which seemed worthy of being used to determine the atomic weight of gold, and it is of course unsatisfactory to know that these were selected out of a much larger number, mainly because, while not known to be in any way vitiated by apparent defects, they lead to values for the atomic weight in question close to those obtained by other methods and other experimenters. It is possible that this near approach to agreement may merely result from a balance of errors in opposite directions, which taken separately would have caused the experiments to be rejected. Some other experiments, under apparently similar conditions, gave figures for the atomic

weight differing from those reported by one or two whole units.

These only admissible results are the following:—

Experiment.	Character of gold in solution.	Character of gold in plates.	Gold deposited. Grms.	Silver deposited. Grms.
I.	A, b	B	5'2721	2'8849
II.	"	"	6'3088	3'4487
III.	"	"	4'2770	2'3393
IV.	"	"	3'5123	1'9223
V.	"	"	3'6804	2'0132

Aside from other difficulties liable to be encountered in carrying out this electrolytic method, the two most important sources of possible inherent error which suggest themselves are the occlusion of hydrogen by the metallic deposit and the instability of the atomicity of gold in the solution electrolysed.

The separation of hydrogen on the cathode plate, whether in bubbles (which may be avoided by proper regulation of the current) or occluded by the metal (which does not seem to be completely avoidable with any current, although the amount of occluded gas was extremely small in a number of my experiments), must be ascribed to decomposition, simultaneous with that of the cyanide of gold, either of water or, more probably, of cyanide of potassium, with secondary action of the potassium on the water. In either case, it is by no means clear that the proportion of current giving rise to this liberation of hydrogen can be counted upon as the same in the gold solution and in that of silver; and hence, even though it be fairly assumed that Faraday's principle of equivalent electrolysis by the same current is strictly correct for the *ensemble* of chemical actions in the two cells, the portion of current actually concerned in depositing gold or silver only in each of the respective cells may conceivably not be quite the same, so that the weights of the two metals thrown down may not be strictly equivalent.* It was, therefore, deemed important to work with feeble currents, and, while heating all the plates in a Sprengel vacuum before weighing, to reject the results of all those experiments in which the quantity of gas thus discharged amounted to more than the merest trace. But, if the source of error in question still exist at all, it might affect the atomic weight of gold in comparison with that of silver, either by making the former appear higher or lower than the truth.

The source of error most to be feared, however, in connection with the application of this electrolytic method to the determination of the atomic weight of gold, is the uncertainty of having all the gold throughout the process in the form of potassium auro-cyanide in the solution, in view of the transition observed to auri-cyanide during electrolysis, although change in the opposite direction occurs with even greater ease. Each of the two salts appears to admit of electrolytic decomposition, and the presence of any traces of the auri-cyanide, in which the gold has triad character, while the calculation is based on the supposed presence of monad gold only would, of course, tend to make the atomic weight of the metal appear lower than the truth.

(To be continued).

* As bearing on the question of the simultaneous decomposition of two electrolytes in the same solution, the following results may be recorded of an experiment made with a solution of mixed zinc and copper sulphates, with excess of potassium cyanide, the anode plate being of brass and the cathode plate of platinum, and an analysis made of the proportions of the two metals in the anode plate, in the solution as first taken, and in the alloy deposited on the cathode plate and subsequently dissolved off from it by means of nitric acid

Proportion of copper to zinc.	In the brass anode plate.	In the solution electrolysed.	In the alloy deposited on the cathode plate
Copper	68'74	13'81	73'34
Zinc	31'26	86'19	26'66
	100'00	100'00	100'00

Different results would undoubtedly have been obtained by substituting some other metal for one of those taken.

* Hittorf (Poggendorff, *Annalen*, [4], vol. xvi., p. 523), in the simultaneous electrolysis of gold and silver solutions, the gold as potassium auri-chloride, obtained results which showed that this metal was deposited at the rate of 1 atom for 3 of silver. Calculating on this basis from his two experiments, the atomic weight of gold comes out = 196'311 and 194'197; for silver 107'66.

In one experiment of my own, using sodium auri-chloride, the result showed that the gold was thrown down for the most part as a triad, but partly as a monad, element.

the last-mentioned mode of formation being analogous to that in which lepidin (tetraphenylfurfuran) is obtained from benzoin.

18. "Studies on Isomeric Change, No. IV. Halogen-Derivatives of Quinone (First Notice)." By ARTHUR R. LING.

The experiments of Hantzsch and of Nietzki have proved in opposition to those of Levy, that the "anilic" acids are paradihydroxyl-derivatives, and Hantzsch and Schnitter have shown that an isomeric change occurs when paradichloroquinone is brominated, the product being metadichlorometadibromoquinone. The author has made several attempts to prepare the paradichlorodibromoquinone, but hitherto unsuccessfully; in so doing he has obtained results which confirm Hantzsch and Schnitter's conclusion.

Metadichlorodibromoquinone is formed on brominating paradichloroquinone or diacetylparadichloroquinone in acetic acid solution, also by the chlorination of paradibromoquinone, the isomeric change apparently occurring in the first and last mentioned cases at the ordinary temperature. By brominating diacetylparadichloroquinol dissolved in carbon tetrachloride in the presence of a trace of iodine, a diacetyldichlorobromoquinol has been obtained, which melts at 260—270°; this may, however, be a mixture of isomerides.

Metadichlorobromoquinone is obtained by brominating metadichloroquinone, and also together with the paradichloro-derivative by brominating paradichloroquinone. It forms yellow plates which do not show a sharp melting point (175—180°); it is sparingly soluble in cold alcohol, easily in boiling. On treatment with potash it yields chlorobromanilic acid. The quinol formed by reducing it with sulphurous acid separates from chloroform in white needles melting at 135°, sparingly soluble in cold water or in chloroform but easily in the boiling liquids. On acetylation it yields a diacetyl-derivative which crystallises from alcohol in white needles melting at 174—180°.

Paradichlorobromoquinone is formed, together with its isomeride, on brominating paradichloroquinone. It is somewhat more soluble in the ordinary solvents than its isomeride, and melts at 158—159°. On treatment with potash it yields chloranilic acid.

Paradichlorobromoquinol crystallises from water in long transparent monohydrated needles which melt at 124—126°; they easily lose their water, becoming opaque, and then melt at 132—135°. Re-crystallised from chloroform, the substance melts at 135.5°: it possesses about the same solubility in all the solvents tried as its isomeride. Hence the two cannot be separated by crystallisation. On acetylation it yields an acetyl-derivative, which crystallises in silky needles melting at 148—159°, sparingly soluble in cold dilute alcohol, but easily in boiling.

When paradichlorobromoquinone is brominated at the ordinary temperature, a product is obtained which may perhaps contain paradichlorodibromoquinone, since, on treatment with potash, it affords a mixture of chlorobromanilic and bromanilic acid. In this way the author hopes to succeed in isolating paradichlorodibromoquinone.

19. "Note on a Phenyl Salt of Phenylthiocarbamic Acid." By AUGUSTUS E. DIXON, M.D.

When heated together in equimolecular proportions at 140—150°, phenol and phenylthiocarbamide interact, forming phenyl phenylthiocarbamide, $\text{NHPh}\cdot\text{CSOPh}$, but the yield is very small; this salt forms octahedral crystals resembling sulphur in appearance, melting at 150°.

20. "Contributions to the Chemistry of Thiocarbamides. Interaction of Benzyl Chloride and of Allyl Bromide with Thiocarbamide, Phenyl- and Diphenylthiocarbamides." By EMIL A. WERNER.

An account is given of the first part of an investigation of the action of benzyl chloride and allyl bromide on thiocarbamide and its different phenylated homologues. After reviewing the results already obtained by Claus,

Berthsen and Klinger, and Will and Rathke in the same direction, the following compounds are described:—

$\text{C}_8\text{H}_{10}\text{N}_2\text{S}\cdot\text{HCl}$, m. p. 174°, and the base $\text{C}_8\text{H}_{10}\text{N}_2\text{S}$, m. p. 88°, from benzyl chloride and thiocarbamide.

$\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}\cdot\text{HCl}$, m. p. 112°, and the base $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}$, m. p. 81—82°, from benzyl chloride and phenylthiocarbamide.

$\text{C}_{20}\text{H}_{18}\text{N}_2\text{S}\cdot\text{HCl}$, m. p. 152—153°, and the base—
 $\text{C}_{20}\text{H}_{18}\text{N}_2\text{S}$,

a viscid liquid, from benzyl chloride and diphenylthiocarbamide.

$\text{C}_4\text{H}_8\text{N}_2\text{S}\cdot\text{HBr}$, m. p. 84°, from allyl bromide and thiocarbamide; the base could not be isolated in a pure state.

$\text{C}_{10}\text{H}_{12}\text{N}_2\text{S}\cdot\text{HBr}$, a viscid liquid, from allyl bromide and phenylthiocarbamide; the base forms a syrupy fluid which is very unstable.

$\text{C}_{16}\text{H}_{16}\text{N}_2\text{S}\cdot\text{HBr}$, m. p. 170—171°, and the base—
 $\text{C}_{16}\text{H}_{16}\text{N}_2\text{S}$,

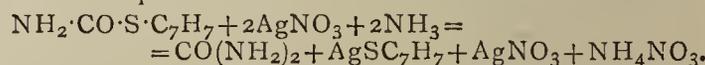
m. p. 57°, from allyl bromide and diphenyl thiocarbamide.

The decomposition of the bases by dilute sulphuric acid at 170° (Will's reaction), and it is shown that the primary thiocarbamide-derivatives behave in a different manner to the homologues.

Characteristic mercurio-chlorides possessing somewhat similar properties have been obtained from the several compounds: the compound $\text{C}_8\text{H}_{10}\text{N}_2\text{S}\cdot\text{HCl}\cdot\text{HgCl}_2$ may be taken as an example; it melts at 112°, and at 136° decomposes with loss of a molecular proportion of HCl and simultaneous alteration in the position of the alkyl-group (benzyl).

The sulphates and picrates of the bases are described, and in the case of the compound $\text{C}_4\text{H}_8\text{N}_2\text{S}\cdot\text{HBr}$, from $\text{C}_3\text{H}_5\text{Br}$ and CSN_2H_4 , a chromium alum has been obtained, $(\text{C}_4\text{H}_9\text{N}_2\text{S})_2\text{Cr}_2(\text{SO}_4)_4\cdot 24\text{H}_2\text{O}$.

Benzyl thiocarbamate ($\text{CONH}_2\cdot\text{SC}_7\text{H}_7$) and benzyl phenylthiocarbamate ($\text{CONHC}_6\text{H}_5\cdot\text{SC}_7\text{H}_7$) were incidentally prepared: both compounds combine with two molecular proportions of AgNO_3 ; the resulting products are immediately decomposed by ammonia in accordance with the equation—



At the Meeting on March 20 Professor Judd, F.R.S., will deliver a lecture on "The Evidence afforded by Petrographical Research of the Occurrence of Chemical Change under Great Pressures."

PHYSICAL SOCIETY.

March 7, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

SIR H. MANCE and Messrs. L. R. Shorter, C. Thompson, and A. D. Waller were elected Members.

Dr. S. P. THOMPSON described "Bertrand's Refractometer," and exhibited the capabilities of the instrument before the Society.

Its action depends on total reflection. The refractometer consists of an hemisphere of glass about 8 m.m. diameter set at the end of a tube, the plane face being outwards and inclined at about 30° with the axis. One side of the convex surface of the hemisphere is illuminated through a piece of ground glass set about perpendicular to the plane face. The hemisphere is viewed through an eyepiece focussed on a scale divided to tenths of millimetres, placed within the tube. The instrument is particularly useful for mineralogical specimens and liquids. The procedure in the latter case is to smear a film of the liquid over the plane face of the hemisphere, and, by

looking through the eyepiece, determine the scale reading of the line which separates the light and darker portions of the field. A reference to a calibration table gives the refractive index.

In experimenting with solids, a thin film of very dense liquid (supplied with the instrument) is placed between the specimen and the glass, and the procedure is then as above. The refractive index of opaque solids can be determined in this way. In using the instrument for minerals, great care must be taken not to scratch the glass. The handiness of the refractometer and its perfect portability (its dimensions being about 5 c.m. long by 2½ c.m. diameter) are great recommendations.

Mr. BLAKESLEY asked to what accuracy the scale could be read, and whether the sensitiveness of the instrument was at all comparable with that of other methods.

Prof. DUNSTAN enquired if it could be used with volatile liquids.

In reply, Dr. THOMPSON said that with non-homogeneous light the scale could be read to one division, but, with a sodium flame, one-tenth of a division could be estimated. For volatile liquids a drop may be used instead of a film, or the evaporation of a thick film may be retarded by a cover-glass.

Mr. H. TOMLINSON'S paper on "The Villari Critical-Point in Nickel" was postponed.

Prof. DUNSTAN described an "*Apparatus for Distilling Mercury in a Vacuum*," devised by himself and W. Dymond, and showed the working of the arrangement.

It consists of a 3 m.m. soft glass tube, rather more than a metre long, having an oblate spheroidal bulb blown at the upper end. The bulb is placed over a ring burner. At the top of the bulb a tube of 1.5 m.m. diam. is attached, and this passes outside the bulb, and descends close to the larger tube. The part of the smaller or fall tube just below the bulb is enlarged, so as to form a condensation chamber, and the lower part serves as a Sprengel tube. A conical reservoir, containing the mercury to be distilled, is in flexible connection with the lower end of the large tube, as in Clark's well-known apparatus. The advantages claimed for the new apparatus are its relative shortness and portability, the small quantity remaining undistilled, and its non-liability to derangement if left unsupplied with mercury.

To ensure satisfactory working, a constant pressure of gas is necessary, and this is obtained by inserting a Sugg's dry governor in the supply pipe. During distillation, peculiar green flashes are seen within the condensation chamber, and these are intensified by bringing it near an electric machine in action. The apparatus also serves well to show the character of an electric discharge through mercury vapour, for the mercury in the two tubes may be used as electrodes.

Prof. THOMPSON said he devised a simple form of distilling apparatus some time ago, which answered fairly well, and could be made by any amateur glass-worker. It consisted of a double barometer, one leg of which was of small bore, so as to act as a Sprengel tube. The rising part of the bend at the top of the larger tube was expanded, and served as the evaporating chamber, below which a burner was placed.

The PRESIDENT asked why Clark's apparatus is made so lengthy.

In reply to this question Mr. Boys said that, as the fall tube goes down within the rising one, the mercury near the top of the latter is heated by the condensing mercury (thus economising gas), and hence condensation does not take place until the vapour has passed a considerable distance down the fall tube.

Prof. S. U. PICKERING read a paper on "*The Theory of Osmotic Pressure, and its Bearing on the Nature of Solution*."

The author said that considerable doubt exists as to the accuracy of the premises on which the theory is

based, and if the theory is to be regarded as true, and not merely a rough working hypothesis, the following conditions must be fulfilled by weak solutions:—

(1). The molecular depression of the freezing-point must be independent of the nature of the dissolved substance.

(2). Any deviations from (1) must be in the direction indicated by the theory.

(3). The depression must be independent of the nature of solvent.

(4). The depression must be independent of the amount of solvent (all solutions being weak).

(5). The deviations with strong solutions should be in the theoretical direction, and

(6). They should be regular.

Prof. PICKERING proceeded to show that experiment, instead of confirming the above statements, disproves them all.

As regards (1), without counting abnormally low (half) values, Raoult's results show variations of 60, 40, 30, &c., per cent in different cases, and the author quoted other values where the variations were 500, 260, 230, &c., per cent. These variations he considered were too great to be explained by the fact of the solutions used being three or four times too strong.

Referring to (2), he said that low values are reasonably explained by the polymerisation of the dissolved molecules, high values by their dissociation into ions. He then argued that there are no abnormally high values, for the view that such exist and that they are explainable by dissociation involves the following conclusions:—
(a) That the more stable a substance is, the more easily is it dissociated; (b) that solution dissociates molecules which we know can exist undissociated as gases; (c) that water must consist of 1½H₂O, and the atomic theory is wrong; (d) that energy can be created, and therefore the theory of its conservation is untenable.

With respect to (3) it was pointed out that in many instances the same dissolved substance gives the full depression with one solvent and half depression with another. Cases were quoted where the depression produced by the same dissolved body in different solvents showed variations of 36,000, 21,000, and 28,000 per cent.

In discussing (4) the author said that even with solutions weaker than that corresponding to a gas, the law is not fulfilled. Taking the case of sulphuric acid (the only one at present fully investigated), the variations amount to 40 per cent, or about 28 times the experimental error.

With reference to (5) it was stated that with strong solutions the molecular depression should become smaller, but in every known case (nine were quoted) it becomes larger, the increase in one instance being 3200 per cent.

As regards (6) all experimental data available, especially those relating to sulphuric acid, show that the deviations are neither regular nor always in the same direction.

Mr. T. H. BLAKESLEY said he was greatly interested with Prof. Pickering's paper, for some time ago he was induced to make experiments on the volume of salts in solution by reading Joule's papers on that subject. Some of the results confirmed, but others did not agree with Joule's theory, that the molecular volume in solution was a whole number. If this theory was true then, he said, it would be possible to pre-determine the density of solutions, and from the measured density of any known solution we could determine the water of crystallisation of the salt from the formula—

$$n = \frac{1 - \frac{W}{w}(D - 1)}{D} \left(\frac{A}{H_2O} + x \right)$$

where W and w are the masses of the water and salt respectively, D the density of the solution relative to water at the same temperature, A the molecular weight of the dehydrated portion of the salt, x the number of molecules of water, and n the molecular volume of the salt in solution, the two latter being whole numbers.

CORRESPONDENCE.

PRIESTLEY AND LAVOISIER.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS (vol. lxi., p. 84) I notice an interesting letter from H. C. B., giving some French versions—or perversions?—of the persecutions of Joseph Priestley. It is curious that the authors did not feel themselves on perilous ground, since, if England mobbed and drove out Priestley, France guillotined Lavoisier outright! Strictly speaking, neither Priestley nor Lavoisier can rank as a “martyr of science.” If the former had followed the wise counsel of Edward Gibbon, and “stuck to physics and chemistry,” not a dog would have barked at him. And Lavoisier suffered, not as a *savant*, but as a “*fœrmier général*.”—I am, &c.,

J. W. SLATER.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 7, February 17, 1890.

Electrolysis by the Igneous Fusion of Aluminium Oxide and Fluoride.—Adolphe Minet.—The author seeks to utilise this kind of electrolysis as the point of departure of a series of applications of electricity to chemistry with especial reference to the production of metallic aluminium. His best results have been obtained with an iron cathode, the intensity of the current being 975 ampères and the difference of potential at the electrodes 6.1 volts. Under these circumstances the weight of aluminium deposited was 1900 grms., as against a calculated quantity of 2320 grms., or a yield of 82 per cent.

On Sodium Silicoglucinate.—P. Hautefeuille and A. Perrey.—The authors caused neutral sodium vanadate to act upon mixtures of silica, glucina, and alkali. The sodium silico-glucinate differ in composition and form from the corresponding potassium compounds.

Part Played by Foreign Bodies in Irons and Steels; Relation between their Atomic Volumes and the Allotropic Transformations of Iron.—F. Osmond.—Prof. W. C. Roberts-Austen, in his researches on the effect produced on the mechanical properties of gold by the addition of 0.20 per cent of one of seventeen foreign metals, had pointed out a curious relation between the results obtained and the position of the alloying metals in the periodic classification, and had suggested that an analogous relation should occur in iron. M. Osmond has elaborated this idea, and finds that foreign bodies of low atomic volume tend to cause iron to assume or to retain that one of its molecular forms in which it possesses the least atomic volume; substances of high atomic volume produce an inverse effect. Carbon, whilst obeying the general law, undergoes, at a certain critical temperature, a transformation, the nature of which is still doubtful, though its existence is incontestable.

On Dibromo-Carballylic Acid.—E. Guinochet.—Not adapted for useful abstraction.

Determination of Uric Acid in Urine by Means of a Solution of Sodium Hypobromite, with the Aid of Heat.—M. Bayrac.—The author evaporates 50 c.c. of urine in the water-bath; in the residue he precipitates the uric acid by 5 or 10 c.c. of a solution of hydrochloric acid at $\frac{1}{2}$ and washes with alco-

hol. This treatment removes urea and creatinine and leaves pure uric acid. This latter body is dissolved in the water-bath with 20 drops of soap-boiler's soda (!) and treated at 90°–100° with 15 c.c. of a concentrated solution of sodium hypobromite. The nitrogen is given off quantitatively from a hot solution.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., January, 1890.

Study of Various Questions of General Chemistry. Lecture by Prof. Schützenberger, of the College of France.—This paper is too long for insertion.

Gallisine, a Non-Fermentible Ingredient of Commercial Glucose.—Dr. Schmidt.—It is found that the glucose obtained by the action of non-arsenical sulphuric acid upon starchy matters is not pure, but contains a substance incapable of fermentation, gallisine. It is obtained as a very fine white powder, perfectly amorphous and very hygroscopic. It is insoluble in anhydrous ether, chloroform, and the hydrocarbons, except absolute alcohol (which dissolves it with difficulty), methylic alcohol, and glacial acetic acid. Its aqueous solution has a distinctly acid reaction. It is not precipitated by lead acetate and basic acetate, by mercury chloride and acetate, iron chloride, tincture of iodine, barium and calcium chloride. Its composition is represented by the formula $C_{12}H_{24}O_{10}$. The author has examined a number of derivatives, especially barium gallisate, hexacetyl-gallisine, potassium and lead gallisates. He has further studied the behaviour of gallisine with chlorosulphonic acid and with bromine and when heated in a current of hydrogen: the products of the dry distillation of gallisine with lime, its oxidation by nitric acid, its transformation under the influence of the pancreatic secretion, its conversion into glucose; its behaviour with the liquors of Fehling and of Knapp, and its optical properties. It is dextro-rotatory, the deflection ranging from 25.67° to 84.40°, according to the strength of the solution. In the analysis of eleven samples of commercial starch-sugar the quantities of gallisine found were from 22.49 to 6.82 per cent.

The Molecular Weights of the Metals.—From the *Journal of the Chemical Society*.

Determination of the Specific Gravity of Salts Soluble in Water.—J. W. Retgers.—From the *Zeitschrift für Physikalische Chemie*.

Absorption of Carbonic Acid by Mixtures of Alcohol and Water.—O. Müller.—The coefficient of absorption decreases as the proportion of alcohol in the mixture augments and reaches its minimum, when the mixture contains 28 of alcohol. It then increases until it reaches the coefficient of absorption of pure alcohol.

Determination of the Molecular Weights of Substances in Solution.—H. H. Will and Bradig.—From the *Berichte D. Chem. Gesell.*

Decolourising Effects observed during the Electrolysis of Acidulated Water.—H. N. Warren.—From the CHEMICAL NEWS.

Some Phosphates of Polyvalent Metals.—K. R. Johnson.—The author has examined the composition, crystalline form, specific gravity, and molecular volume of lanthanum and cerium metaphosphate, uranium phosphate, iron (ferric) chrome, aluminium and thorium metaphosphate, and yttrium pyrophosphate.—*Berichte*.

Solubility of Glass in Water.—H. H. Mylius and Foerster.—Water does not dissolve glass, but decomposes it into silica and free alkali. Glass containing lead is least attacked by boiling water.

On Melezitose.—M. Alechine.—The author concludes that melezitose has the molecular composition $C_{18}H_{32}O_{16}$. These two papers are from the *Journal Rousskago Physico-chimicheskago Obekttohestra*.

Synthesis of Glycerins by the Aid of Hypochlorous Acid.—Sergius Reformatsky.—This paper does not admit of useful abstraction.

Combinations of Raffinose with Bases.—MM. Beythien and Tollens (*Berichte*).—Raffinose forms with bases compounds some of which are less soluble in water and alcohol than raffinose.

Xylose and Wood-Gum.—MM. Wheeler and Tollens (*Berichte*).—Xylose, like arabinose, gives the well-known cherry-red colour when heated with phloroglucinol and hydrochloric acid.

Action of Chloral upon Glucose.—A. Heffter (*Berichte*).—A mixture of glucose and chloral heated to 100° for one to two hours is resolved into two compounds, $C_8H_{11}O_6Cl_3$.

Constitution of Primuline.—HH. Pfitzinger and Gattermann.—Not adapted for useful abstraction.

Electrolytic Separation of Cadmium and Zinc.—Edgar E. Smith and Lee K. Frankel.—From the *American Chemical Journal*.

Presence of Tin in Certain Sugars.—Dr. T. L. Phipson.—From the *CHEMICAL NEWS*.

Determination of Sulphuric Acid in Presence of Iron.—HH. Jannasch and T. W. Richards.—From the *CHEMICAL NEWS*.

Determination of Silica and Iron in Cryolite.—R. Fresenius and E. Hintz.—Already inserted.

Condensation of Hydrochloric Acid.—Dr. Hurter.—From the *Journal of the Society of Chemical Industry*.

The Chilian Manganese Ore.—J. Pattinson and H. S. Pattinson.—From the *Journal of the Society of Chemical Industry*.

On the So-called Resin Colours.—A. Muller-Jacobs (*Dingler's Polyt. Journal*).—The precipitates obtained by treating the aqueous solution of a resin soap are treated with a metallic salt. They combine with all the basic aniline colours, forming compounds known as resin-colours.

The Density Numbers of the Elements.—J. A. Groshans.—Already noticed.

Metallurgical Review.—An account of nickel steel, of the tenacity and ductility of aluminium bronzes and brasses, an examination of boiler-plates while working, and a notice of ferro-silicon alloyed with white cast-iron.

A Lake of Borax in California.—Napier Hake.—From the *Journal of the Society of Chemical Industry*.

Preparation of Artificial Meerschaum.—A. von Loseke.—From the *Zeitschrift für Angewandte Chemie*.

Crossing Varieties of Cinchona.—From the *Pharm. Journal*.

Canaiigre.—Henri Tremble.—This product, now coming into use in tanning in America, is the root of *Rumex hymnosepalum*. Sturk found in this root 28.57 per cent of tannin, but the author finds only 17.33.

New Application of Potassium Ferricyanide.—G. Kassner (*Chemiker Zeitung*).—A mixture of hydrogen peroxide, and a solution of potassium ferricyanide rendered alkaline by potassa, soda, or caustic baryta, may be used for giving off a rapid and regular current of pure oxygen.

Industrial Review and Various Patents.—Brief notices of patents relating chiefly to artificial colours.

MISCELLANEOUS.

Chemical Society Anniversary Meeting.—The Anniversary Meeting will be held at 4 p.m. on Thursday, March 27th. Fellows and their friends will dine together at the Whitehall Rooms, Hôtel Méropole, at 7 p.m. the same evening.

Royal Institution of Great Britain.—The following are the probable arrangements for the Friday Evening Meetings after Easter:—

Sir Frederick Bramwell, Bart., D.C.L., F.R.S., on "Welding by Electricity"; on Friday, April 18th.

Sir John Lubbock, Bart., M.P., D.C.L., LL.D., F.R.S., on "The Shapes of Leaves and Cotyledons"; on Friday, April 25th.

Walter H. Pollock, M.A., on "Théophile Gautier"; on Friday, May 2nd.

R. Brudenell Carter, F.R.C.S., on "Colour-Vision and Colour-Blindness"; on Friday, May 9th.

Professor Raphael Meldola, F.R.S., on "The Photographic Image"; on Friday, May 16th.

Professor A. C. Haddon, M.A., M.R.I.A., Dean of Royal College of Science, Dublin, on "Manners and Customs of the Torres Straits Islanders"; on Friday, May 23rd.

A. A. Common, F.R.S., Treas. R.A.S., on "Astronomical Telescopes"; on Friday, May 30th.

Professor W. Boyd Dawkins, M.A., F.R.S., on "The Search for Coal in the South of England"; on Friday, June 6th.

Absorption of Gases in Liquid Mixtures.—O. Müller and O. Lubarsch (*Annalen der Physik und Chemie*).—The absorption-coefficient of carbon dioxide, hydrogen, oxygen, and carbon monoxide in mixtures of alcohol and water falls as the concentration of the alcohol increases, reaches a minimum of 28 per cent (by weight), and then increases.

Determination of Mercury.—J. Volhard.—In a solution containing the mercury as a mercuric salt the acid is almost entirely neutralised with pure sodium carbonate, and the mercury is completely precipitated with ammonium sulphide, avoiding too great excess. It is advantageous to use ammonium sulphide recently prepared with the strongest ammonia. Soda-lye is then added with agitation until the liquid begins to clear; it is then heated to boiling, adding more lye until the sulphide is entirely dissolved and the liquid is quite clear. The caustic soda used should be that prepared from the metal, ascertaining previously the absence of silver. From the alkaline solution the sulphide is precipitated at a boiling heat by ammonium nitrate, keeping up the boiling until the ammonia is nearly expelled, and the precipitate is let settle in heat. It is denser, and deposits more rapidly than the precipitate obtained with sulphuretted hydrogen. If the precipitate has to be brought upon a tared filter, it is best first to wash by decantation with boiling water until the washings no longer react with a solution of silver nitrate. If, after the precipitation of the sulphide, it has been boiled so long that it may be possibly contaminated with sulphur, a little sodium sulphite is added and it is again boiled for a short time.—*Liebig's Annalen*.

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.

Hydropyridines.—Will any reader kindly inform me where I can obtain a full account of the *hydropyridine* series of organic compounds?—INTERESTED.

Schäfer's Beta-naphthol Beta-sulphonic Acid.—I should feel grateful for any information respecting the mode of preparation of the above, or reference to any works dealing with the subject.—"Q."

Are Cast-iron Stoves Prejudicial?—I have heard it stated (1) that carbon contained in the cast-iron is driven off, when the stove is sufficiently heated, in the form of carbonic oxide; (2) that the iron, thus becoming more porous, absorbs carbonic oxide (CO) from the fire itself, and again poisons the air of one's room with it. As I have lately taken into use a cast-iron stove (slow combustion—burning coke—sides lined with firebrick), and infer that a quantity of CO is formed in it, from the blue flames which ignite as soon as the feed door at the top is opened, I should be greatly obliged for any information on either of the above points.—C. E. H.

MEETINGS FOR THE WEEK.

- MONDAY, 17th.—Medical, 8.30.
— Society of Arts, 8. "Some Considerations Concerning Colour and Colouring," by Prof. A. H. Church, M.A., F.R.S.
- TUESDAY, 18th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
— Society of Arts, 5. "Brazil," by James Wells, M.Inst.C.E.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
- WEDNESDAY, 19th.—Society of Arts, 8. "Commercial Geography," by J. S. Keltie
— Meteorological, 7.
- THURSDAY, 20th.—Royal, 4.30.
— Royal Institution, 3. "The Early Developments of the Forms of Instrumental Music" (with Musical Illustrations), by Frederick Niecks.
— Royal Society Club, 6.30.
— Institute of Electrical Engineers, 8.
— Chemical, 8. "The Evidence Afforded by Petrographical Research of the Occurrence of Chemical Change under Great Pressures," by Prof. Judd, F.R.S.
- FRIDAY, 21st.—Royal Institution, 9. "Electro-magnetic Radiation," by Prof. G. F. Fitzgerald, M.A., F.R.S.
— Physical, 5. "On the Villari Critical-point of Nickel," by Herbert Tomlinson, F.R.S. "On Bertrand's Idiocylophanous Prism," by Prof. Sylvanus Thompson.
- SATURDAY, 22nd.—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.
— Society of Arts, 3. "The Atmosphere," by Prof. Vivian Lewes.

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FREDERIC H. MADDEN, School Secretary.

BOROUGH OF DARLINGTON.

SPENT OXIDE.

The Gas Works Committee invite offers for the Purchase of about 100 Tons (more or less) of SPENT OXIDE.

Samples and Particulars may be had on application to the Gas Works Engineer, Town Hall.

Tenders, endorsed "Tender for Spent Oxide," to be sent to me not later than the 20th instant.

No pledge is given that the highest or any offer will be accepted.

(By Order) F. T. STEAVENSON.

Darlington, 7th March, 1890. Town Clerk.

BOROUGH OF DARLINGTON.

The Gas Works Committee invite Tenders for the Supply of 100 Tons of PEROXIDE OF IRON for Gas Purification, delivered at the Darlington North Road Station; delivery to extend over a period of not exceeding six months from the acceptance of the Tender.

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(By Order) F. T. STEAVENSON,

Darlington, 7th March, 1890. Town Clerk.

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This Exhibition will be held at the Crystal Palace from July 2 to September 30, 1890, and will comprise Machinery, Metals, Minerals, Metallurgical processes, Assaying, Chemical Industry, Electricity, Practical Mining, Quarrying, &c. Prospectuses and Application forms for space may be had from the Hon. Secretary (Geo. A. Ferguson, Editor of the *Mining Journal*) at the Offices, 18, Finch Lane, E.C.

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THE CHEMICAL NEWS.

Vol. LXI. No. 1582.

THE NITRIFYING PROCESS AND ITS
SPECIFIC FERMENT.*

By PERCY F. FRANKLAND, Ph.D., B.Sc. (Lond.),
A.R.S.M., &c.
Professor of Chemistry in University College, Dundee,
and GRACE C. FRANKLAND.

The process of nitrification has been practically studied for centuries, but it was first in the year 1878 that it was shown by Schloësing and Müntz to be dependent upon the presence of certain minute forms of life, or micro-organisms, or, in other words, to be a fermentation change.

The authors have been engaged during the last three years in endeavouring to isolate the nitrifying organism, and the present memoir gives in detail an account of the numerous experiments which were made in this direction.

Nitrification, having been in the first instance induced in a particular ammoniacal solution by means of a small quantity of garden soil, was carried on through twenty-four generations, a minute quantity on the point of a sterilised needle being introduced from one nitrifying solution to the other. From several of these generations gelatin-plates were poured, and the resulting colonies inoculated into identical ammoniacal solutions, to see if nitrification would ensue; but, although these experiments were repeated many times, on no occasion were they successful.

It appeared, therefore, that the nitrifying organism either refused to grow in gelatin, or that the authors had failed to find it, or that, growing in gelatin, it refused to nitrify after being passed through this medium.

Experiments were, therefore, commenced to endeavour to isolate the organism by the dilution method. For this purpose a number of series of dilutions were made by the addition, to sterilised distilled water, of a very small quantity of an ammoniacal solution which had nitrified. It was hoped that the attenuation would be so perfect that ultimately the nitrifying organism alone would be introduced.

After a very large number of experiments had been made in this direction the authors at length succeeded in obtaining an attenuation consisting of about 1-1,000,000th of the original nitrifying solution employed, which not only nitrified, but, on inoculation into gelatin-peptone, refused to grow, and was seen, under the microscope, to consist of numerous characteristic bacilli hardly longer than broad, which may be described as bacillo-cocci.

These results are the more striking, for, in the case of the two other bottles similarly diluted, one had not nitrified, but, on inoculation into gelatin-peptone, produced a growth already on the second day, whilst the remaining bottle not only produced a growth, but had also nitrified, thus clearly showing that the number of organisms had been reduced to two, *i.e.*, one which nitrified and did not grow in gelatin, and another which had nothing to do with nitrification, but which grew in gelatin. In the case where nitrification took place and a growth also appeared in the gelatin-tube, it was obvious that both the nitrifying and non-nitrifying organisms were present. These inoculation tests, together with the microscopical appearances, were confirmed by repeated experiments, with invariably the same results.

It is, however, very remarkable that, although this bacillo-coccus obstinately refuses to grow in gelatin when inoculated from these dilute media, yet in broth it pro-

duces a very characteristic growth, which, although slow in commencing, often requiring three weeks before it makes its appearance, is very luxuriant.

The authors have, moreover, been successful in inducing nitrification in ammoniacal solutions inoculated from such broth cultivations, the extent of which has been quantitatively determined.

Although microscopically its form differs slightly when grown in broth and the ammoniacal solution respectively, yet its identity was established beyond question by its returning to its characteristic bacillo-coccus form when grown again in the ammoniacal solution.

The authors have also been able to induce its tardy growth in gelatin-peptone by passing it first through broth cultivations.

The paper is accompanied by carefully executed drawings of the nitrifying organism when grown in the various media employed.

NOTE ON THE
ISOLATION OF THE NITRIFYING ORGANISM.

By R. WARINGTON, F.R.S.

ON March 13, Prof. P. F. Frankland and Mrs. Frankland communicated to the Royal Society an account of their investigation on the isolation of the nitrifying organism. As I have myself been working for some time on the same subject, I desire to make a few remarks on their communication.

The medium they made use of was an ammoniacal solution containing no organic matter; this was originally seeded with a small quantity of garden soil. From this solution, when nitrified, a second solution was seeded, from the second a third, and so on, through 24 cultures.

From these nitrified solutions gelatin plates were prepared. The organisms which appeared upon the gelatin were introduced into ammoniacal solutions perfectly similar to those from which they had been originally obtained, but in no case did any nitrification take place.

The authors next resorted to the dilution method, and after many trials succeeded, by seeding from a nitrified solution diluted to one million times its volume, in obtaining nitrification in an ammoniacal solution, which, when nitrified, yielded no growth on gelatin. This nitrifying organism they describe as a small bacillo-coccus; one of its special characteristics, as already mentioned, is that it will not grow on gelatin.

My own work, which is as yet unpublished, has been conducted on similar lines; and, as far as it has gone, entirely confirms the statements made in the earlier part of Frankland's communication.

Having prepared successive cultures of the nitrifying organism in weak solutions of ammonium carbonate, containing the necessary nutritive salts, but no organic matter, I proceeded to isolate the bacteria present by means of plate cultures, or by Klein's method of spreading with a loop of platinum wire an extremely thin film of the solution, diluted if necessary, over a sloping surface of nutrient gelatin contained in a test-tube. The growths on gelatin were in all cases simple in character, and from three solutions only one organism was obtained. As these solutions had actively nitrified, and were fully capable of setting up nitrification in other solutions to which they were added, the probability seemed strong that the single organism obtained from them was in fact the nitrifying agent. This organism, however, and also all the other organisms previously separated by culture on gelatin from nitrifying solutions, obstinately refused to nitrify when introduced either alone or in mixture into fluids susceptible of nitrification. In a written Report made to the Managing Committee of the Rothamsted Agricultural Trust on Feb. 14, I gave an outline of these results, and said "We must therefore assume either—

* Abstract of a Paper read before the Royal Society, March 13, 1890.

(1) That the nitrifying organism does not grow on gelatin, or (2) that it loses its property of nitrification when so grown." The experiments I had then in hand were specially designed to test the truth of the second alternative.

I have employed the dilution method to a limited extent. Seeding with a nitrified solution diluted to 500 times its volume, I failed in two instances to obtain nitrification, while in three instances nitrification took place; in all the latter cases I obtained the usual growth on gelatin.

The nitrifying organism described by Frankland appears to agree in form with the small oval coccus originally mentioned by Schläesing and Müntz, but the isolation and characters of which were so imperfectly described that it was difficult to know what amount of weight should be given to their statement.

It is important to note that the bacterium isolated by Frankland produces only nitrous acid. This is quite in accordance with my own long experience of what occurs when successive cultures are made from a nitrifying fluid; the product soon becomes purely nitrous, and the nitrites thus produced are quite permanent. We must therefore suppose either that the production of nitric acid requires the presence of two organisms, one of which disappears during successive cultures; or else that the nitrifying bacterium suffers a diminution of power during artificial cultivation. That the formation of nitric from nitrous acid may be brought about by a second organism I am in a position to assert, but this of course does not exclude the possibility of the second alternative.

I hope, before long, to communicate to the Chemical Society the full results of my investigation.

ON THE PERIODIC LAW.

By JOHN A. R. NEWLANDS, F.I.C., F.C.S.

IN the *Chemical Society's Journal* for October last (No. 323, p. 638), in the Faraday Lecture, by Prof. Mendeleeff, on the Periodic Law of the Chemical Elements, an erroneous statement occurs which is doubtless due to an accidental oversight on the part of the distinguished lecturer. He refers to a Table of mine published in the *CHEMICAL NEWS* (vol. xii., p. 83), and gives its first and last horizontal lines in the following way:—

1st Octave of
Newlands H F Cl Co and Ni Br Pd I Pt and Ir
7th ditto.. .. O S Fe Se Rh and Ru Te Au Os or Th

Now the complete table from which the above lines were taken was as follows:—

No.	No.	No.	No.	No.	No.	No.	No.	No.	No.
H 1	F 8	Cl 15	Co & Ni 22	Br 26	Pd 36	I 42	Pt & Ir 50		
Li 2	Na 9	K 16	Cu 23	Rb 30	Ag 37	Cs 44	Tl 53		
G 3	Mg 10	Ca 17	Zn 25	Sr 31	Cd 38	Ba & V 45	Pb 54		
Bo 4	Al 11	Cr 19	Y 24	Ce & La 33	U 40	Ta 46	Th 56		
C 5	Si 12	Ti 18	In 26	Zr 32	Sn 39	W 47	Hg 52		
N 6	P 13	Mn 20	As 27	Di & Mo 34	Sb 41	Nb 48	Bi 55		
O 7	S 14	Fe 21	Se 28	Ro & Ru 35	Te 43	Au 49	Os 51		

NOTE.—Where two elements happen to have the same equivalent, both are designated by the same number.

This Table contained the whole of the then known elements, numbered off in the order of their atomic weights and arranged with a few slight transpositions so as to bring members of the same group on the same horizontal line.

A similar Table was shown at the Meeting of the Chemical Society, March 1, 1866, except that the last vertical column of elements in it was given absolutely in numerical order, thus:—

	No.
Pt and Ir	50
Os	51
Hg	52
Tl.. ..	53
Pb	54
Bi	55
Th	56

It will be seen that in Prof. Mendeleeff's illustration of my table, the ordinal numbers have been entirely omitted. In addition, the symbols on his upper line are described as my "1st octave," and those on the lower line as my "7th octave," whereas on my system, which follows the natural order of the atomic weights, the 1st octave comprises the eight elements from H to F, as shown in the above table.

I have long since pointed out that when the elements are arranged in the natural order of their atomic weights "the difference between the number of the lowest member of a group and that immediately above it is 7; in other words, the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note of an octave in music" (*CHEM. NEWS*, vol. x., p. 94, Aug. 20, 1864). Now there could be no eighth note in the octave unless there were seven consecutive notes preceding. In fact, an octave in music has been defined as "a collection of eight consecutive notes." Taking the natural notes on the key-board of a piano for instance, commencing with the first note, say A, it, and all consecutive notes up to and including the next A, would be termed the first octave, but it would be incorrect and quite inadmissible to describe all the A's on the key-board as belonging to the first octave, or all the G's as belonging to the seventh octave.

Laboratory, 27, Mincing Lane, E.C.,
March 18, 1890.

A NEW METHOD FOR THE ANALYSIS OF ZINC AND COPPER ALLOYS.

By H. N. WARREN, Research Analyst.

THE following method of separation of zinc from copper and other allied metals, which was introduced by the author at the commencement of the present year, and is now being satisfactorily worked in several commercial laboratories, depends chiefly upon the superior affinity of magnesium to replace not only copper and metals of the same group, but, by suitable means, to effect a complete separation of such oxidisable metals as zinc, iron, &c. The method, although speedy and accurate, is perhaps

better suited in cases where an approximate idea is known as to the nature of the alloy qualitatively. In the case of the sample presented being a brass alloy, which should, for convenience sake, be obtained in the form of filings, a suitable weighed quantity is introduced into a small conical flask, to which is added strong H_2SO_4 in proportion to the quantity of sample taken. On applying a gentle heat from a sand-bath for a few minutes the alloy is quickly rendered soluble, and the whole diluted with

water to a convenient bulk. A few coils of magnesium tape are now introduced into the solution and the solution maintained at about 100° F., until the whole of the copper is precipitated, which is ascertained by the absence of a red precipitate upon the addition of a drop of potassium sulphocyanide to the filtrate. The precipitated copper, which should be of a perfect red colour, is filtered, and finally washed into a tared platinum dish by the aid of a small quantity of ether, and dried in the air-bath, from whence the weight is readily obtained by the usual method. If tin, antimony, or other metals of the same group are suspected, the copper must necessarily be further examined.

To the filtrate is added a somewhat strong solution of sodium acetate, and the whole raised to the boiling-point; by this means any free sulphuric acid is neutralised, all the iron that may be present is precipitated as tribasic acetate, and the sulphate of zinc present converted into acetate. Into this is introduced a further quantity of magnesium, and, in this instance, the form of thick sheet or rod is better adapted than that of tape, the precipitated zinc being the more readily detached from the same. Upon the introduction of the magnesium a brisk reaction follows, accompanied by a copious supply of hydrogen, the zinc being entirely precipitated, inasmuch that not the slightest precipitate is obtained on the addition of ammonia and ammonium sulphide to the filtrate, the zinc thus obtained being treated as in the former instance, which, if successfully performed, shows very slight signs of oxidising.

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

THE VOLUMETRIC DETERMINATION OF COPPER.

By A. ETARD and P. LEBEAU.

WE cannot estimate copper accurately by any rapid method, for the electrolytic method, which is perfect, requires some time. Various volumetric processes have been proposed, but in none of them is the end of the operation shown with certainty.

One of the most expeditious methods is that in which the yellow colour of a copper salt dissolved in an excess of strong hydrochloric acid is made to disappear by means of a stannous solution. The colouration observed is due to a cupric chloride hydrochlorate,—



The yellow colour not being very intense, it is not easy to note the end of the determination.

Recently there has been pointed out a colour reaction of copper produced in presence of sulphuric acid and potassium bromide. The reaction, however, is due to the cupric bromide in presence of strong hydrobromic acid, without the participation of sulphuric acid. There is probably formed a violet hydrobromate of cupric bromide.

The colouration is developed in mediums containing only CuBr_2 , HBr , and H_2O as necessary elements. A small excess of water turns the violet colour to an ordinary copper green.

The authors use this bromo-cupric colouration as an indicator for the volumetric determination of copper.

Any salt of copper whatever, in a strong solution, treated with an excess of concentrated hydrobromic acid, takes a violet colour like that of permanganate. Such a solution, if mixed with a standard solution of stannous bromide or chloride dissolved in strong hydrobromic acid, scarcely grows paler, and at the end it is abruptly decolourised by a single drop of the stannous liquid. The time during which the stannous liquid is run in must not be too prolonged, as on contact with air the violet colour is reproduced.

The process is relatively costly, but we may use, with-

out inconvenience, a solution of stannous chloride in strong hydrochloric acid, free from iron.

The stannous solution is, in any case, run into the concentrated solution of the cupric salt after the addition of a few c.c. of strong hydrobromic acid. The portion taken for analysis must be free from oxidising and reducing agents.

The standard of the stannous solution must be verified from time to time.—*Comptes Rendus*, vol. cx., p. 408.

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLET, F.R.S.,
Professor of Chemistry in the University of Virginia.

(Continued from p. 128).

Sixth Series of Experiments.

THESE experiments consisted merely in the further application of electrolysis to the deposition of metallic gold from a solution of potassium auro-cyanide, comparing the weight of the metal thrown down, however, not with the weight of silver, but with the volume of hydrogen gas liberated by the action of the same current, the object being to thus secure, with an assumed knowledge of the density of hydrogen, a direct comparison of the atomic weight of gold with that of the element most generally taken as the basis of the numerical constants in question.

A cell containing the same solution of potassium auro-cyanide as was used in the fifth series of experiments, and having immersed in it a pair of plates of "proof" gold, as already described, was employed for the deposition of the gold. The same current which traversed this cell was passed through a hydrogen voltameter of special construction,† made of glass, in a single piece, the general character of which will be seen from Fig. 5.

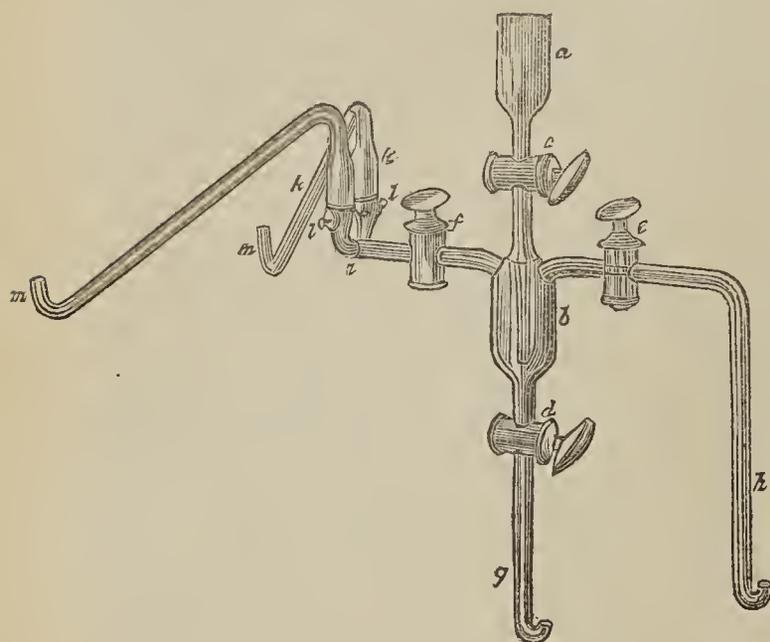
When this instrument was to be prepared for use, it was cautiously heated pretty strongly in an air-bath to remove the film of moisture and air from the internal surface, drawing dry air through by means of an aspirator. Clean mercury, previously heated, was then poured in through the funnel *a*, going down to nearly the bottom of the cylindrical vessel *b*, until this vessel—about 30 m.m. in diameter, and 60 m.m. in height—was completely filled, and also the tubes and stop-cocks, *c*, *d*, *e*, and *f*, each of these in succession being opened to allow escape of air, and afterwards closed; *f* was a three-way stop-cock, which could either be made to open communication between the parts of the tube on either side of it, or to simply close this tube, or to close this tube and establish communication between the vessel *b* and the outside air through the base of the stop-cock; it was in this last-named way that air and surplus mercury were allowed to escape, filling the tube between *b* and *f* with mercury, but not allowing of any of the metal going further along the tube towards *i*. The stop-cock *c* was closed, with the tube on which it was situated completely full with mercury, and leaving surplus mercury in the funnel *a*. In filling *b* and its connected tubes, care was taken to leave no visible bubbles of air. Pure water mixed with one-twelfth its weight of pure sulphuric acid was boiled for some time in a small flask, to dispel all dissolved air, keeping up the volume by additions from time to time of water kept boiling in a second flask; the lower turned-up end of the tube *h* was then immersed in the dilute acid, and the lower end of *g* in a cup of mercury; on opening the stop-cocks *e* and *d* mercury ran out from *g*, and the dilute acid came in

* A Paper read before the Royal Society, May 9, 1889.

† This piece of apparatus—an excellent specimen of skilful glass-blowing—was made, from drawings furnished by me, by Mr. Emil Greiner, 63, Maiden Lane, New York.

through *h*, filling about half-full the cylinder *b*. Closing *d* and *e*, opening *c*, and keeping up a supply of mercury in the funnel *a*, *f* was now turned so as to force out through the base of this stop-cock the little mercury in the tube behind it, and fill this tube with the acidulated water. Then *f* was turned so as to allow of this acidulated water being forced on to the bend, *i*, and into the two little voltameter tubes, *k* and *k*, filling these about one-third full. While these tubes were being thus filled, the extremities of the delivery tubes, *m* and *m*, were in communication with a Sprengel pump, so that they were very nearly exhausted of air. The stop-cock *f* having been closed, *e* was opened, and by suitable tilting of the apparatus, and running in of mercury from the funnel, *a*, nearly all of the acidulated water from *f* backwards was expelled through the tube *h*. A repetition of the procedure by which the cylinder, *b*, had been partially filled with acidulated water now served to partially fill it with well-boiled and still hot distilled water, to which no acid had been added. The two delivery tubes, *m* and *m*, were severally detached from the Sprengel pump, after allowing (by a special separate arrangement of tubes with stop-cocks) hydrogen to enter one of the two and oxygen the other, and when thus filled the ends of these two tubes

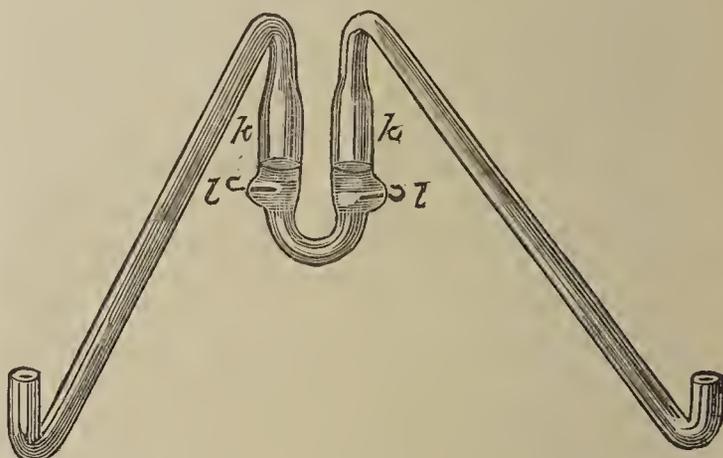
FIG. 5.



from time to time a little tapping of the apparatus to get rid of the effect of irregular adhesion of the liquid to the walls of the voltameter tubes.

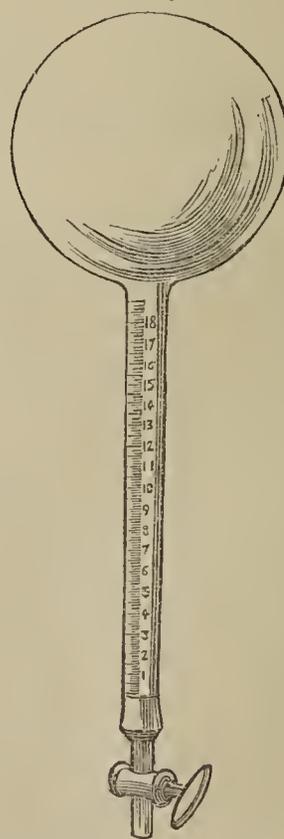
It will be seen that, with the arrangement described, the electrolysis could be effected of acidulated water, thoroughly deprived in advance of dissolved air, and in

FIG. 6.



quantity so small as to be capable of retaining in solution but infinitesimal quantities of the hydrogen and oxygen electrolytically separated. As the decomposition proceeded, the quantity of liquid in the voltameter tubes could be maintained constant by opening the stop-cock *c*, with a supply of mercury in the funnel *a*, and then cautiously opening *f*, so as to feed forward a little of the air-free water from the cylinder *b*, thus leaving the proportion of acid unaltered. The surface presented by the

FIG. 7.



were dipped under mercury, and the two platinum wires *l* and *l*, sealed into the voltameter tubes were connected by the little rings on their outer ends with the terminals of the galvanic cells whence the electric current was to be derived, taking care, of course, to connect to the negative pole the wire of the tube already filled in its upper part with hydrogen, and to the positive pole the wire of the oxygen tube. Viewed from the front, the two voltameter and delivery tubes presented the appearance shown in Fig. 6. The little voltameter tubes, *k* and *k*, had an external diameter of about 12 m.m. and a length of 40 m.m. The platinum wires, *l* and *l*, serving as electrodes, were 1 m.m. in diameter, and extended beyond the interior surface of the glass (into which they were sealed) for only 3 m.m. in length. They could be well covered, and the voltameter tubes filled to one-third their capacity, with only about 2 c.m. of the acidulated water. By careful tilting of the apparatus laterally it was found to be possible to so regulate the pressure of mercury at the ends of the delivery tubes, and therefore the gaseous tension in the two voltameter tubes, that the acidulated water was not forced over from the one to the other, which, had it occurred, would have allowed admixture of the two gases; this required constant watching, however, and there was needed

platinum wire electrodes was so small as to allow of occlusion of the gases to only an extremely minute extent, and both the hydrogen and oxygen were allowed to escape for some time before any was collected for measurement.

The hydrogen only was collected and measured. I had hoped to apply this form of voltameter to a more exact

determination of the relative volumes of hydrogen and oxygen derived from water by electrolysis than is possible with the voltameters of more common construction. But I have not yet seen my way to getting over the difficulties connected with the presence of ozone, hydrogen dioxide, Berthelot's per-sulphuric acid, or other by-products in the oxygen gas evolved at the positive pole. If this could be accomplished, a useful contribution might possibly be made to the question, revived and worked upon of late by several chemists, of the exact atomic weight of oxygen. The vessel for collecting and measuring the hydrogen, shown in Fig. 7, consisted of a spherical globe of tolerably stout glass, with a capacity of about 250 c.m., having a neck of about 1 c.m. internal diameter, and 22 c.m. long. This neck had etched upon it a simple linear scale of millimetres. At the mouth it was fitted with a well-ground perforated glass stopper, forming part of a glass stop-cock with an outer orifice of about 1 m.m. bore. The exact capacity of the whole globe and neck was ascertained by heating it in an air-bath to remove air and moisture condensed on the interior surface, drawing dry air through with an aspirator, then filling the globe with heated mercury, allowing it to cool to an accurately noted temperature, immersing the body of the globe in an outer vessel of mercury so as to prevent extension or flexure of the glass by the weight of the contained metal, filling up to the very mouth with mercury, inserting the stopper with the stop-cock open, thus forcing out through its orifice the last of the air, closing the stop-cock, removing from the orifice tube, by an iron wire, the drop or two of mercury remaining in it, and then emptying the flask, and carefully weighing in successive portions the mercury which it had held. The hydrogen from the voltameter was collected in this flask, without its stopper, the flask having been previously filled with mercury, with the needful precautions for removal of all air, and inverted over a mercury trough. In each experiment the process of electrolysis was arrested when the hydrogen had filled the body of the globe and reached to a point rather more than half-way down the length of the neck, the gold plates being of course withdrawn at the same moment from their cell of gold solution, set away to soak in distilled water, and afterwards thoroughly washed, dried, heated in the Sprengel vacuum, cooled, and weighed. The portion of hydrogen collected was dried by successive balls of fused potash introduced and withdrawn by means of platinum wire. The neck of the flask having, in advance of the collection of hydrogen, been passed through a cork, this was used to close the mouth, placed downwards, of a vessel through which a stream of water was caused to flow rapidly from the pipes supplying the University buildings. The atmospheric temperature of the day on which the electrolysis experiment was made having been such as not to differ too much from the temperature of the water from the pipes, the gas occupied such a volume after effectual exposure to this latter temperature that the mercury marked a point somewhere within the length of the neck, which point was noted by the millimetre scale, the thermometer immersed in the flowing water, and the barometer and its attached thermometer being read at the same time. It remained only to insert the stop-cock stopper under the mercury of the little mercury trough, close the stop-cock, withdraw the flask from the trough, reject the drop or two of mercury from the stopcock orifice by means of a wire, remove the portion of mercury left in the neck of the flask, and weigh it carefully. Its weight, with considera-

tion of its temperature when the stop-cock was closed, gave the volume of the portion of the flask not occupied by hydrogen, and this, subtracted from the whole volume of the interior of the flask, as found by the original calibration, gave the volume, under known conditions of temperature and pressure, of the hydrogen which had been collected. From two calibrations at different temperatures a correction was obtained for the expansion of the glass of the flask, but it was hardly necessary to take this into account, in view of the small limits within which temperature varied in all the experiments made.

But three experiments carried out by this method led to results which seemed worthy of confidence. These results were as in Table below.

In calculating the weight of hydrogen from its observed volume, Regnault's value for the weight of a litre of this gas at 0° C. and 760 m.m. was taken as the basis. The correction, of which Lord Rayleigh not long since pointed out the need—namely, for the compression of the vacuum glass flask by atmospheric pressure—was adopted from the experiments of J. M. Crafts (*Comptes Rendus*, vol. cvi., p. 1662); and his corrected value, 0.08988 grm., was still further corrected for the difference in the force of gravity at Paris and at the University of Virginia (in C.G.S. units, 980.94 : 979.95), giving as the value to be used 0.08979 grm.

The electrolysis of the water was carried on very slowly, so as to keep the density of the current low with such small electrodes as were used. Nevertheless, as the hydrogen voltameter required constant watching, it became necessary to bring the whole time of an experiment within moderate limits, and hence a considerably stronger current was used than in the simultaneous deposition of gold and silver in the fifth series, this circumstance being less favourable to the satisfactory deposition of the gold. It would have been desirable to use a larger flask, and to collect a greater volume of hydrogen; but this, on account of the time required, would have made an experiment exceedingly troublesome and difficult.

In the work of this series the same unsatisfactory need for selecting only such results as came fairly close to the figures expected, and rejecting several others on the ground of very considerable departure therefrom, and the same sources of possible constant error in regard to the gold deposit present themselves which have already been noticed under the head of the fifth series. As regards the hydrogen, one is led to consider possible diffusion of hydrogen and oxygen between the two little voltameter tubes, and slight imperfection in the drying of the hydrogen obtained. The former would, on the whole, probably tend to diminish the volume of gas collected, and hence to raise the apparent value of the atomic weight of gold. The latter would have the opposite tendency. That neither can have had more than an extremely minute influence was fairly proved by testing a part of the hydrogen obtained, on the one hand, by passing it through a red-hot glass tube, and on the other by submitting it to more extended drying by contact with phosphorus pentoxide both before and after such heating; in neither case was there appreciable change of volume.

Notwithstanding the desirability of comparing the atomic weight of any other element directly with that of hydrogen, the difficulty is not to be overlooked of doing this for an element having so high an atomic weight as that of gold. There is a manifest objection to the necessity of dealing with such minute quantities of hydrogen as those concerned in these experiments. A

Experiment.	Character of gold in solution.	Character of gold in plates.	Gold deposited. Grms.	Hydrogen liberated.	
				Vol. at 0° C. and 760 m.m. C.m.	Weight. Grm.
I.	A, b	C	4.0472	228.64	0.02053
II.	A, b	C	4.0226	227.03	0.02039
III.	A, b	C	4.0955	231.55	0.02079

very small error in the determination of the hydrogen greatly affects the value found for an atomic weight nearly two hundred times as large. It is true that the measurement of the volume of the hydrogen admits of being made with such precision as to leave room for but an extremely minute error in the corresponding weight, yet this measurement is not one of *limitless* delicacy, particularly if the difficulty be properly appreciated of ascertaining with certainty the precise temperature of the gas at the time its volume is read. Moreover, in measuring the volume of the gas, and thence deducing its weight, there is need not merely for a knowledge of changes of temperature and pressure, but for *absolutely* correct readings of the barometer and thermometer, so that there must usually be a degree of hesitation in accepting the readings of even fairly standard instruments, when temperature and pressure come to be placed in comparison with these conditions as affecting the results of Regnault for gaseous density. Nor can the results of that great physicist be assumed as themselves free from all possible need of further correction.

The error of direct comparison with so small an atomic weight as that of hydrogen is, however, after all only *masked* by substituting an *indirect* comparison through some larger atomic weight, since the assumed value of the latter is uncertain within limits which depend upon its comparison with the atomic weight of hydrogen.

(To be continued).

THE GLOW OF PHOSPHORUS.*

By Professor THORPE, F.R.S.

THE word *phosphorus* originally applied to any substance, solid or liquid, which had the property of shining in the dark, has gradually lost its generic sense, and is nowadays practically restricted, as a designation, to the wax-like inflammable substance which plays such an important part in the composition of an ordinary lucifer match. Phosphorus, indeed, is one of the most remarkable of the many remarkable substances known to the chemist. The curious method of its discovery, the universality of its distribution, its intimate connection with the phenomena of animal and vegetable life, its extraordinary physical properties and chemical activity, its abnormal molecular constitution, the protean ease of its allotropic transformations, all combine to make up a history which abundantly justifies its old appellation of the *phosphorus mirabilis*. Godfrey Hankewitz, more than 150 years ago, wrote:—"This phosphorus is a subject which occupies much the thoughts and fancies of some alchemists who work on microcosmical substances, and out of it they promise themselves golden mountains." Certainly no man of his time made more in the way of gold out of phosphorus than Mr. Hankewitz, for at his little shop in the Strand he enjoyed for many years the monopoly of its sale, guarding his *arcana* with all the jealousy of a modern manufacturer of the element.

Phosphorus, or, as it was then called, *noctiluca*, was first seen in this country in 1677. It was shown to Robert Boyle, who had already worked on phosphorescence in general, and who seems to have been specially struck with the remarkable peculiarity of a factitious body which could be made "to shine in the dark without having been before illumined by any lucid substance, and without being hot as to sense." In these respects the substance differed from all the *phosphori* hitherto known. The conditions which determine its glow were the subject of the earliest observations on phosphorus, and Boyle has left us a minute account of his work on the point. In the first place, he noticed that

the substance was only luminous in presence of air. He accurately describes the nature of the light, and noticed that "the water in which the phosphorus was partially immersed acquired a strong and penetrant taste, . . . and relished a little like vitriol. On evaporation it would not shoot into crystals, . . . but coagulated into a substance like a Gelly, or the Whites of Eggs, which would be easily melted by heat. On heating this 'Gelly' 'it gave off flashes of fire and light,' and had a 'garlick smell.'" He also found that the *noctiluca* was soluble in certain oils, and he particularly mentions oil of cloves as a convenient means of showing the luminosity as it is "rendered more acceptable to the standers-by by its grateful smell. In Oyl of Mace it did not appear luminous, nor in Oyl of Aniseeds." Boyle describes a number of experiments showing how small a quantity of the phosphorus is required to produce a luminous effect. "A grain of the *noctiluca* dissolved in Alkohol of Wine and shaken in Water; it render'd 400,000 times its weight luminous throughout. And at another Tryal I found that it impregnated 500,000 times its weight; which was more than one part of Cochineel could communicate its colour to. And one thing further observable was that when it had been a long time exposed to the air it emitted strong and odorous exhalations distinct from the visible fumes." The strong and odorous exhalations we now know to be ozone.

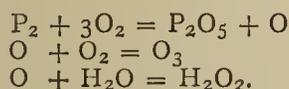
The earlier volumes of the *Philosophical Transactions of the Royal Society* contain several papers on the luminosity of phosphorus, and one by Dr. Frederic Slare is noteworthy, as giving one of the earliest, if not actually the earliest, account of what is one of the most paradoxical phenomena connected with the luminosity of phosphorus, namely, its increase on rarefying the air. "It being now generally agreed that the fire and flame [of phosphorus] have their pabulum out of the air, I was willing to try this matter *in vacuo*. To effect this, I placed a considerable lump of this matter (phosphorus) under a glass, which I fixed to an engine for exhausting the air; then presently working the engine, I found it grow lighter [*i.e.*, more luminous], though a charcoal that was well kindled would be quite extinguished at the first exhaustion; and upon the third or fourth draught, which very well exhausted the glass, it much increased in light, and continued so to shine with its increased light for a long time; on re-admitting the air, it returns again to its former dulness." This observation was repeated and its result confirmed by Hawksbee, in this country, and by Homberg, in France, and seems subsequently to have led Berzelius, and after him Marchand, to the conclusion that the luminosity of phosphorus was altogether independent of the air (*i.e.*, the oxygen), but was solely due to the volatility of the body. Many facts, however, combine to show that the air (oxygen) is necessary to the phenomenon. Lampadius found that phosphorus would not glow in the Torricellian vacuum, and Lavoisier, in 1777, showed that it would not inflame under the same conditions; and the subsequent experiments of Schrotter, Meissner, and Müller are decisive on the point that the glow is the concomitant of a chemical process dependent upon the presence of oxygen. It is, however, remarkable that phosphorus will not glow in oxygen at the ordinary atmospheric pressure and temperature, but that if the oxygen be rarefied the glow at once begins, but ceases again immediately the oxygen is compressed. Indeed, phosphorus will not glow in compressed air, and the flame of feebly burning phosphorus may be extinguished by suddenly increasing the pressure of the gas. Phosphorus, however, can be made to glow in oxygen at the ordinary pressure, or in compressed air if the gases be gently warmed. In the case of oxygen, the glow begins at 25° and becomes very bright at 36°. In compressed air the temperature at which the glow begins depends upon the tension. If the oxygen be absolutely deprived of moisture the phosphorus refuses to glow under any conditions. This fact, strange as it may seem, is not with-

* A Lecture delivered at the Royal Institution, on Friday, March 14, 1890.

out analogy; the presence of traces of moisture appears to be necessary for the initiation or continuance of chemical combination in a number of instances.

It was observed by Boyle that a minute quantity of the vapour of a number of essential oils extinguished the glow of phosphorus. The late Professor Graham confirmed and extended these observations; he showed that relatively small quantities of olefiant gas and of the vapours of ether, naphtha, and oil of turpentine entirely prevented the glow, and subsequent observers have found that many essential oils, such as those of peppermint and lemon, and the vapours of camphor and asafetida, even when present in very small quantity, stop the absorption of oxygen, and the slow combustion of phosphorus in air.

It has been established that whenever phosphorus glows in air, or in rarefied oxygen, ozone and hydrogen peroxide are formed, but it is not definitely known whether the formation of these substances is the cause or the effect of the chemical process of which the glow is the visible sign. That there is some intimate connection between the luminosity of the phosphorus and the production of these bodies is highly probable. Schonbein, as far back as 1848, sought to demonstrate that the glow depends on the presence of ozone. It is certainly true that many of the substances, such as the essential oils, which prevent the glow of phosphorus, also destroy ozone. At a low temperature phosphorus produces no ozone in contact with air, neither does it glow. It has been found, in fact, that with air ozone is produced in largest quantity at 25°, at which temperature phosphorus glows brightly. On the assumption that the oxidation of the phosphorus consists in the immediate formation of the highest oxide, the production of the ozone and the hydrogen peroxide has been represented by the following equations:—



Both these reactions may, of course, go on simultaneously; ozone and hydrogen peroxide are not mutually incompatible; the synthesis of hydrogen peroxide by the direct oxidation of water seems to occur in a number of processes. But such symbolic expressions can at most be only very partial representations of what actually occurs. It is highly probable that the combination which gives rise to the glow only occurs between the vapour of phosphorus and the oxygen. Phosphorus is sensibly volatile at ordinary temperatures, and by rarefying the atmosphere in which it is placed its volatilisation is increased, which serves to account for the increased glow when the pressure of the gas is diminished. When phosphorus is placed in an atmosphere of hydrogen, nitrogen, or carbonic acid, these gases, when brought into contact with oxygen, become luminous from the oxidation of the vapour of phosphorus diffused through them. The rapidity of volatilisation varies with the particular gas; it is greatest in the case of hydrogen, and least in that of carbonic acid. Indeed, a stream of hydrogen gas at ordinary temperatures carries away comparatively large quantities of phosphorus, which may be collected by appropriate solvents. No ozone and no glow is produced in oxygen gas at ordinary temperatures and pressures, but on warming the oxygen both the ozone and the glow are formed. On passing ozone into oxygen at temperatures at which phosphorus refuses to glow, the phosphorus at once becomes luminous, oxygen is absorbed, and the characteristic cloud of oxide is produced, and the effect continues so long as the supply of ozone is maintained. A drop of ether at once extinguishes the glow.

Phosphorus combines with oxygen in several proportions, and the study of the mode of formation and properties of these oxides is calculated to throw light upon the nature of the chemical process which attends the glow of phosphorus.

Certain of these oxides have recently been the subject

of a considerable amount of study in the chemical laboratories of the Normal School of Science.

When phosphorus is slowly burned in air, there is produced a considerable quantity of a volatile substance having a characteristic garlic-like smell, which solidifies, when cooled, in beautiful arborescent masses of white crystals. It melts at about 23° and boils at 173°. In a sealed tube, kept in the dark, it may be preserved unchanged, but on exposure to light, and especially to bright sunshine, it rapidly becomes deep red. It slowly absorbs oxygen at the ordinary temperature and pressure, but from the mode in which the solid product of the reaction (P₂O₅) is deposited, it is evident that the union only takes place between the vapour of the oxide and the oxygen gas. Under diminished pressure the act of combination is attended with a glow, which increases in brilliancy if ozone be present. On compressing the oxygen the glow ceases. No ozone is formed during the act of oxidation. The degree of rarefaction needed to initiate the glow depends upon the temperature of the oxide; the warmer the oxide the less is the diminution of pressure required. By gradually warming the oxide the luminosity steadily increases, both in area and intensity, until at a certain temperature the mass ignites. The change from glow to actual flame is perfectly regular and gradual, and is unattended with any sudden increase in brilliancy. In this respect the process of oxidation is analogous to the slow and barely visible burning of fire-damp which is sometimes seen to occur in the Davy lamp, or to the slow combustion of ether and other vapours which has been specially studied by Dr. Perkin. Other instances of what may be called *degraded combustion* are known to chemists. Thrown into warm oxygen, the substance burns into flame at once and burns brilliantly, and it also takes fire in contact with chlorine. Alcohol also ignites it, and when it is warmed with a solution of potash it evolves spontaneously inflammable phosphoretted hydrogen. In contact with water it suffers only a very gradual change, and many days may elapse before even a comparatively small quantity is dissolved. This substance has long been known; it was discovered, in fact, by the French chemist Sage, but its true nature has only now been determined; its chemical formula is found to be P₄O₆, hence its composition is similar to that of its chemical analogue, arsenious oxide.

The study of the properties of this remarkable substance enables us to gain a clearer insight into the nature of the chemical process attending the glow of phosphorus. When phosphorus is placed in oxygen, or in an atmosphere containing oxygen, under such conditions that it volatilises, the phosphorus oxidises, partly into phosphoric oxide and partly into phosphorous oxide. Ozone is formed, possibly by the reaction already indicated, and this reacts upon the residual phosphorus vapour and the phosphorus oxide, with the production of the luminous effect to which the element owes its name. The glow itself is nothing but a slowly burning flame, having an extremely low temperature, caused by the chemical union of oxygen with the vapours of phosphorus and phosphorous oxide. By suitable means this glow can be gradually augmented until it passes by regular gradation into the active vigorous combustion which we ordinarily associate with flame. Many substances, in fact, may be caused to phosphoresce in a similar way. Arsenic, when gently heated, glows in oxygen, and sulphur may also be observed to become luminous in that gas at a temperature of about 200°.

A Contribution to the Chemical Study of the Truffle.—Ad. Chatin.—The author determines the absolute weight of nitrogen, its proportion to the totality of the organic matter, the weight of the ash, and the proportion of each of the mineral elements. An analysis of the soils was carried on simultaneously. In the ash of the truffle the phosphoric acid ranges from 20 to 30 per cent.—*Comptes Rendus*, Vol. cx., No. 8.

SMOKELESS EXPLOSIVES.*

By Sir FREDERICK ABEL, C.B., D.C.L., D.Sc., F.R.S., V.P.R.I.

THE production of smoke which attends the ignition or explosion of gunpowder is often a source of considerable inconvenience in connection with its application to naval or military purposes, its employment in mines, and its use by the sportsman, although occasions not unfrequently arise during naval and military operations when the shroud of smoke produced by musketry or artillery fire has proved of important advantage to one or other, or to both, of the belligerents during different periods of an engagement.

Until within the last few years, however, but little, if any, thought appears to have been given to the possibility of dispensing with or greatly diminishing the production of smoke in the application of fire-arms, excepting in connection with sport. The inconvenience and disappointment often resulting from the obscuring effects of a neighbouring gun-discharge, or of the first shot from a double-barrel gun, led the sportsman to look hopefully to gun-cotton, directly after its first production in 1846, as a probable source of greater comfort and brighter prospects in the pursuit of his pastime and in his strivings for success.

A comparison between the chemical changes attending the burning, explosion, or metamorphosis of gun-cotton and of gunpowder, serves to explain the cause of the production of smoke in the latter case, and the reason of smokelessness in the case of gun-cotton. Whilst the products of explosion of the latter consist exclusively of gases and of water which assumes the transparent form of highly-heated vapour at the moment of its production, the explosive substances classed as gunpowder, composed of mixtures of saltpetre or another nitrate of a metal, with charred wood or other carbonised vegetable matter, and with variable quantities of sulphur, furnish products of which very large proportions are not gaseous, even at high temperatures. Upon the ignition of such a mixture, these products are in part deposited in the form of a fused residue, which constitutes the fouling in a fire-arm, and are in part distributed, in an extremely fine state of division, through the gases and vapours developed by the explosion, thus producing smoke.

In the case of gunpowder of ordinary composition, the solid products amount to over fifty per cent by weight of the total products of explosion, and the dense white smoke which it produces consists in part of extremely finely divided potassium carbonate, which is a component of the solid products, and, to a great extent, of potassium sulphate, produced chiefly by the burning of one of the important solid products of explosion—potassium sulphide—when it is carried in a fine state of division into the air by the rush of gas.

With other explosives, which are also smoke-producing, the formation of the smoke is due to the fact that one or other of the products, although existing as vapour at the instant of its development, is immediately condensed to a cloud composed of minute liquid particles or of vesicles, as in the case of mercury vapour liberated upon the explosion of mercuric fulminate, or of the aqueous vapour produced upon the ignition of a mixture of ammonium nitrate and charcoal, or ammonium nitrate and picric acid.

Until within the last half-dozen years, the varieties of gunpowder which have been applied to war purposes in this and other countries have exhibited comparatively few variations in chemical composition. The proportions of charcoal, saltpetre, and sulphur, employed in their production, exhibit slight differences in different countries, and these, as well as the character of the charcoal used, its sources and method of production, underwent but

little modification for very many years. The same remark applies to the nature of the successive operations pursued in the manufacture of black powder for artillery purposes in this and other countries.

The replacement of smooth-bore guns by rifled artillery, which followed the Crimean war, and the increase in the size and power of guns consequent upon the application of armour to ships and forts, soon called for the pursuit of investigations, having for their object the attainment of means for variously modifying the action of fired gunpowder, so as to render it suitable for the different calibres of guns, whose full power could not be effectively, or in some instances safely, developed by the use of the kind of gunpowder previously employed indiscriminately in artillery of all known calibres.

In order to control the violence of explosion of gunpowder, by modifying the rapidity of transmission of explosion from particle to particle, or through the mass of each individual particle, of which the charge of a gun is composed, the accomplishment of the desired results was, in the first instance, and indeed throughout practical investigations extending over many years, sought exclusively in modifications of the size and form of the individual masses composing a charge of powder, and of their density and hardness; it being considered that, as the proportions of saltpetre, charcoal, and sulphur, generally employed in the production of gunpowder, very nearly correspond to those required for the development of the greatest chemical energy by those incorporated materials, it was advisable to seek for the attainment of the desired results by modifications of the physical and mechanical characters of gunpowder, rather than by any modification in the proportions and chemical characters of its ingredients.

The varieties of powder, which, as the outcome of careful, practical, and scientific researches in this direction, have been introduced into artillery service from time to time, and some of which, at any rate, have proved fairly efficient, have been of two distinct types. The first of these, produced by breaking up more or less highly-pressed cakes of black powder into grains, pebbles, or boulders of approximately uniform size and shape, the sharp edges and rough surfaces being afterwards removed by attrition (reeling and glazing), are simply a further development of one of the original forms of granulated or corned powder, represented by the old F. G., or small arms and L. G., or cannon powder. Gunpowders of this class, ranging in size from about 1000 pieces to the ounce to about six pieces to the pound, have been introduced into artillery service, and certain of them, viz., R. L. G. (rifle large grain), which was the first step in advance upon the old cannon powder (L. G.), pebble powder (P), and large pebble or boulder powder (P 2), are still employed more or less extensively in some guns of the present day.

The other type of powder has no representative among the more ancient varieties; it has its origin in the obviously sound theoretical view that uniformity in the results furnished by a particular powder, when employed under like conditions, demands not merely identity in regard to composition, but also identity in form, size, density, and structure of the individual masses composing the charge used in a gun. The practical realisation of this view should obviously be attained, or at any rate approached, by submitting equal quantities of one and the same mixture of ingredients, presented in the form of powder of uniform fineness and dryness to a uniform pressure for a fixed period in moulds of uniform size, and under surrounding conditions as nearly as possible alike. The fulfilment of these conditions would, moreover, have to be supplemented by an equally uniform course of proceeding in the subsequent drying and other finishing processes to which the powder masses would be submitted.

The only form of powder, introduced into our artillery service for a brief period, in the production of which

* A Lecture delivered before the Royal Institution of Great Britain, Friday, January 31, 1890.

these conditions were adhered to as closely as possible, was a so-called pellet powder, which consisted of small cylinders, having semi-perforations with the object of increasing the total inflaming surface of the individual masses.

Practical experience with this powder, and with others prepared upon the same system, but with much less rigorous regard to uniformity in such details as state of division and condition of dryness of the powder before its compression into cylindrical or other forms, showed that uniformity in the ballistic properties of black powder could be as well and even more readily secured by the thorough blending or mixing together of batches presenting some variation in regard to density, hardness, or other features, as by aiming at an approach to absolute uniformity in the characters of each individual mass composing a charge.

At the time that our attention was first actively given to this subject of the modification of the ballistic properties of powder, it had already been to some extent dealt with in the United States by Rodman and Doremus, and the latter was the first to propose the application, as charges for guns, of powder masses produced by the compression of coarsely grained powder into moulds of prismatic form. In Russia the first step was taken to utilise the results arrived at by Doremus, and to adopt a prismatic powder for use in guns of large calibre.

Side by side with the development and perfection of the manufacture of prismatic powder in Russia, Germany, and in this country, new experiments on the production of powder masses suitable, by their comparative gradual action, for employment in the very large charges required for the heavy artillery of the present day, by the powerful compression of mixtures of more or less finely broken up powder-cake into masses of greater size than those of the pebble, pellet, and prism powders, were actively pursued in Italy, and also by our own Government Committee on Explosives, and the outcome of very exhaustive practical investigations were the very efficient Fossano powder, or *poudre progressif*, of the Italians, and the boulder and large cylindrical powders known as P² and C², produced at Waltham Abbey, which scarcely vied, however, with the Italian powder in the uniformity of their ballistic properties.

Researches carried out by Captain Noble and the lecturer some years ago with a series of gunpowders differing considerably in composition from each other, indicated that advantages might be secured in the production of powders for heavy guns by so modifying the proportions of the constituents (*e.g.*, by considerably increasing the proportion of charcoal and reducing the proportion of sulphur) as to give rise to the production of a much greater volume of gas, and at the same time to diminish the heat developed by the explosion.

These researches served, among other purposes, to throw considerable light upon the cause of the wearing or erosive action of powder-explosions upon the inner surface of the gun, which in time produces so serious a deterioration of the aim that the velocity of projection and accuracy of shooting suffer very greatly, an effect, the extent of which increases in an increasing ratio to the size of the guns in consequence, obviously, of the large increase in the weight of the charges fired.

Several causes undoubtedly combine to bring about the wearing away of the gun's bore, which is especially great where the products of explosion, while under the maximum pressure, can escape between the projectile and the bore. The great velocity with which the very highly heated gaseous and liquid (fused solid) products of explosion sweep over the heated surface of the metal, gives rise to a displacement of the particles composing it, which increases as the surface becomes roughened by the first action upon the least compact portions of the metal, and thus opposes greater resistance; at the same time, the effect of the high temperature to which the surface is raised is to reduce its rigidity and power of resisting the

force of the gaseous torrent, and lastly some amount of chemical action upon the metal by certain of the highly heated non-gaseous products of explosion, contributes towards an increase in the erosive effects. A series of careful experiments made by Captain Noble with powders of different composition, and with other explosives, afforded decisive evidence that the explosive agent which furnished the largest proportion of gaseous products, and the explosion of which was attended by the development of the smallest amount of heat, exerted least erosive action.

It is probable that important changes in the composition of powders manufactured by us for our heavy guns would have resulted from those researches, but in the meantime, two eminent German gunpowder manufacturers had occupied themselves independently and simultaneously with the important practical question of producing some more suitable powder for heavy guns than the various new forms of ordinary black powder, the rate of burning of which, especially when confined in a close chamber, was, after all, reduced only in a moderate degree by the increase in the size of the masses, and by such increase in their density as it was practicable to attain. The German experimenters directed their attention not merely to an alteration of the proportions of the powder ingredients, but also to a modification in the character of charcoal employed, and the success attending their labours in these directions led to the practically simultaneous production, by Mr. Heidemann at the Westphalian Powder Works, and Mr. Düttenhofer at the Rottweil Works, near Hamburg, of a prismatic powder of cocoa-brown colour, consisting of saltpetre in somewhat higher proportion, of sulphur in much lower proportion than in normal black powder, and of very slightly burned charcoal, similar in composition to the charcoal (*charbon roux*) which Violette, a French chemist, first produced in 1847 by the action of superheated steam upon wood or other vegetable matter, and which he proposed for employment in the manufacture of sporting powder. These brown prismatic powders (or "cocoa powders," as they were termed from their colour) are distinguished from black powder, not only by their appearance, but also by their very slow combustion in open air, by their comparatively gradual and long-sustained action when used in guns, and by the simple character of their products of explosion as compared with those of black powder. As the oxidising ingredient, saltpetre, is contained, in brown or cocoa powder, in larger proportion relatively to the oxidisable components, sulphur and charcoal, than in black powder; these become fully oxidised, while the products of explosion of the latter contain, on the other hand, larger proportions of unoxidised material or of only partially oxidised products. Moreover, there is produced upon the explosion of brown powder a relatively very large amount of water-vapour, not merely because the finished powder contains a larger proportion of water than black powder, but also because the very slightly charred wood or straw used in the brown powder is much richer in hydrogen than black charcoal, and therefore furnishes by its oxidation a considerable amount of water. The total volume of gas furnished by the brown powder (at 0° C. and 760 m.m. barometer) is only about 200 volumes per kilogramme of powder, against 278 volumes furnished by a normal sample of black powder, but the amount of water-vapour furnished upon its explosion is about three times that produced from black powder, and this would make the volume of gas and vapour developed by the two powders about equal if the heat of its explosion were the same in the two cases; the actual temperature produced by the explosion of brown powder is, however, somewhat the higher of the two.

Although the smoke produced upon firing a charge of brown powder from a gun appears at first but little different in denseness to that of black powder, it certainly disperses much more rapidly, a difference which is probably due to the speedy absorption, by solution, of the

finely divided potassium salts by the large proportion of water-vapour distributed throughout the so-called smoke.

This class of powder was substituted with considerable advantage for black powder in guns of comparatively large calibre; nevertheless, it became desirable to attain even slower or more gradual action in the case of the very large charges required for guns of the heaviest calibres, such as those which propel shot of about 2000 lbs. weight. Accordingly, the brown powder has been modified in regard to the proportions of its ingredients to suit these conditions, while, on the other hand, powder intermediate with respect to rapidity of action between black pebble powder and the brown powder has been found more suitable than the former for use in guns of moderately large calibre.

The recent successful adaptation of machine guns and comparatively large quick-firing guns to naval service, more especially for the defence of ships against attack by torpedo boats, &c, has rendered the provision of a powder for use with them, which would produce comparatively little or no smoke, a matter of very considerable importance, inasmuch as the efficiency of such defence must be greatly diminished by the circumstance that, after a very brief use of the guns with black powder, the objects against which their fire is destined to operate become more or less completely hidden from those directing them by the dense veil of powder-smoke produced. Hence much attention has been directed during the last few years to the production of smokeless, or nearly smokeless, powders for naval use in the above directions. At the same time, the views of many military authorities regarding the importance of dispensing with smoke in land engagements has also created a demand, the apparent urgency of which has been increased by various circumstances, for a smokeless powder suitable for field artillery and small arms.

The properties of ammonium nitrate, of which the products of decomposition by heat are, in addition to water-vapour, entirely gaseous, have rendered it a tempting material to work upon in the hands of those who have striven to produce a smokeless powder; but its deliquescent character has been the chief obstacle to its application as a component of an explosive agent susceptible of substitution for black powder for service purposes.

A German chemical engineer, F. Gäns, conceived that, by incorporating charcoal and saltpetre with a particular proportion of ammonium nitrate, he had produced an explosive material which did not partake of the hygroscopic character common to other ammonium nitrate mixtures, and that by its explosion the potassium in the saltpetre formed a volatile combination with nitrogen and hydrogen, a *potassium amide*, so that, although containing nearly half its weight of potassium salt, it would furnish only volatile products. The views of Mr. Gäns regarding the changes which his so-called *amide powder* undergoes upon explosion were not borne out by existing chemical knowledge, while the powder compounded in accordance with his views proved to be by no means smokeless, and was certainly not non-hygroscopic. Mr. Heidemann has, however, been successful, by modifications of Gäns' prescription and by application of his own special experience in power-manufacture, in producing an ammonium nitrate powder possessed of remarkable ballistic properties, furnishing comparatively little smoke, which speedily disperses, and exhibiting the hygroscopic characteristics of ammonium nitrate preparations in a decidedly less degree than any other hitherto prepared. The powder, while yielding a very much larger volume of gas and water-vapour than black or brown powder, is considerably slower than the latter; the charge required to produce equal ballistic results is less, while the chamber-pressure developed is lower, and the pressures along the chase of the gun are higher, than in the case of brown powder,

The ammonium nitrate powder contains, in its normal dried condition, more water than even brown powder; it does not exhibit any great tendency to absorb moisture

from an ordinarily dry or even a somewhat moist atmosphere, but if the amount of atmospheric moisture approaches saturation it will rapidly absorb water, and when once the process begins it continues rapidly, the powder masses becoming speedily quite pasty. The charges for quick-firing guns are enclosed in metal cases, in which they are securely sealed up; the powder is therefore prevented from absorbing moisture from the external air, but it has been found that if the cartridges are kept for long periods in ship's magazines, in which, from their position relatively to the ship's boilers, the temperature is more or less elevated, sometimes for considerable periods, the expulsion of water from some portions of the powder-masses composing the hermetically sealed charge, and its constant irregular distribution, may give rise to a want of uniformity in the action of the powder, and to the occasional development of high pressures. Although, therefore, this ammonium nitrate powder may be regarded as the first successful advance towards the production of a comparatively smokeless artillery-powder, it is not uniformly well adapted to the requirements which it should fulfil in naval service.

(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, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, March 6th, 1890.

SIR,—We submit herewith the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from February 1st to February 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

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

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

Excepting two samples which were recorded as "very slightly turbid," the whole of the 168 samples examined were found to be clear, bright, and well filtered.

Judged by the determinations of colour-tint, and of oxygen required for oxidation, the character of the water-supply to the Metropolis during the month of February has scarcely differed appreciably from that manifested during the previous months of December and January. But the proportion of organic carbon found in the water, though still low, both absolutely and in regard to the period of the year, has not continued to be of the exceptional degree of lowness for the season taken note of in our reports for the previous two months. As regards the Thames-derived supply, the mean proportion of organic carbon was found to be 0.160 part in 100,000 parts of the water, with a maximum of 1.74 part in any single sample examined, this maximum proportion of organic carbon

corresponding to about three-tenths of a grain of organic matter in 70,000 grains, *i.e.*, a gallon of the water.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

CORRESPONDENCE.

SULPHIDE OF ANTIMONY.

To the Editor of the Chemical News.

SIR,—Having precipitated Sb as Sb_2S_3 in order to expel H_2S , I passed a current of CO_2 through the solution, and found, about three or four hours afterwards, that no precipitate was visible, the Sb_2S_3 being apparently dissolved in aqueous solution of CO_2 . On boiling the solution no precipitate came down, but on again passing H_2S through the liquid the Sb came down as Sb_2S_5 (the red variety), and, on filtration, it was found that there was still some of the Sb in solution as Sb_2S_3 , which came down when separated from the Sb_2S_5 .

This may prove a useful reaction in the separation of the second group sulphides.—I am, &c,

G. W. ENGLAND.

Claremont, Grove Road, Woodford,
Essex, March 16, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 8, February 24, 1890.

Composition of the Linear Spectra of the Chemical Elements.—J. R. Rydberg.—The author's researches have, so far, extended only to the Group I., II., and III. of the Periodic System. He designates by $n = 10^8 \lambda^{-1}$ (λ being expressed in Angström units) the number of waves in 1 c.m. of air. His conclusions are:—(1) The long rays form double or triple rays defined by the property that the difference (ν) of the number of waves of the corresponding components is constant in each element. (2) The corresponding components of the double or triple rays form series, the terms of which are functions of consecutive whole numbers. Each series may be approximately expressed by an equation of the form—

$$n = n_0 - \frac{N_0}{(m + \mu)^2}.$$

Here n is the number of waves, m any whole number whatever (the number of the order of the term), $N_0 = 109721.6$, a constant common to all the series and to all the elements, n_0 , μ , are specific constants of the series. (3) The different series of one and the same group (nebulous or narrow) have the same value of μ ; the difference of the values of $n_0 = \nu$. The series of the same number of order in the different groups have the same value of n_0 ; they are distinguished by the values of μ . (4) The wave-lengths of the corresponding rays, the same as the values of the constants ν , n_0 , μ in the corresponding series of the different elements are periodic functions of the atomic weight. The periodicity of the constants renders it possible to calculate by interpolation the spectrum of an element if we know the spectra of the adjoin-

ing elements in the periodic system. The hypotheses of Mr. Lockyer on the Dissociation of the Elements are quite incompatible with the results of these investigations.

Vapour-Tension of Solution made in Acetic Acid.—F. M. Raoult and A. Recoura.—In all probability, at a given temperature the constitution of the physical molecule of a body is the same in the liquid state and in that of a saturated vapour.

The Action, in the Dry Way, of the Different Potassium and Sodium Arseniates upon the Oxides of the Magnesian Series.—C. Lefèvre.—The oxides of the magnesian series always give with the potassium arseniates, as final products, a double arseniate of the composition $2MO.KO.AsO_5$, thus behaving like the earthy-alkaline metals. With the sodium arseniates some give a double arseniate of a composition similar to the above; the others yield another double salt, poorer in oxide $Mo.2NaO.AsO_5$. The first series includes magnesium, zinc, and nickel; the second, cobalt, manganese, and cadmium.

The Volumetric Determination of Copper.—A. Etard and P. Lebeau.—(See p. 137).

Preparation of Hydroxycamphocarbonic Acid, setting out from Camphocarbonic Acid.—A. Haller and M. Minquin.—Not adapted for useful abstraction.

A New Putrefaction-Ptomaine obtained by the Culture of Bacterium Allii.—A. B. Griffiths.—The microbe concerned is chromogenous, producing a green pigment on the surface of putrid onions. The pigment is soluble in alcohol, and the solution gives an absorption spectrum consisting of a band which extends from the extreme violet to the blue (almost to the line F of the solar spectrum). There is also an absorption band in the green and one in the yellow. The end of the latter coincides with the line D. The ptomaine is a white solid, soluble in hot water, alcohol, ether, and chloroform. From water it crystallises in microscopic prismatic needles, very deliquescent. It gives with sodium phosphomolybdate a white precipitate; with iodine dissolved in potassium iodide, a maroon; with Nessler's solution, a yellowish maroon; with tannin, a maroon; with picric acid, a yellow; with gold chloride, a dense yellow; sulphuric acid, slightly diluted, gives a violet-red colour. The base forms a yellow crystalline chloroplatinate. The analysis of the base leads to the formula $C_{10}H_{17}N$. It is still uncertain whether it ought to be attached to pyridin or to the series $C_n H_{2n-5} N$.

Chromogenous Functions of the Pyrocyanic Bacillus.—C. Gessard.—The chromogenous function of this bacillus varies with the medium.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 1.

Observations on a New Method of Analysis, applicable to Industrial Water and to Water used for Feeding Steam-Boilers.—Leo Vignon.—The author refers to two earlier papers describing his method of analysis. He determines the carbonic acid volumetrically in a known volume of water by means of a standard solution of lime, using phenolphthalein as indicator. He then determines directly the quantity of sodium carbonate necessary to transform the calcium and magnesium chlorides and sulphates into the corresponding sodium salts. This result is obtained by adding to the water (which must be previously boiled to expel its free or semi-combined carbonic acid) a standard solution of sodium carbonate. Phenolphthalein is used as an indicator. In both operations colorimetric comparisons are made with distilled water. The author now adds the precaution that the distilled water used for comparison must have been recently boiled. Further, to expel the free carbonic acid

from the sample it is better to boil it in a porcelain or platinum vessel (not in glass) rather than use the lime-water.

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.

Dynamite.—Would any of your readers inform me the best published work on the manufacture of dynamite?—"EXPLOSIVES."

MEETINGS FOR THE WEEK.

- MONDAY, 24th.—Medical, 8.30.
— Society of Arts, 8. "Some Considerations Concerning Colour and Colouring," by Prof. A. H. Church, M.A., F.R.S.
- TUESDAY, 25th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
— Society of Arts 8. "Engraving in Wood, Old and New," by W. J. Linton.
— Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
- WEDNESDAY, 26th.—Society of Arts, 8. "Carriage-building and Street Traffic in England and France," by G. N. Hooper.
— Geological, 8.
- THURSDAY, 27th.—Royal, 4.30.
— Chemical, 8. (Anniversary).
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "The Early Developments of the Forms of Instrumental Music" (with Musical Illustrations), by Frederick Niecks.
- FRIDAY, 28th.—Royal Institution, 9. "Foam," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.
— Quekett, 8.
- SATURDAY, 29th.—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.
— Society of Arts, 3. "The Atmosphere," by Prof. Vivian Lewes.

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This Exhibition will be held at the Crystal
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THE CHEMICAL NEWS.

VOL. LXI. No. 1583.

SMOKELESS EXPLOSIVES.*

By Sir FREDERICK ABEL, C.B., D.C.L., D.Sc., F.R.S., V.P.R.I.

(Concluded from p. 144).

ATTENTION was first seriously directed to the subject of smokeless powder by the reports received about four years ago of remarkable results stated to have been obtained in France with such a powder for use with the magazine rifle (the Lebel) which was being adapted to military service. These Reports were speedily followed by others, descriptive of marvellous velocities obtained with small charges of this powder, or some modifications of it, from guns of very great length. As in the case of mélinite, the fabulously destructive effects of which were much vaunted at about the same time, the secret of the precise nature of the smokeless powder was so well preserved by the French authorities, that surmises could only be made on the subject, even by those most conversant with these matters. It is now well known, however, that more than one smokeless explosive has succeeded the original powder, the perfection of which was reported to be beyond dispute, and that the material now adopted for use in the Lebel rifle bears, at any rate, great similarity to preparations which have been made the subject of patents in this country, and which are still experimental powders in other countries.

So far as smokelessness is concerned, no material can surpass *gun-cotton* pure and simple; but, even if its rate of combustion in a firearm could be controlled with certainty and uniformity, although only used in very small charges, such as are required for military rifles, its application as a safe and reliable propulsive agent for military and naval use is attended by so many difficulties, that the non-success of the numerous attempts, made in the first twenty-five years of its existence, to apply it in this direction, is not surprising.

Soon after its discovery by Schönbein and Böttger in 1846, endeavours were made to apply gun-cotton wool, rammed into cases, as a charge for small arms, but with disastrous results. Subsequently von Lenk, who made the first practical approach to the regulation of the explosive power of gun-cotton, produced small arm cartridges by superposing layers of gun-cotton threads, these being closely plaited round a core of wood. Von Lenk's system of regulating the rapidity of burning of gun-cotton, so as to suit it either for gradual or violent action, consists, in fact, in converting coarse or fine, loosely or lightly twisted, threads or rovings of finely carded cotton into the most explosive form of gun-cotton, and of arranging these threads or yarns in different ways, so as to modify the mechanical condition, *i.e.*, the compactness and extent and distribution of enclosed air-spaces, of the mass of gun-cotton composed of them. Thus, small arm cartridges were composed, as already stated, of compact layers of tightly-plaited fine gun-cotton thread; cannon cartridges were made up of coarse loose gun-cotton yarn wound very compactly upon a core; charges for shells consisted of very loose cylindrical hollow plaits (like lamp wicks) along which fire flashed almost instantaneously; and mining charges were made in the form of a very tightly twisted rope with a hollow core. While the two latter forms of gun-cotton always burned with almost instantaneous rapidity in open air, and with highly destructive effects if they were strongly confined, the tightly wound or plaited masses burned slowly in air, and

would frequently exert their explosive force so gradually when confined in a firearm, as to produce good ballistic results without appreciably destructive effect upon the arm. Occasionally, however, in consequence of some slight unforeseen variation in the compactness of the material, or in the amount and disposition of the air-spaces in the mass, very violent action would be produced, showing that this system of regulating the explosive force of gun-cotton was quite unreliable.

Misled by the apparently promising nature of the earliest results which von Lenk obtained, the Austrian Government embarked, in 1862, upon a somewhat extensive application of von Lenk's gun-cotton to small-arms, and provided several batteries of field guns for the use of this material. The abandonment of these measures for applying a smokeless explosive to military purposes soon followed upon the attainment of unsatisfactory results, and was hastened by the occurrence of a very destructive explosion at gun-cotton stores at Simmering, near Vienna, in 1862.

It was at about this time that the attention of the English Government, and through them of the lecturer, was directed to the subject of gun-cotton, the Austrian Government having communicated details regarding improvements in its manufacture accomplished by von Lenk, and results obtained in the extended experiments which had been carried out on its application to the various purposes above indicated, according to the system devised by that officer. One of the results of the lecturer's researches, subsequently carried on at Woolwich and Waltham Abbey, was his elaboration of the system of manufacture and employment of gun-cotton which has been in extensive use at the government works with little, if any, modification for over eighteen years, and has been copied from us by France, Germany, and other countries. By reducing the partially purified gun-cotton-fibre to pulp, as in the ordinary process of making paper, completing its purification when in that condition, and afterwards converting the finely-divided explosive into highly compressed homogeneous masses of any desired form and size, very important improvements were effected in its stability, its uniformity of composition and action, and its adaptability to practical uses, a great advance being made in the exercise of control over the rapidity of combustion or explosion of the material.

No success had attended the experiments instituted in England with wound cannon cartridges of gun-cotton threads made according to von Lenk's plan; on the other hand, a number of results which at first sight appeared very promising were obtained at Woolwich in 1867-8 with bronze field-guns and cartridges built up of compressed gun-cotton masses arranged in different ways (with varied air-spaces, &c.) with the object of regulating the rapidity of explosion of the charge. But although the attainment of high velocities with comparatively small charges of the material, unaccompanied by any indications of injury to the gun, was frequent, it became evident that the fulfilment of the conditions essential to safety to the arm were exceedingly difficult to obtain with certainty; they appeared, indeed, to be altogether beyond absolute control, even in so small a gun as the twelve-pounder. Military authorities not being, in those days, alive to the advantages which might accrue from the employment of an entirely smokeless explosive in artillery, the lecturer received no encouragement to persevere with experiments in this direction, and the same was the case with respect to the possible use of a smokeless explosive in military small arms, with which, however, far more promising results had at that time been obtained at Woolwich.

Abel's system of preparing gun-cotton was no sooner elaborated than its application to the production of smokeless cartridges for sporting purposes was achieved with considerable success by Messrs. Prentice of Stowmarket. The first gun-cotton cartridge, which found considerable favour with sportsmen, consisted of a roll of

* A Lecture delivered before the Royal Institution of Great Britain, Friday, January 31, 1890.

felt-like paper composed of gun-cotton and ordinary cotton, and produced from a mixture of the pulped materials. Afterwards a cylindrical pellet of slightly compressed gun-cotton pulp was used, the rapidity of explosion of which was retarded, while it was at the same time protected from absorption of moisture by impregnation with a small proportion of indiarubber. Neither of these cartridges afforded promise of sufficient uniformity of action to fulfil military requirements, but after a series of experiments which the lecturer made with compressed gun-cotton arranged in various ways, very promising results were attained, especially with the Martini-Henry rifle and a charge of pellet-form, the rapidity of explosion of which was regulated by simple means.

A sporting powder which was nearly smokeless had, in the meantime, been produced by Colonel Schultze, of the Prussian Artillery, from wood cut up into very small cube-like fragments, converted into a mild form of nitro-cellulose after a preliminary purifying treatment, and impregnated with a small portion of an oxidising agent. Subsequently the manufacture of the Schultze powder was considerably modified; it was converted into the granular form and rendered considerably more uniform in character and less hygroscopic, and it then bore considerable resemblance to the E.C. powder, a granulated nitro-cotton powder, produced, in the first instance at Stowmarket, and consisting of a less highly nitrated cotton than gun-cotton (trinitro-cellulose), incorporated in the pulped condition with a somewhat considerable proportion of the nitrates of potassium and barium, and converted into grains through the agency of a solvent and a binding material. Both of these powders produced some smoke when fired, though the amount was small in comparison with that from black powder. They did not compete with the latter in regard to accuracy of shooting, when used in arms of precision, but they are interesting as being the forerunners of a variety of so-called smokeless powders, of which gun-cotton or some form of nitro-cellulose is the basis, and of which those of Johnson and Borland, and of the Smokeless Powder Company, are the most prominent in this country.

In past years, both camphor and liquid solvents, such as acetic ether and acetone, for gun-cotton, and mixtures of ether and alcohol for nitro-cotton, have been applied to the hardening of the surfaces of compressed masses or granules of those materials, by von Förster and others, with a view to render them non-porous, and in the E.C. powder manufacture the latter solvent was thus applied to harden the powder-granules. In the Johnson-Borland powder, camphor is applied to the same purpose; in smokeless powders of French and German manufacture acetic ether and acetone have been used, and the solvent has been applied, not merely to harden the granules or tablets of the explosive, but to convert the latter into a homogeneous horn-like material.

Much mystery has surrounded the nature and origin of the first smokeless powder adopted, apparently with undue haste, by the French Government, for use with the Lebel magazine rifle. A few particles of the Vieille powder, or *Poudre B*, were seen by the lecturer about two years ago, and very small specimens appear to have fallen into the hands of the German Government about that time. They were in the form of small yellowish brown tablets of about 0.07 inch to 0.1 inch square, of the thickness of stout note-paper, and had evidently been produced by cutting up thin sheets of the material. They appear to contain, as an important ingredient, picric acid (the basis of "mélinite") a substance extensively used as a dye, and obtained by the action of nitric acid, at a low temperature, upon carbolic acid and cresylic acid, constituents of coal tar. Originally produced by the action of nitric acid upon indigo, and afterwards by similar treatment of Botany Bay gum, it was first known as carbazotic acid, and is one of the earliest of known explosives of organic origin. When sufficiently heated, or when set light to, it burns with a yellow smoky flame, and even very large

quantities of it have been known to burn away somewhat fiercely, but without exploding. Under certain conditions, however, and especially if subjected to the action of a powerful detonator, it explodes with very great violence and highly destructive effects, as pointed out by Sprengel, in 1873, and recent experiments at Woolwich have shown that it does this even, as in the case of gun-cotton, when it contains as much as 15 per cent of water. It is no longer a secret that picric acid at any rate forms the basis of the much-vaunted and mysterious explosive for shells for which the French Government were said to have paid a very large sum of money, and the destructive effects of which have been described as nothing less than marvellous. M. Turpin patented, in 1875, the use of picric acid alone as an explosive for shells and for other engines of destruction, and whether or not his claims to be the inventor of mélinite are valid, there appears no doubt that his patent in France was the starting-point of the development and adoption of that explosive.

The attention thus directed in France to the properties of picric acid appears to have given rise to experiments resulting in its employment as an ingredient of the first smokeless powder (*Poudre B*) adopted for the French magazine rifle.

The idea of employing picric acid preparations as explosive agents for propulsive purposes originated with Designolle about twenty years ago, but no useful results attended the experiments with the particular mixtures proposed by him. It is certain that the recent adaptation of that substance in France was of a different character, and that, promising as were the results of the new smokeless powder, of which it appears to have formed an ingredient, and a counterpart of which was made the subject of experiments at Woolwich about three years ago, its deficiency in the all-essential quality of stability must have been, at any rate, one cause of its abandonment in favour of another form of smokeless powder, which there is reason to believe is of more simple character.

In Germany, the subject of smokeless powder for small arms and artillery was being steadily pursued in secret, while the sensational reports concerning *Poudre B* were spread about in France, and a small-arm powder giving excellent results in regard to ballistic properties and uniformity, was elaborated at the Rottweil powder-works, and appears to have been adopted into the German service for a time, but its first great promise of success seems to have failed of fulfilment through defects in stability.

Reference has already been made to the conversion of gun-cotton (trinitrocellulose), and to mixtures of it with less explosive forms of nitrated cotton (or cellulose of other description), by the action of solvents, into horn-like materials. These are in the first instance obtained in the form of gelatinous masses, which, prior to the complete evaporation, or removal in other ways, of the solvent, can be pressed or squirted into wires, rods, or tubes, or rolled or spread into sheets; when they have become hardened, they may be cut up into tablets, or into strips or pieces of size suitable for conversion into charges or cartridges. Numerous patents have been secured for the treatment of gun-cotton, nitro-cotton, or mixtures of these with other substances, by the methods indicated; but in this direction the German makers of the powder just now referred to seem to have secured priority. Experiments were made about a year and a half ago with powder produced in this way at Woolwich, and the Wetteren Powder Company, in Belgium, has also manufactured so-called paper powders, or horn-like preparations, of the same kind, which were brought forward as counterparts of the French small-arm and artillery smokeless powder.

Mr. Alfred Nobel, to whom the mining world is so largely indebted for the invention of dynamite and of other very efficient blasting agents, of which nitro-

glycerin is the basis, was the first to apply the latter explosive agent, in conjunction with one of the lower products of nitration of cellulose, to the production of a smokeless powder. This powder bears great resemblance to one of the most interesting of known violent explosive agents, also invented by Mr. Nobel, and called by him blasting gelatine, in consequence of its peculiar gelatinous character. When the nitro-cotton is impregnated and allowed to digest with nitro-glycerin, it loses its fibrous nature and becomes gelatinised while assimilating the nitro-glycerin, the two substances furnishing a product which has almost the character of a compound. By macerating the nitro-cotton with from 7 to 10 per cent of nitro-glycerin, and maintaining the mixture warm, the whole soon becomes converted into a plastic material from which it is very difficult to separate a portion of either of its components. This preparation, and certain modifications of it, have acquired high importance as blasting agents more powerful than dynamite, and possessed of the valuable property that their prolonged immersion in water does not separate from them any appreciable proportion of nitro-glycerin.

In the earlier days of the attempted application of blasting gelatin to military uses, in Austria, when endeavours were there made to render the material less susceptible of accidental explosion on active service (as by the penetration of bullets or shell fragments into transport wagons containing supplies of the explosive), this result was achieved by Colonel Hess by incorporating with the components a small proportion of camphor, a substance which had then, for some time past, played an important part in the technical application of nitro-cotton to the production of the remarkable substitutes for ivory, horn, &c., known as Xylenite. By incorporating with nitro-glycerin a much larger proportion of nitro-cotton than used in the production of blasting gelatin, and by employing camphor as an agent for promoting the union of the two explosives, as well as, apparently, for deadening the violence or reducing the rapidity of explosion of the product, Mr. Nobel has obtained a material of almost horn-like character, which can be pressed into pellets or rolled into sheets while in the plastic condition, and which compares favourably with the gun-cotton preparations of somewhat similar physical characters just referred to, as regards ballistic properties, stability, and uniformity, besides being almost absolutely smokeless. The retention in its composition of some proportion of the volatile substance camphor, which may gradually be reduced in amount by evaporation, renders this explosive liable to undergo some modification in its ballistic properties in course of time; it is believed that this point has been dealt with by Mr. Nobel, and accounts from Italy speak favourably of the results of trials of his powder in small arms, while Mr. Krupp is reported to be carrying on experiments with it in guns of several calibres.

The Government Committee on Explosives, in endeavouring to render the above defect of Nobel's original powder, were led by their researches to the preparation of other varieties of nitro-glycerin powder, which when applied in the form of wires or rods, made up into sheaves or bundles, have given, in the service small-bore rifle, excellent ballistic results. The most promising of them, which fulfils, besides, the conditions of smokelessness and of stability, so far as can be guaranteed by the application of special tests of exposure to elevated temperatures, &c., is now being submitted to searching experiments with the view of so applying it in the arm as to overcome certain difficulties attending the employment, in a very small-bore rifle, of an explosive developing much greater energy than the black powder charge, which therefore gives very considerably higher velocities even with much smaller charges, and consequently heats the arm much more. Thus, the service black powder charge furnishes, with the small-bore rifle, an average (and variable) velocity of 1800 f.s., together with pressures ranging from

18 to 20 tons per square inch; on the other hand, with considerably less of the explosive referred to, there is no difficulty in securing a very uniform velocity of about 2200 f.s. with pressures not exceeding 17 tons, while velocities as high as 2500 f.s. are obtainable with pressures not greater than the maximum allowed with the black powder charge.

It is obvious, from what has already been said respecting the causes of the erosive action of powder in guns, that comparatively considerable erosive effects would be expected to be produced by powders of high energy as compared with black powder. Moreover, the freedom of the products of explosion from any solid substances, and consequently the absence of any fouling or deposition of residue in the arm, causes the heated surfaces of the projectile and of the interior of the barrel to remain clean, and in a condition, therefore, very favourable to close adherence together. If to these circumstances be added the fact that the behaviour of the smokeless powder has to be adapted to suit an arm, a cartridge, and a projectile originally designed for use with black powder, it will be understood that the devising of an explosive which shall be practically smokeless, sufficiently stable, and susceptible of perfectly safe use in the arm under all service conditions, easy of manufacture and not too costly, is, after all, but a small part of the difficult problem of adapting a smokeless powder successfully to the new military rifle—a problem which, however, appears to be on the near approach to satisfactory solution.

The experience already acquired in guns ranging in calibre from 1.85 inches to 6 inches, with the smokeless powder devised for use in our service, has been very promising, and indicates that the difficulties attending its adaptation to guns designed for black powder are likely to prove considerably less than in the case of the small-arm. But here again, the circumstance that much smaller charges are required to furnish the same ballistics as the service black powder charges, and that the comparatively gradual and sustained action of the new powder gives rise to lower pressures in the chamber of the gun, and higher pressures along the chase, demonstrate that the full utilisation of the ballistic advantages, and the increase in the power of guns of a given calibre and weight, with the new form of powder, are only attainable by some modifications in the designs of the guns—such as a reduction in size of the charge-chamber, and some additions to the strength, and perhaps, in some cases, of the length of the chase.

When, however, the smokeless powder has been adapted with success in all respects to artillery, from small machine guns to guns of comparatively heavy calibre, and when its ballistic advantages have been fully utilised in guns of suitable design, it will remain to be determined how far such a powder—undeniably of much more sensitive constitution than black powder, or any of its modifications—will withstand, unchanged and unharmed, the various vicissitudes of climate, and the service storage conditions in ships and on land in all parts of the world—a condition essential to its adaptability to naval and military use, and especially to the service of our Empire; and whether sufficient confidence can be placed in its stability for long periods under these extremely varied conditions to warrant the necessary freedom from apprehension of possible danger, emanating from within the material itself, to allow of its being substituted for black powder wherever its use may present advantages.

Possibly it might be that the storage, with perfect safety, of such a powder in ships, forts, or magazines, might demand the adoption of precautionary measures which might place some comparatively narrow limits upon the extent of its practicable service applications; even then, however, an imperative need for the introduction of special arrangements to secure safety and immunity from deterioration may be of small importance as compared with the great advantages which the provision of a

thoroughly efficient smokeless powder may secure to the possessor of it, especially in naval warfare.

That the opinions respecting the importance of such advantages are founded upon a sound basis one can hardly doubt, after the views expressed by several of the highest military and naval authorities, although opinions as to their extent may differ very considerably even among such authorities.

The accounts furnished from time to time from official and private sources of the effects observed at some considerable distance by witnesses of practice with the smokeless powders successively adopted in France, have doubtless been regarded by military authorities as warranting the belief that the employment of such powders must effect a great revolution in the conduct of campaigns. Not only have the absence of smoke and flame been dwelt upon as important factors in such a revolution, but the recorders of the achievements of smokeless powder—whose descriptions have doubtless been to some extent influenced by the vivid pictures already presented to them of what they *should* anticipate—have even been led to make such explicit assertions as to the *noiselessness* of these powders that high military authorities have actually been thereby misled to portray, by vivid word-painting, the contrast between the battles of the future and the past—to imagine the terrific din caused by the discharge of several hundred field-guns and the roar of musketry in the great battles of the past, giving place to noise so slight that distant troops will no longer receive indications where their comrades are engaged, while sentries and advanced posts will no longer be able to warn the main body of the approach of an enemy by the discharge of their rifles, and that battles might possibly be raging within a few miles of columns on the march without the fact becoming at once apparent to them.

It is somewhat difficult to conceive that in these comparatively enlightened days—an acquaintance with the first principles of physical science having for many years past constituted a preliminary condition of admission to the training establishments of the future warrior—the physical impossibility of such fairy tales as appear to be considered necessary in France for the delusion of the ordinary public, would not at once have been obvious. Yet even in professional publications in Germany, where we are led to expect that the judgment of experts would be comparatively unlikely to be led astray through lack of scientific knowledge, we have, during the earlier part of last year, read in articles upon the influence of smokeless powder upon the art of war (based evidently upon the reports received from France) such passages as these:—"The art of war gains in no way as far as simplicity is concerned; on the contrary, it appears to us that the absence of so important a mechanical means of help as *noise* and smoke were to the commander, requires increased skill and circumspection in addition to the qualities demanded by a general. . . ." "The course of a fight will certainly be mysterious on account of the *relative stillness* with which it will be carried on."

In an amusing article, in imitation of the account of the Battle of Dorking, which appeared in the *Deutsche Heeres Zeitung* of April last, the consternation is described with which a battalion receives the information from a wounded fugitive from the outposts that the enemy's bullets have been playing havoc among them, without any visible or audible indications as to the quarter of attack. Later in the year, and especially since the manœuvres before the German and Austrian Emperors, when the employment of the new smokeless powder was the event of the day, the absurdity of the assertions as to the noiselessness of the new powders became a theme for strong observations in the German service papers; the assumed existence of a noiseless powder was ridiculed as a thing equally impossible with a recoilless powder; the violence of the report, or explosion, produced upon the discharge of a firearm being in direct relation to the

volume and tension of the gaseous matter projected into the surrounding air.

The circumstance that blank ammunition was alone used in the smokeless powder exhibition at the German manœuvres may have served to lend some support to the assertions as to *comparatively* little noise made by the powder—the report of blank cartridges being slight on account of the small and lightly confined charges used. It is said that the sound of practice with blank ammunition at the German manœuvres was scarcely recognised at a distance of 100 metres. In a recently published pamphlet on the results of employment of the latest German smokeless powder in the manœuvres, it is stated, on the other hand, that the difference between the violence of the report of the new powder and of black powder is scarcely perceptible; that it is sharper and more ringing, but not of such long duration. This description accords exactly with our own experience of the reports produced by different varieties of smokeless powder, and of the lecturer's earlier experience with gun-cotton charges fired from rifles and field guns. The noise produced by the latter was decidedly more ringing and distressing to the ear in close proximity to the gun, but also of decidedly less volume, than the report of a black-powder charge when heard at a considerable distance from the gun.

As regards smokelessness, the present German service powder is not actually smokeless, but produces a thin, almost transparent, bluish cloud which is immediately dissipated. Independent rifle-firing was not rendered visible by the smoke produced at a distance of 300 metres, and at shorter ranges the smoke presented the appearance of a puff from a cigar. The most rapid salvo-firing during the operations near Spandau did not have the effect of obscuring those firing from distant observers.

That in future warfare, if smokeless, or nearly smokeless, powders have maintained their position as safe and reliable propelling agents for small arms and field artillery, belligerents of both sides will be alike users of them, there can be no doubt. The consequent absence of the screening effect of smoke—which, on the one hand, removes an important protection and the means of making rapid advances or sudden changes of position in comparative safety, and, on the other hand, secures to both sides the power of ensuring to the fullest extent accuracy of shooting, and of making deadly attack by individual fire through the medium of cover with comparative immunity from detection—can scarcely fail to change more or less radically many of the existing conditions under which engagements are fought.

As regards the naval service, it is especially and, at present at any rate, exclusively for the new machine and quick-firing guns that a smokeless powder is wanted; for such service the advantages which would be secured by the provision of a reliable powder of this kind can scarcely be over-estimated, and their realisation within no distant period may, it is believed, be anticipated with confidence.

The Chemical Laboratory of Wiesbaden.—In the Winter Term 1889-90 there were 62 students on the books. Of these 46 were from Germany, 3 from England, 2 from Austro-Hungary, 2 from France, 2 from Spain, 2 from Russia, 2 from North America, 1 from Holland, 1 from Norway, 1 from Chili. Besides the Director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged as teachers in the establishment Prof. Dr. H. Fresenius, Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, and Architect J. Brahm. The assistants in the instruction laboratory are two in number, in the private laboratory 16, and in the Versuchsstation 3. The next Summer Term begins on the 24th of April. Besides the scientific researches, a great number of analyses were undertaken in the different Departments of the Laboratory, and in the Versuchsstation on behalf of manufacture, trade, mining, agriculture, and hygiene.

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLET, F.R.S.,
Professor of Chemistry in the University of Virginia.

(Continued from p. 140).

Seventh Series of Experiments.

IN pursuance of the attempt to connect directly the atomic weight of gold with that of hydrogen, metallic zinc was prepared as nearly as possible in a state of purity, and, a known quantity of the metal having been dissolved in dilute sulphuric acid, the amount of hydrogen evolved was determined by volume. A solution of pure auric chloride or bromide was then treated with a known quantity of the same zinc, more than sufficient for the complete precipitation of all the gold present; the excess of zinc was dissolved by dilute sulphuric acid, and the volume of hydrogen given off was determined. The precipitated gold was carefully collected, washed, dried, ignited, and weighed. The difference between the volume of hydrogen which the zinc gave when thus partly used to replace a known quantity of gold and the volume which it would have given if replacing hydrogen alone, represented, of course, the volume of a quantity of hydrogen equivalent to the gold precipitated and weighed. From this volume, under known conditions of temperature and pressure, the weight of the hydrogen was calculated on the basis of Regnault's results for the density of the gas, after application of the needful corrections, as in the sixth series of these experiments.

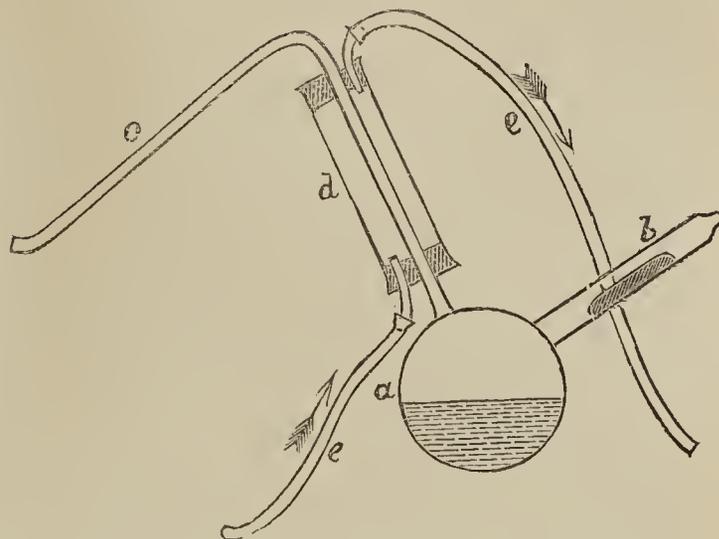
In a preliminary notice of my work read before the Chemical Section of the British Association at the Manchester meeting of 1887, it was pointed out that the method just described has certain advantages in principle. It does not require that the weight of the gold salt in solution be known, so that all difficulties in regard to drying such salt without decomposition are disposed of. It does not depend upon a knowledge of the atomic weight of the halogen in combination with gold, or upon a knowledge of the atomic weight of zinc. It does not even require that the zinc be of assured purity, provided only it be uniform in character, so that a given weight of it can be trusted to yield always the same quantity of hydrogen, and there be no impurities present capable of interfering with the collection of the whole of the precipitated metallic gold in a state of purity. The chief difficulty consists in the accurate ascertainment of the total volume of hydrogen evolved from the solution of a satisfactorily large quantity of zinc; when the gold solution comes to be used, as the volume of hydrogen given off on solution of the *surplus* zinc may be made quite small, its measurement becomes both easy and exact.

The pure zinc required was obtained by fractionally distilling in a Sprengel vacuum some very nearly pure metal from the Bertha Zinc Works, in South-Western Virginia, using a long combustion-tube of hard Bohemian glass, and substantially the same arrangement of apparatus as that described by Morse and Burton† in connection with their work on the atomic weight of zinc. The original metal was found, by an analysis in the laboratory of the University of Virginia, to contain less than 0.04 per cent of foreign matter, almost solely consisting of lead and iron. It was four or five times re-distilled *in vacuo*, rejecting each time about one-third of the quantity treated. The process is easily carried out, and in the final product, completely soluble in dilute sulphuric acid without visible residue, no trace of detectable impurity could be found.

For the evolution of hydrogen on solution of this zinc

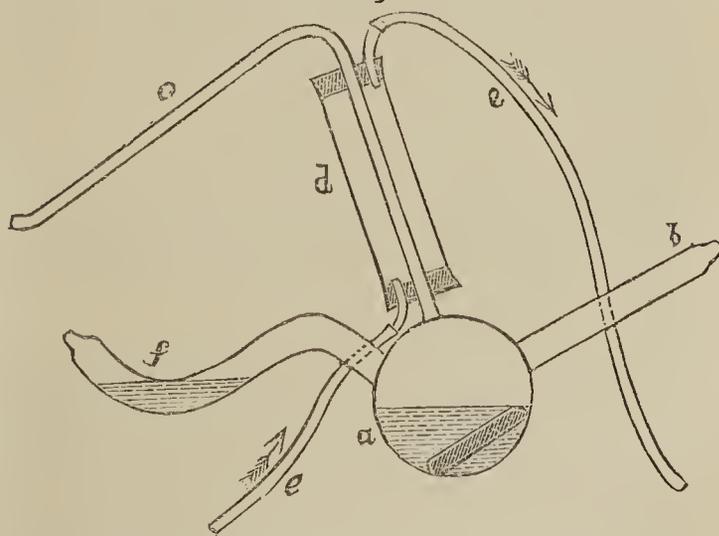
in acid the little piece of apparatus represented in Fig. 8 was used, the same that I had used in my work of several years ago on the atomic weight of aluminum.* The description formerly given of the details of an experiment with this apparatus may be repeated with but trifling change of language. A rather more than sufficient quantity of diluted sulphuric acid, its volume accurately measured, having been introduced into the bulb *a* by means of a little tube-funnel passed through the tube *b*,

FIG. 8.



the outer end of which was originally open, taking care to leave the surface of *b* clean, the metallic zinc, in a single piece of elongated shape, and having a little piece of slender platinum wire wrapped round it, was passed into *b*, held nearly horizontal, so that the metal did not slip down into the bulb, but rested 40 or 50 m.m. from it; *b* was now drawn off in the lamp flame, and sealed with a well-rounded end. The bulb was touched for a moment or two with the hand, so as to expel a very little air, and the outer end of the small tube *c* was introduced into the mercury of the trough, taking care that *b* was

FIG. 9.



still kept in such a position as to prevent the zinc coming in contact with the dilute acid. After a sufficient lapse of time for the apparatus to have acquired the temperature of the room, the barometer and thermometer and the difference of level of the mercury in the trough and in *c* were read off;† so that, knowing the volume of dilute acid introduced and of metallic zinc (the latter from its weight), calibration of the bulb and tubes after the experiment was over completed the data necessary to

* A Paper read before the Royal Society, May 9, 1889.

† *American Chemical Journal*, vol. x., p. 312. Tubes of glazed porcelain, closed at one end, had been specially procured for use in thus distilling zinc, but it was found that they were quite unnecessary.

* *Phil. Trans.*, 1880, p. 1026.

† All readings were, of course, made from a distance with the aid of a small telescope.

determine the volume of air which the apparatus contained at the beginning. The piece of zinc was now made to slide down into the bulb, the end of the gas delivery-tube *c* having been brought under the mouth of the measuring flask. Over-rapid evolution of hydrogen and any considerable rise of temperature were prevented, partly by tilting the bulb so that the little piece of zinc rested against one side and exposed but a part of its surface to the action of the liquid, and partly by cooling the outside of the bulb with water. To guard against more than traces of aqueous vapour being carried away with the hydrogen, a rapid current of ice-water was kept up through *d*.

As soon as the last of the zinc had disappeared, leaving the liquid quite clear, *c* was brought up into a nearly vertical position, and the apparatus left to itself until the temperature of the room had been attained. The barometer and thermometer and the height of the mercury in *c* above that in the trough were now read and recorded.

Lifting *c* straight up from the trough, the mercury in this tube was got out by running a wire up and down in it, and inverting it, the whole of the remaining space in *a*, *b*, and *c* was filled up with solution of zinc sulphate and free acid of the same strength with that already contained, this liquid being run in from a graduated burette through a slender tube-funnel, and the volume used noted, so as to show how much liquid had been already present.

The apparatus having been now emptied, washed out, and calibrated (with water, instead of mercury, on account of the difficulty of getting the interior quite dry), the volume of gas remaining in it at the close of the experiment was had from the difference between the total capacity (to the level of the mercury in *c*) and the volume of liquid which the bulb had contained at the close of the experiment, these taken together with the data for pressure and temperature.

The dilute acid was saturated with pure hydrogen just before being used (and in the experiments with auric chloride or bromide the main portion of water holding this salt in solution was similarly treated), and a preliminary experiment showed that there was but an extremely minute difference between the amount of gas removable from such liquid by heating in a Sprengel vacuum and from that containing zinc sulphate after the solution of the metal; so that, practically, the question of retention of gas in solution by the liquid might be neglected.

The sulphuric acid was diluted to 25 per cent by weight, only a small bit of platinum wire was wrapped round the zinc, and the temperature of the bulb was not allowed to rise beyond about 20° C. Thus the risk of evolving other gaseous products than hydrogen*—as hydrogen sulphide or sulphur dioxide—was avoided, and on testing for these impurities the hydrogen collected no traces of them were found.

The measuring-flask used to collect the hydrogen was of the same character as that used for the experiments of the sixth series, but of much larger size, holding about a litre. The quantity of zinc taken for each experiment was calculated to give a volume of gas which, under the conditions of temperature and pressure of the day, would bring the mercury to somewhere near the middle of the neck, and the gas, previously dried by balls of fused potash, was measured after the temperature had been rendered as nearly as possible fixed by the circulation round the outside of the flask of an active stream of water from the laboratory supply pipes. On account of slight rise of temperature during the solution of the metal, the volume of hydrogen left in the bulb and tubes was always less than that of the air in the same at the beginning; and, after reduction to normal temperature and pressure, the difference had to be subtracted from the gas collected in the flask.

* Muir and Adie: "On the Interaction of Zinc and Sulphuric Acid," *Chem. Soc. Journ.*, Jan., 1888, p. 47.

In the experiments with auric chloride or bromide the quantity of hydrogen given off on solution of the *surplus* zinc was so small that it could be easily measured in a little gas tube, the same method of double calibration with mercury being used as for the larger volumes. In these experiments the bulb used had a second side tube, *f*, as shown in Fig. 9, to hold the sulphuric acid, while *a* contained the aqueous solution of the gold salt; this acid was already somewhat diluted, and was introduced into *a*, after complete precipitation of the gold, very gradually, so as to avoid any considerable rise of temperature. The quantity of water used was such as to make the whole volume of liquid very nearly the same in the experiments with zinc alone and in those with zinc and the auric salt. Care was taken to ascertain, after measurement of the hydrogen, that it had been effectually freed by the potash balls not only from moisture, but from any traces of hydrochloric acid formed and carried over.

In order to connect the weight of the zinc with that of the hydrogen produced by its solution, it was necessary that the weight of the metal should be *absolute*, or in terms of equal value with those used in Regnault's researches on the density of hydrogen; hence, as has been already stated, the weights used were such as had had their real values determined, and the precaution of double weighing was applied. The quantities of metal used being small, the centre of gravity of the balance beam was so adjusted as to give great sensitiveness. In calculating the weight of the hydrogen from its volume, the same value for the weight of a litre of the gas was assumed, as has been already stated, viz., 0.08979 grm., being the result of Regnault's determinations, with the correction pointed out by Lord Rayleigh and numerically estimated by Crafts, and further corrected for the force of gravity at the University of Virginia.

The haloid salts of gold were prepared as for the experiments of the first and second series, and the careful filtration of their solutions was followed by long-continued standing at rest before the portions required were gently drawn off for use. Great care was taken in removing the last traces of precipitated gold from the bulb—to facilitate which the connected tubes were all cut off short—and in repeatedly washing the metal, first with dilute sulphuric acid, then with pure hydrochloric acid, and finally with water, before drying, heating (in the Sprengel vacuum), cooling, and weighing.

The results obtained by this method were much more free from irregularity, and much more satisfactory, than those of the electrolytic experiments. All are reported, except one or two cases obviously vitiated by mechanical defects of manipulation, and in consequence, not carried out to the end.

Experiments with Zinc alone.

Exper.	Zinc dissolved. Grm.	Hydrogen obtained at 0° C. and 760 m. m. C. c.	Hydrogen at 0° C. and 760 m. m. for 1 grm. of zinc. C. c.
I.	2.6990	922.64	Equivalent to { 341.85 341.91 341.93 342.04
II.	2.6771	915.33	
III.	2.7029	924.20	
IV.	2.7117	927.51	

Or a total amount of 10.7907 grm. of zinc gave 3689.68 c. c. of gas,* equivalent to 341.93 c. c. of hydrogen for 1

* These figures represent an atomic weight for zinc = 65.142, taking the weight of a litre of hydrogen at 0° C. and 760 m. m. as 0.08979 grm., and assuming the zinc used to have been absolutely pure, and the quantity of hydrogen collected to have been strictly equivalent to it; neither of the two latter assumptions is essential to the use made in this paper of the experiments. Reynolds and Ramsay, in their recent paper (*Chem. Soc. Journ.*, Dec., 1887, p. 854) on the atomic weight of zinc, arrive at a somewhat higher value on the basis of a like comparison of the weight of the metal with the volume of hydrogen liberated by it, but they assume the weight of the litre of hydrogen under normal temperature and pressure as 0.0896 grm., which must be considered too low in view of the recently applied correction of Lord Rayleigh.

Experiments with Gold Salt and Zinc.

Exper.	Character of gold used.	Character of gold salt.	Gold precipitated. Grm.	Hydrogen at 0° C. and 760 m.m.		Hydrogen equivalent to gold.	
				Corresponding to total zinc. C.c.	Obtained from residual zinc. C.c.	Vol. at 0° C. and 760 m.m. C.c.	Weight. Grm.
I.	A, b	AuCl ₃	10.3512	1779.44	-23.34	=1756.10	=0.15768
II.	A, b	AuBr ₃	8.2525	1428.99	-28.61	=1400.38	=0.12574
III.	A, b	AuCl ₃	8.1004	1393.43	-18.56	=1374.87	=0.12345
IV.	C	AuCl ₃	3.2913	582.82	-24.18	=558.64	=0.05016
V.	C	AuBr ₃	3.4835	606.20	-15.27	=590.93	=0.05306
VI.	D	AuBr ₃	3.6421	643.31	-25.20	=619.11	=0.05550

gram. of zinc. This value was adopted in calculating the fifth column of the above Table.

In considering possible causes of constant error in the experiments of this last series, it seems most likely that they would affect the exact determination of the weight of the precipitated gold, either by mechanical loss of some minute particles of the metal, tending to lower the atomic weight, or by incomplete washing out of the zinc salt, with an influence in the opposite direction. Any failure to remove the last traces of moisture from the hydrogen was, I think, effectually guarded against, at any rate within such limits as would have sensibly affected the resulting atomic weight; and any error due to retention of hydrogen in solution by the liquid must also have been inappreciably small, in view of the precautions taken and the close similarity of conditions in the experiments with zinc alone and with zinc and the auric salt.

(To be continued).

SOME LECTURE EXPERIMENTS.

By A. A. BRENEMAN.

1. *The Dissociation of Soap by Water.*—A well-filtered alcoholic solution of soap containing a little phenolphthalein is poured carefully into a glass cylinder half filled with distilled water, which also contains phenolphthalein. The line of contact of the liquid is coloured bright red, and, on carefully stirring with a long rod, a pink flush is diffused through the mixed liquids. As both are free from colour before contact, the liberation of alkali by the water is plainly shown, and the theory of the action of soap is thus illustrated. The alcohol may be of fifty to eighty per cent, and should contain a large quantity of soap in solution. The cylinder is tilted at forty-five degrees in pouring in the soap solution so that the layers of liquid may be distinct.

2. *Dissociation of Ammonium Chloride by Heat.*—The following experiment is easily performed and requires much less apparatus than such as require the separation of the dissociated constituents by diffusion through a porous cylinder. It depends simply upon the greater solubility of ammonia gas in water as compared with gaseous hydrochloric acid.

Into a long-necked, round-bottomed Bohemian flask is put three to five grms. solid NH₄Cl, and the flask is heated over a gas lamp (best a triple burner) until the solid has nearly disappeared and the bulb of the flask is filled with transparent gas. A glass rod having a strip of moistened red litmus-paper wound spirally around it for four inches of its length is then introduced as far as the bulb. On withdrawing it after ten seconds the paper will be entirely blue, and, if still moist, will then turn red on quickly exposing it to the fumes issuing from the mouth of the flask.

After cooling, the residual NH₄Cl may be dissolved in water and tested with litmus to show its faintly acid reaction. Ordinary sublimed NH₄Cl is faintly acid, but a sample purified by solution and re-crystallisation will be so nearly neutral that the greater acidity of the sample from the flask will be quite apparent. If, during the

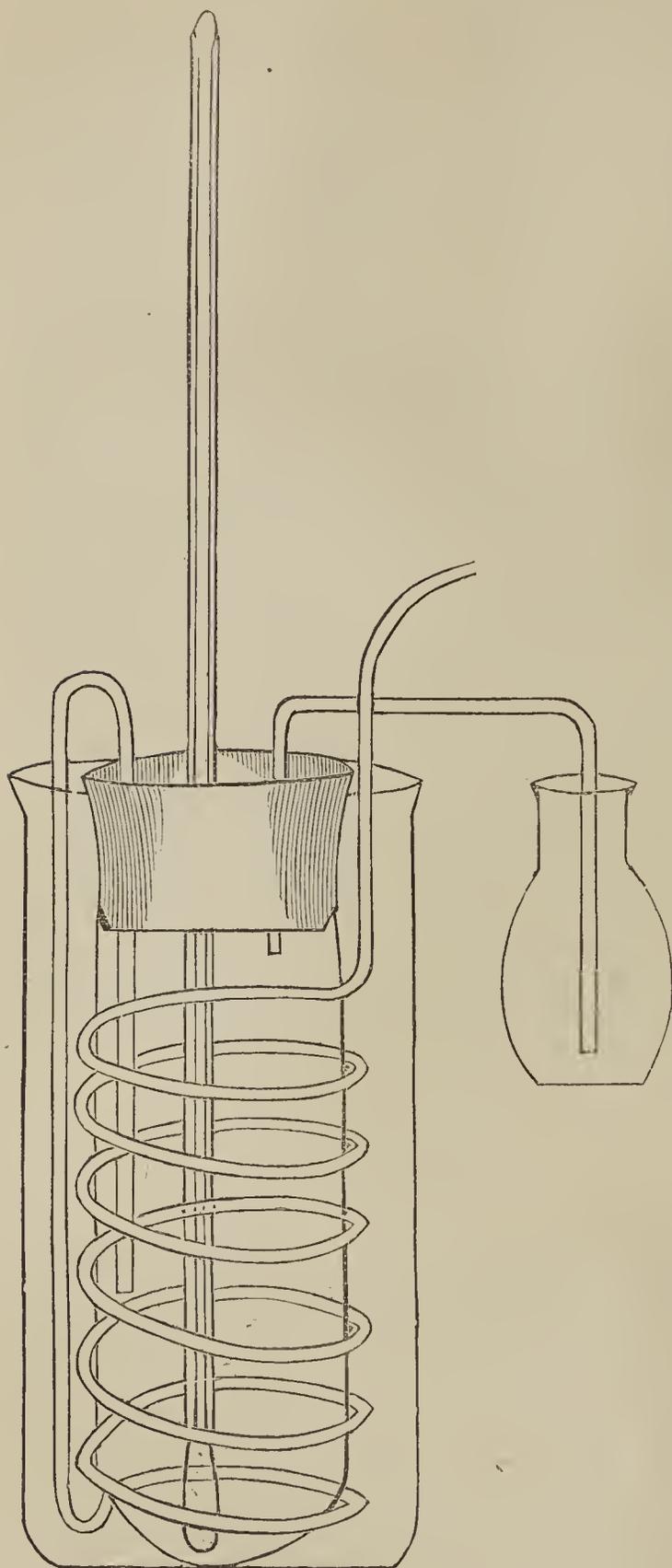
heating of the flask, a thick dry rod, previously cooled by ice or ether, be inserted into the transparent gases of the heated flask, heavy clouds of NHCl are produced.

3. *Opaque Soap Bubbles for many Forms of Gas Experiment.*—Two flasks, arranged like gas-washing bottles and tied together so as to be handled as one, are filled to the depth of 1.5 c.c. with strong NH₃ and HNO₃ respectively. The long tube of each bottle reaches to within one c.m. of the surface of the liquid, but does not touch it; the short tube ends just below the stopper in each bottle. On forcing any gas first through the long tube into the bottle containing HNO₃, and from that through the connecting tube against the surface of the NH₃ solution in the other flask, dense white fumes of NH₄NO₃ are produced and bubbles may be blown with the gas from the second bottle. Nitric acid is preferable to HCl, as fumes of NH₄Cl soon choke the exit tube, while NH₄NO₃ is deliquescent in presence of moist NH₃ gas. Also, the gas must pass last through the NH₃ bottle, as otherwise nitric acid fumes will be in excess in the mixture and the soap will be decomposed, preventing formation of bubbles. Such bubbles are more readily visible by daylight or gas-light, and much more satisfactory for use before large audiences. The quantity of vapour added is too trifling to affect the density of the gas, and the properties of weight, combustibility, &c., may be illustrated as usual. With CO₂, however, the rapid formation of ammonium carbonate in the second bottle necessitates a little practice in manipulating the apparatus.—*Journal of the American Chemical Society*, Vol. xii., No. 2.

THE IGNITING-POINT OF SULPHUR.

By BERTRAM BLOUNT.

AFTER writing my last letter on this subject, which appeared in the CHEMICAL NEWS, vol. lxi., p. 108, my attention was called to a paper by Mr. J. Rutherford Hill in the *Pharmaceutical Journal* of March 1st, in which he detailed the method of experiment he had used, and gave as his result a temperature of 248° C. This differed so widely from my own experience that I proceeded, as soon as opportunity presented, to repeat the determination by the method he had adopted. The apparatus employed by Mr. Rutherford Hill is figured in the CHEMICAL NEWS, vol. lxi., p. 125, and it was there that I first saw it, while that which I fitted up was based on his written description in the *Pharmaceutical Journal*. The accompanying figure shows the arrangement. The sulphur is contained in a test-tube immersed in a beaker of sulphuric acid. The test-tube is provided with a three-holed cork, through which pass a thermometer whose bulb dips into the sulphur, a glass tube extending downwards nearly to the surface of the sulphur, and another glass tube terminating at the under side of the cork. The free end of the former of these tubes is wound spirally round the test-tube, and is finally connected with a water-pump (not shown), supplying a blast of air, the arrow indicating the entrance of the steam. The latter (the exit tube) leads into a small flask containing a little water. In performing the experiment the temperature of



the sulphur is gradually raised by heating the sulphuric acid bath, and the stream of air is regulated by a screw-clip until about three bubbles per second pass, the rate being shown by the end of the exit tube dipping into water in the small flask. The air-supply is heated by passing through the spiral of glass tubing coiled round the test-tube, and the stream of air being kept fairly small, cooling of the sulphur or sulphur vapour is avoided.

Using this apparatus, I found that the *air* took fire in sulphur vapour at 266° C., burning with a blue flame at the mouth of the ingoing tube, and, on allowing the temperature to fall, ceased to ignite at 261° C. These tem-

peratures are not far removed from those obtained by Mr. Rutherford Hill, and the difference between his and my results probably lies in the different temperature of the air current, and perhaps in the actual dimensions and arrangement of the apparatus and the area of the surfaces of glass in contact with the mixed gases. I do not think that my higher figures are due to any heating of the thermometer by the flame, as the bulb of the instrument was protected from it by immersion in the fused sulphur, and, moreover, no sudden rise was observed at the point of ignition.

It is plain from this that my former statement of what I believed to be the igniting-point of sulphur is erroneous, there being no doubt as to the superiority of this plan over that I formerly used. In the light of more recent experience I am inclined to regard the higher result then obtained as due to the exclusion of the air from the capsule containing the sulphur by sulphur vapour, thus hindering ignition.

In conclusion I must thank Mr. Rutherford Hill for the very excellent and accurate method he has devised, and the satisfactory termination to which he has brought this question.

Laboratory, Broadway,
Westminster, S.W.
March 15, 1890.

DETERMINATION OF POTASSA AND HUMUS IN SOILS.

By J. RAULIN.

THE author's process depends on the very slight solubility of potassium phosphomolybdate in aqueous liquids, whilst the corresponding sodium, magnesium, calcium, iron, and aluminium salts are more or less soluble. A relatively small sample of the soil may be taken for analysis, since the phosphomolybdate weighed is nineteen times as heavy as the potassa to be determined.

A solution of phosphomolybdic acid is prepared by dissolving 100 grms. pure crystalline ammonium molybdate in a minimum of water, and adding 6.5 grms. neutral crystalline ammonium phosphate dissolved in a little water. Aqua regia is added when ammonium phosphomolybdate is thrown down. It is then heated, adding aqua regia from time to time, until the precipitate is re-dissolved. It is evaporated to dryness, first over the naked flame, and then in the water-bath at about 70°. The author adds 400 c.c. of water, 5 c.c. of nitric acid, heats, and filters, when the phosphomolybdic reagent is ready.

A liquid for washing the potassium phosphomolybdate is obtained by dissolving 20 grms. sodium nitrate in 1 litre of water, 2 c.c. of pure nitric acid, and 1.2 c.c. of a solution of nitre, at 80 grms. per litre, slightly heated, to saturate the liquid with potassium phosphomolybdate. It is stirred up, let settle, and the clear liquid is decanted.

To prepare the solution in which the potassa is to be determined, a portion of the soil in question, containing about 15 m.grms. of anhydrous potassa, is accurately weighed off. The potassium salts are extracted by the usual means, they are separated from the larger part of the calcareous, ferruginous, and aluminous salts, and converted into nitrates. The liquid is concentrated down to a few c.c., and slightly acidulated with nitric acid. The author then adds 4 c.c. of the phosphomolybdic reagent for every 10 m.grms. of anhydrous potassa supposed to be present. It is evaporated to dryness at 50°, and then filtered through very small counterpoised double filters, each double, washing the precipitate with the solution mentioned above. The counterpoise is washed with the same liquid, and the filters are dried at 50° and weighed. The weight multiplied by $\frac{5.2}{100}$ gives the potassium oxide.

A volumetric determination of humus in soils by a solution of permanganate would be practical if the combustion of the organic matter were complete, and if the end of the reaction were not masked by the brown colour.

The author modifies the process of J. H. Schmidt as follows:—

In a small flat-bottomed flask, holding one-fourth litre, he introduces 10 c.c. of a solution of manganese sulphate (16 grms. of the anhydrous salt per litre), and 10 c.c. of a solution of permanganate, at 10 grms. per litre, and heats for a few moments, when the liquid is decolourised and "manganese bronze" is precipitated. He adds 100 c.c. water, and 4 c.c. of sulphuric acid (150 c.c. of the monohydrated acid per litre). He further adds an exactly measured volume of a humic liquid suitably prepared, so that when becoming completely oxidised it may destroy at most half the manganese peroxide. The mixture is gently boiled for eight hours, renewing the water as it is driven off.

The manganese peroxide not attacked is dissolved in heat in a small measured excess of decinormal oxalic acid, and the excess of the latter is destroyed by a solution of permanganate at 1 gm. per litre, which is dropped in until a slight rose tint appears.

The volume of oxalic acid not destroyed is calculated from the volume of permanganate dropped in, the correspondence of the two liquids having been found by a previous trial. The volume of oxalic acid which destroys the same quantity of peroxide which the humus introduces is calculated by taking the difference between the volume of oxalic acid required to destroy all the peroxide formed by 10 c.c. of permanganate at 10 grms. per litre, and the volume of oxalic acid which has destroyed the peroxide remaining after the action of the humus. The former volume of oxalic acid, *i.e.*, that which has destroyed the peroxide formed by 10 c.c. of permanganate, has been determined by a previous trial.

As for the humic liquor, it is prepared from 10 grms. of soil treated with soda in the usual manner. It will be easy to calculate the volume of oxalic acid equivalent to the total volume of the humic liquid, of which a known fraction has been tried, and consequently the volume of oxalic liquid equivalent to the humus of 10 grms. of dry soil.

This number of c.c. of the oxalic liquid multiplied by 0.8 m.grm. will express in m.grms. the weight of oxygen necessary to burn the humus of 10 grms. of dry soil.—*Comptes Rendus*, cx., p. 289.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

March 21, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

MR. A. E. CHILDS was elected a member of the Society.

The following communications were read:—

"The Villari Critical Point in Nickel and Iron." By HERBERT TOMLINSON, F.R.S.

Villari has shown that the permeability of iron is increased by longitudinal traction, provided the magnetising force does not exceed a certain limit, but beyond this limit traction produces a decrease of permeability. The value of the force for which traction produces no change in the permeability is known as the Villari critical point.

As far as the author is aware, no previous observer has found a similar critical point for nickel, but by confining his attention to temporary magnetisation, he has detected such a point with comparative ease. He has also examined the variation of the Villari critical points in iron and nickel with change of load, and has investigated the

influence of permanent strain on these points. The experiments were made by the ballistic method, using wires about 400 diameters long. In each set of observations the permeability was obtained with various loads, the magnetising force being kept the same, and with each load the circuit was closed and opened until the swings on make and break were equal; this swing was taken as a measure of the induction under the given load.

Several diagrams accompany the paper, in which load and percentage change of permeability are plotted, regard being had to sign.

The author finds that for annealed unstrained iron the critical value of the force decreases as the load increases, and that the Villari point is much lower for temporary than for total magnetisation. With a load of 4.7 kilos. on a 1 m.m. wire, the value of the force giving the temporary point was 2.8 C.G.S. units. He also found that for a given magnetising force there were generally two loads, which have no effect on the temporary magnetisation.

With unstrained nickel the critical value of the force is much greater than in iron, being about 114 C.G.S. units for a load of 10 kilos. on a wire 0.8 m.m. diameter, and 67 for a load of 6.6 kilos.; for a force of 21 units no critical point exists.

Experiments on a permanently strained iron wire show that for magnetising forces ranging from 0.03 to 0.3 there is no critical point, and all the resulting curves are identical. There is, however, considerable difference in the observations taken during loading and those taken on unloading. For greater magnetising forces the curves cease to be identical, and the maximum increase of permeability becomes less and less, until for a certain force the curves begin to cut the load line. As the force increases beyond this value the point of cutting approaches the zero, and the curves begin to cut the load line in two points. Further increase of force to 3 C.G.S. units causes the first point to disappear and the second point recedes from the origin. Finally, with sufficiently high magnetising forces, the second point cannot be reached before the wire breaks, and the curve lies entirely below the load line.

With nickel the curves for very minute forces, like those of iron, are exactly the same for different values of the force, but they lie below the load line, *i.e.*, the permeability is diminished by loading; there is no difference, however, in the loading and unloading curves. Beyond a certain value of the force, the identity of the curves ceases, and that part of the curve near the origin bulges towards the load line. For a force a little over 21 C.G.S. units the permeability begins to increase with load, and the curve cuts the line in one point, which point recedes from the origin as the force increases.

Mr. SHELFORD BIDWELL said that Prof. J. J. Thomson, reasoning from the change of length by magnetisation, had predicted a Villari point in cobalt when compressed, and this was verified experimentally. On applying similar reasoning to nickel, he (the speaker) did not expect to find a Villari point, and both Sir W. Thomson and Prof. Ewing had searched in vain for one. In some experiments, not yet completed, he had examined the behaviour of nickel, both loaded and unloaded, when subjected to various magnetising forces. These show that the metal always contracts when magnetised. For no load the contraction at first increases with the magnetising force, but attains a maximum. With a moderate load the contraction is less for small forces, but for larger forces becomes equal, and then exceeds the contraction of the unloaded wire. For greater loads the contraction is less than when unloaded for all values of the force.

"On Bertrand's Idiocylophanous Prism." By Prof. S. P. THOMPSON, D.Sc.

This hitherto undescribed prism is a total reflection one, made of calc spar, which shows to the unaided eye the rings and crosses such as are seen when a slice of

spar is examined by convergent light in a polariscope. The space is cut so that the light after the first reflection passes along the optic axis, and after the second reflection emerges parallel to the incident light. The rings and brushes are present in pairs, but two pairs may be seen by tilting the prism to one side or the other. This was demonstrated before the Society.

Prof. Thompson also exhibited a similar prism cut from quartz. Owing to the feeble double-refracting of the substance no conspicuous rings could be seen, but when examined by the lantern traces of such rings were visible.

"On the Shape of Movable Coils used in Electrical Measuring Instruments." By T. MATHER.

The object of this note is to determine the best shape of the horizontal section of swinging coils, such as are used in D'Arsonval galvanometers, electro-dynamometers, Wattmeters, &c. Assuming constant period and constant moment of inertia about the axis of rotation, it is shown that for zero instruments the best shape of the section is two circles, tangential to the direction of the deflecting field at the point about which the coil turns. A table accompanies the paper, in which various forms of section are given together with their relative deflecting moments per unit moment of inertia; the coils being taken of equal lengths, and the current density being constant. From this table it appears that ordinary D'Arsonval coils only give about 45 per cent of the maximum deflecting moment, and ordinary Siemens dynamometers from 40 to 53 per cent.

The various assumptions made in the paper are shown to be justifiable in commercial instruments, and the modifications necessary in special cases are pointed out.

Mr. C. V. Boys said he had when working at his radio-micrometer arrived at a shape similar to that recommended in the paper. He also noticed a peculiar relation true for all shapes where the length parallel to the axis of rotation is great compared with the breadth. Suppose a coil of any dimensions, then another coil of half the breadth and double the length and cross section will be dynamically, electrically, and magnetically the same as the original; for the moment of inertia, the electric resistance and the enclosed magnetic field are equal. The above relation is also true where the breadth is not small if the cross-pieces be thickened near the axis, so as to make their moment of inertia proportional to their length. He enquired whether the author had considered the subject of grading the movable coils; he himself was of opinion that, unlike fixed galvanometer coils, the wire near the axis should be thicker than that further away.

The PRESIDENT remarked that, in 1881, Prof. Perry and himself exhibited a Wattmeter at the Society of Arts whose movable coil somewhat resembled one of those in the paper, which gave a deflecting moment of 95 per cent of the maximum. In designing the instrument they had felt that the ordinary method of using a comparatively large swinging coil was not the best, and this led them to the shape adopted.

NOTICES OF BOOKS.

Electricity: Theoretically and Practically Considered.
By ARTHUR RUST. London: E. and F. N. Spon.

WHAT is electricity? So far is this question yet from being answered that there still exists a heretic in Science—there are such persons!—who maintains that electricity is a form of matter, one of the components of water which escapes on freezing. This escape or decomposition the individual in question proclaims to be the reason why ice is specifically lighter than water! Hence Mr. Rust, in his special study of thermo-electricity, has done good work. Here, surely, we have a means of generating or liberating electricity in which water cannot be supposed to play a part.

Our author regards electricity as "a mode of motion, a flow of molecular vibrations produced by the friction of molecules against molecules, which, by various methods, have been brought into different conditions and conveyed away by the best conductor." This theory he endeavours to prove by means of thermo-electricity.

His thermo-couples are made of soft iron and of an alloy of zinc and antimony. In forming these couples great care seems to have been taken, and the majority of the experiments have been repeated more than a dozen times.

We cannot describe Mr. Rust's interesting experiments without reproducing the numerous cuts with which they are illustrated. He concludes, as the law of thermo-electricity, that the electromotive force is proportional to the rate of speed at which heat passes the two junctions. He holds that there are not two electricities, but one; further, that there is "only one material force, viz., heat; and that electricity and light proceed from it." He considers that the results of the electrical experiments in high vacua made by Mr. Crookes are precisely what might have been expected, whilst, in an absolute vacuum, no electric current could pass.

His thermo-electric furnace of 6000 elements generated such a heat that the lower iron parts melted like wax. With various improvements, some of them suggested by Prof. Silvanus P. Thompson, he hopes that this "magnopile" will become a commercial success.

Synoptical Tables of Inorganic and Organic Chemistry.

Compiled by CLEMENT J. LEAPER, F.C.S. London: G. Gill and Sons.

THIS work is avowedly examinational, being "adapted to the requirements of students preparing for the South Kensington Examinations." On this point we do not need to repeat the opinion which we have so often been compelled to express. But we feel bound to signalise the ingenuity of those authors who still contrive to present the familiar facts of elementary chemistry in some new form.

The tables, we find, are to be committed to memory.

In the glossary of chemical terms a non-metal is defined as "a substance yielding an oxide which, by admixture with water, produces an acid." Hence, accordingly, chromium, manganese, molybdenum, tungsten, &c., must in future rank as non-metals.

Amongst the laws, that of the conservation of energy is omitted.

Nitric anhydride is said to be a "whole crystalline solid," an expression not sufficiently clear.

Passing over not a few questionable statements, we find the formic, acetic, oxalic, tartaric, and salicylic acids enumerated as "the commoner organic acids." Mr. Leaper must be aware that, e.g., the citric and malic acids are far commoner, as well as more important, than the salicylic. It may, perhaps, seem hypercritical in us to point out such trifling errors. But in tables which are to be committed to memory "as a solid groundwork for future reading and research," no inaccuracy should, we submit, be suffered to exist.

Detection of the Elements of the Tissues of Wheat and Rye Meal.—P. Soltsien (*Pharm. Zeitung*).—The sample is comminuted, and a large quantity is then heated in a tall narrow glass upon the water-bath with a little water, adding gradually hydrochloric acid and potassium chlorate until the whole, after the larger particles have been crushed with a glass rod, becomes clear and thin, and any fat present collects on the surface. If too little fat is present a little pure butter fat is added. The mixture is diluted with hot water, well stirred up, and let stand until completely cold. Most of the hairs and other characteristic tissues will be found entangled in the fat, which is lifted off and examined with the microscope.

CORRESPONDENCE.

LARD.

To the Editor of the Chemical News.

SIR,—I should not have troubled you with a further letter upon this subject were it not for the following facts:—I was turning over the pages of vol. lii., 1885, of the CHEMICAL NEWS when I came across "Notes and Queries," under which head (dated April 2, 1885), was "Watered Lard;" this is signed "W. Brown," and, without wishing to create further correspondence on the matter, I should like those few remarks in "Notes and Queries" to be compared with what I have already written. What I have previously said is light itself on this matter of "lard." I reiterate that the whole of the fat of the hog melted down is nothing more or less than pork dripping, and to bring it up to anything like proper lard it is mixed with *other substances* and sold as "Refined Leaf Lard." The above reference proves that it is done. It is but five years ago that it troubled someone to ask those who had to deal with such adulterations to endeavour to put a stop to such matters; yet we find, when I interest myself in the question, that it brings forth a reply which, I contend, is simply saying lard (?) and *all things are pure*.

I commenced this correspondence with no other object whatever than of pointing out what my experience of lard had been during the last thirty years. We have, "like the poor," sophisticators always with us, but should we allow them to follow their ways without taking some action to counteract their *modus operandi*. My remarks hitherto have not, I see, been without effect; for it seems that some of my statements have been transferred to the *Grocer*, and, of course, all against my ideas.

I am obliged to you, Mr. Editor, for the insertion of my former letters, and, in conclusion, trust that Mr. Allen, of Sheffield, and others would thoroughly corroborate all I have written respecting "lard."—I am, &c.,

JOHN H. SWINDELLS, Ph.D., D.Sc.

13, Keogh Road,
Maryland Point, Essex.

LARD.

To the Editor of the Chemical News.

SIR,—I have read the letters which have appeared in recent numbers of the CHEMICAL NEWS on the subject of lard. Permit me to state, for the benefit of your readers who may be interested in this subject, that the United States Department of Agriculture, Division of Chemistry, has recently made a series of studies on lard and lard adulterants. The result of these studies is presented in a Bulletin, in which, to quote the words of the Chemist of the Department, "It is believed that the present state of our knowledge of lard and its compounds is fully set forth." This Bulletin is known as "No. 13, Lard and Lard Adulterations." It may be obtained, gratis, I believe, on application to the Department of Agriculture, Washington, D.C., United States of America.—I am, &c.,

J. T. DONALD, M.A.

124, St. James Street, Montreal,
March 11, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 9, March 3, 1890.

Absorption of Atmospheric Ammonia by Vegetable Soils.—Th. Schloësing.—The author, as far back as

1876, concluded that in the exchanges of ammonia between the atmosphere and the soil the latter is the gainer, and acquires, in this manner, quantities of ammonia which are not unimportant. Lately, this conclusion has been contested. Not only doubts have been raised on the origin of the ammonia acquired by soils exposed to the air, but it has been urged that the property of absorbing the ammonia of the air, though admissible in acid soils, cannot exist in calcareous soils. In a series of experiments with different soils there has been found in every case a gain of total nitrogen. A series of further experiments, announced as to appear in the author's next communication, will show that the presence of limestone does not interfere with the fixation of atmospheric nitrogen.

A Contribution to the Chemical Study of the Truffle.—Ad. Chatin.—The riches of the truffle in phosphoric acid, lime, and magnesia is remarkable in comparison with the poverty of the soils. Six elements, nitrogen, phosphorus, potassa, lime, iron, and sulphur, appear characteristic of the truffle. The author considers that the nitrogen is derived in great part from the air confined in the soil. Phosphoric acid forms a mean of more than 50 per cent of the ash of the truffle, and it is closely followed by potassa. Lime forms 7—8 per cent of the ash, whether the earth contains 50 per cent of calcareous matter or scarcely 1 per cent. The proportion of iron oxide is about 5 per cent. Soda is present to about 1 per cent, but rises in some cases to 6 per cent. Magnesia rises and falls along with soda. Manganese is present in all truffles; as are chlorine and iodine.

Historical Note on Batteries with Melted Electrolytes.—Henri Becquerel.—The author shows that the system of batteries proposed by M. Lucien Poincaré is not novel. Electric currents have been obtained by using a salt in fusion as one of the electrolytes by A. C. Becquerel thirty-five years. They have been also proposed by M. Jablochkoff, in 1877, by M. Brand in 1882, and by MM. Fabringi and Farkas in 1888.

The Vapour-Density of the Selenium Chlorides.—C. Chabré.—The vapour-density of the chloride SeCl_4 at 360° is 3.86; calculation gives 3.84. In opposition to Messrs. Evans and Ramsay he concludes that 2SeCl_4 is resolved into $\text{Se}_2\text{Cl}_2 + 3\text{Cl}_2$.

Certain Derivatives of Erythrite.—E. Grimaux and Ch. Cloez.—The derivatives studied are hydrofurfuran and the erythrite bromhydrines.

Derivatives of Heptamethylene.—M. Markownikoff.—Not adapted for useful abstraction.

The Preparation and Properties of Aricine.—H. Moissan and E. Landrin.—The arica bark operated upon contained neither quinine nor cinchonine. The base obtained is insoluble in water, soluble in alcohol at 90° and in ether. It melts at 188° — 189° . Its melting-point and rotatory power ($-58^\circ 18'$ in an alcoholic solution) distinguish it clearly from its isomer, cusconine.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 1.

On the Constitution of Manganese Peroxide.—W. Spring and M. Lucion.—Manganese peroxide should not be represented by the formula MnO_2 , but by Mn_2O_4 , and it is very probably a manganous manganate MnO , MnO_3 , or a manganese permanganate $\text{Mn}_2\text{O}_7 \cdot 3\text{MnO} = 5(\text{MnO}_2)$.

Memoir on an Application of Thermochemistry.—Albert Colson.—The author determines the solution- and neutralisation-heats of the bases piperidin, pyridin, and nicotin, and draws conclusions as to the properties and, the constitution of nicotin. He finds that nicotin possesses a powerful basicity of the order of ammonia and another very faint basicity which scarcely acts upon dimethyl orange when the liquids are diluted.

MISCELLANEOUS.

Analogies between Music and Chemistry.—In the *Chemiker Zeitung* there has appeared a paper on this subject, which can be reproduced only by special permission, and which is intelligible only to persons who are at once chemists and musicians. We, therefore, merely call attention to its occurrence.

Chemical Manufacturers and their Workmen.—At the annual meeting of the Oldbury Alkali Works Provident Society (Messrs. Chance Bros.), held at the works, on Saturday, Mr. A. M. Chance, one of the partners, and manager of the firms' extensive works, laid before the operatives an interesting scheme. He explained that the firm had purchased four acres of land at a place named Tal Bank, for workpeople to build houses on. He (the speaker) and another member of the firm had been appointed trustees, and the disposal of the land was left in their hands. They invited those workpeople who chose to build their own houses to consider the matter, so that some feasible plan of dividing the land might be devised. The workmen could either purchase the freehold of the land or take it on a long or short lease. A committee, consisting of Messrs. A. M. Chance, G. F. Chance, and five workmen, was appointed to consider the building scheme. Mr. Chance intimated that if the proposal was appreciated the firm would assist their workpeople in another direction.

ERRATUM.—P. 136, in table, for "Br 26" read "Br 29."

MEETINGS FOR THE WEEK.

MONDAY, 31st.—Medical, 8.30.
Society of Chemical Industry, 8. "A Separation for Solids and Liquids," by Dr. W. S. Squire. Wool-washing and Wool Fat and Products," by H. Langbeck.
TUESDAY, April 1st.—Institute of Civil Engineers, 8.
Pathological, 8.30.
THURSDAY, 3rd.—Chemical, 8.
Mathematical, 8.

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LECTURES.

Experimental Chemistry (Inorganic) Prof. H. FRESENIUS, Ph.D.
Experimental Physics W. FRESENIUS, Ph.D.
Stoichiometry E. HINTZ, Ph.D.
Organic Chemistry
Chemical Technology
Microscopy, with exercises in Microscopic work E. BORGMANN, Ph.D.
Chemistry and Analysis of Foods Prof. H. FRESENIUS, Ph.D.
E. BORGMANN, Ph.D.
W. FRESENIUS, Ph.D., and
E. HINTZ, Ph.D.
Hygiene Dr. med. G. FRANK.
Practical exercises in Bacteriology
Technical Drawing, with exercises J. BRAHM.

The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to the undersigned.

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THE CHEMICAL NEWS

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PROFESSOR GRÜNWALD'S MATHEMATICAL SPECTRAL ANALYSIS

[Most of our readers will be aware that Prof. Grünwald has been led, by a mathematical examination of the spectra of hydrogen, oxygen, and some other elements, to the conclusion that these bodies are compounds. This view has been subjected to a very hostile criticism by Dr. H. Kayser in the *Chemiker Zeitung* (1889, No. 13, pp. 1655 and 1687), mainly on the ground that the coincidences of the spectral lines are merely what the doctrine of probabilities would lead us to expect. To this criticism Prof. Grünwald has replied in the *Chemiker Zeitung* (1890, vol. xiv., No. 20). The substance of his reply we lay before our readers].

On May 9, 1887, the author foretold to Prof. Liveing, of Cambridge, a long list of lines which, according to his theory, should be found in the spectrum of water, requesting Prof. Liveing to examine this spectrum very closely, to measure even the faintest lines, and to test the accuracy of his predictions. The coincidence was most surprising.

Dr. Kayser, setting out with the assumption that the theory was merely a structure of artificial hypotheses, resting merely on the above-named result, fell to work to submit the author's publications to a—as he thought—destructive criticism, and in particular to show that the above coincidences were merely accidental. To this end he adduced a calculation showing that the number of coincidences was up to about 0.5 Angstrom unit, the same as might have been expected from a purely arbitrary assumption of the wave-lengths predicted.

This calculation, however, proves nothing, because Dr. Kayser takes into account merely the number, and not the kind and the degree of accuracy of the coincidences. He ignores how many complete coincidences occur between 0 and 0.1, 0.1 and 0.2 Angström unit, &c. But, even assuming the calculation as correct, it would be a logical error to argue from the mere probability of a certain number of coincidences up to 0.5 Angström units to the necessity of this number, still more, as Dr. Kayser curiously does, to the necessity of the existing very close coincidences. How much the probability of mere accidental coincidences depends, not merely on their number, but on their kind, will be very plainly seen on supposing that the numbers of the one series were (with the same number and distribution of coincidences) all smaller or greater, say by 0.5 Angström unit, than the corresponding numbers of the other series. Dr. Kayser's calculation would then still remain the same, though the probability that the coincidences were accidental would be very trifling.

Further, a physical cause tends to decrease the number of the experimentally demonstrable coincidences. The rays of the spectrum of water-vapour corresponding to the fainter, and especially to the more refrangible rays of the second hydrogen spectrum, are exceedingly feeble, so that no calculation of probabilities can determine and take into account how many coincidences may in this manner escape observation.

Love's graphic method of distinguishing the accidental from the necessary coincidences of two spectra is not false, as Dr. Kayser alleges, but it is, on the contrary, correct under suppositions which in many cases are admissible, and it is the only method at present known which considers not merely the number but the degree of accuracy of the coincidences. The conditions of its ap-

plicability will appear from the following demonstration:—

Let $\lambda = \lambda_1, \lambda_2, \lambda_3 \dots$ and $\lambda' = \lambda'_1, \lambda'_2, \lambda'_3 \dots$ be two corresponding or approximately identical series of wave-lengths, which are supposed to belong to one and the same substance, so that two corresponding numbers, $\lambda = \lambda_1$ and $\lambda'_1 = \lambda'_1$, are slightly different only from errors of observation, whilst their true values are identical.

Let all numbers of the same series be of equal value (in point of observation), and let the value of the numbers λ of the first series be to the value of the numbers of the second series as $m : m'$.

Then—

$$\frac{m\lambda + m'\lambda'}{m + m'}$$

is the probable value of the corresponding inaccurate numbers λ and λ' , and—

$$\frac{m\lambda + m'\lambda'}{m + m'} - \lambda = \frac{m'(\lambda' - \lambda)}{m + m'} = \gamma(\lambda' - \lambda);$$

$$\gamma = \frac{m'}{m + m'}$$

is the probable value of the error in λ . We find thus—

$$\gamma(\lambda'_1 - \lambda_1), \gamma(\lambda'_2 - \lambda_2), \gamma(\lambda'_3 - \lambda_3) \dots$$

as the probable errors of the figures $\lambda_1, \lambda_2, \lambda_3$, of the first series in case both these and the second series belong to the same substance, as it is suspected.

We further suppose that the probability of any given possible error in the numbers of either series is independent of the magnitude of the single wave-lengths, so that it might have occurred with equal probability in the determination of one wave-length as of all the others of the same series.

The errors $\gamma(\lambda' - \lambda) = \gamma(\lambda'_1 - \lambda_1) \cdot \gamma(\lambda'_2 - \lambda_2) \dots$ could as easily occur in successive determinations of one and the same wave-length, and the probability that an error $z = \gamma(\lambda' - \lambda)$ lies between z and—

$$z + dz = \gamma(\lambda' - \lambda) + \gamma \cdot d(\lambda' - \lambda)$$

would be equal to—

$$\frac{k - k^2 z^2}{\sqrt{\pi}} e^{-dz}$$

where $dz = -\gamma d(\lambda' - \lambda)$ is a constant minimal difference in error, independent of z . The number, γ , of the cases proportional to this probability in which such an error occurs must consequently be represented by an equation of the form—

$$y = b e^{-k^2 z^2} = b e^{-k^2 \gamma^2 (\lambda' - \lambda)^2} = b e^{-\beta^2 x^2}$$

if $\lambda' - \lambda$ is put $= x$, and $\beta = k\gamma$ and b denote constants.

The number of cases in which an error $z = \gamma x$ occurs between γx and $\gamma x + \gamma dx$ is equal to the number of cases in which the deviation x lies between x and $x + dx$. If, therefore, the near coincidences between the two series are not accidental but real, it must then be expected, according to the principles of the calculus of probabilities, and under the above suppositions, and between the number γ of the cases in which the deviations x of the corresponding numbers of the first and second series lie between x and $x + dx$, there must exist approximately a relation of the form $y = b e^{-\beta^2 x^2}$, where dx represents the smallest possible constant alteration of the variable deviation x .

Love's graphic method, depending on the last equation, is consequently, under the suppositions above mentioned, accurate and applicable.

(To be continued).

A New Bismuth and Potassium Iodide.—L. Astre.—This salt, when isolated by means of acetic ether, answers to the formula $(\text{BiI}_3)_2\text{IK}$, and not to that given by Nickles.—*Comptes Rendus*, Vol. cx., No. 9.

THE ACTION OF CHLORINE ON
HÆMATOXYLIN AND THE EXTRACTIVE
MATTER OF LOGWOOD.*

By WM. W. MACFARLANE and PHILIP S. CLARKSON.

It is well known among dyers, who have had any experience in extracting the colouring-matter from logwood by boiling the wood under pressure in closed vessels, that a larger quantity of wood, when so treated, is required for dyeing a given quantity of material, than when the colouring matter is extracted by boiling the wood in an open vessel, such as a dye-tub. It was the desire to discover the cause of this difference, and to avoid the loss of colouring matter, that led to a long series of experiments, and the discovery that chlorine can be used to increase the dyeing power of the extractive matter of logwood; and also that hæmatoxylin and hæmatein have entirely different values for the dyer, depending upon the manner in which they are used; that is, whether used for colouring wool or cotton, and whether the dyeing is done in an acid, alkaline, or neutral bath.

Logwood, before it is used by the dyer, is treated by a process called "curing," which consists in saturating the chipped or ground wood with water, then allowing it to lie in heaps or beds until a kind of fermentation or heating takes place. It is then necessary to move it frequently to avoid any considerable increase in temperature, and to expose all portions of it to the oxidising influence of the air. Exactly what takes place in this curing process is not known, as the composition of the extractive matter of logwood has not been determined. It is known that the wood contains hæmatoxylin, and it is supposed that certain glucosides are present, which, during the process of curing are broken up, yielding hæmatoxylin or hæmatein. Hæmatein is produced during this process, as will be shown later. Wood which has been subjected to this treatment, although it contains from 10 to 25 per cent more water, gives the dyer much better results, particularly on wool, than an equal weight of the wood in the condition it comes from the chipping or grinding machines.

For a long time attempts have been made to develop, or increase, the dyeing power of the extractive matter of logwood, either during the extraction process, or after the extractive matter had been obtained in an aqueous solution. Most of the substances used for this purpose are oxidising agents, and are used probably with the idea of converting hæmatoxylin into hæmatein. In 1885, C. E. Avery obtained a United States patent for the oxidising of logwood liquors or extracts by the action of "oxidants such as a solution of bleaching-powder, hypochlorous acid, chloric acid, chlorates, or nitrates of the alkalies and alkaline earths." He further claims the use, for this purpose, of "oxidising substances, such as solutions of chlorates of potash, or lime, or nitrates of potash, soda, or lime, which, whilst mixing with the logwood liquor at moderate temperatures, oxidise slowly or not at all, but on raising the temperature, particularly under pressure, or by the addition of acid or acid salts, become oxidisers of hæmatoxylin to hæmatein." In the specification of this patent, the quantity of a chlorate or nitrate necessary to convert a given quantity of hæmatoxylin is stated, but no directions are given as to the quantity of bleaching-powder or hypochlorous acid to be used to effect the desired result. The authors made many experiments, both following closely the specification of this patent, and with variation of the quantity of oxidants, and of the method of using them, but were not able to obtain any results which would pay for the labour and material used. In using a solution of bleaching-powder for this purpose, it was assumed that the combined or available chlorine was the oxidising agent intended to convert the

hæmatoxylin to hæmatein, and although many experiments were tried, the result was invariably a dull grey shade of black.

In Wurtz's "Dictionnaire de Chemie" (vol. i., Pt. 1, p. 645) it is stated that chlorine converts hæmatoxylin into a brown amorphous mass. Erdmann (*Four. für Prak. Chemie*, xxvi., 202), Reim (*Berichte der Deut. Chem. Gesell.*, 1871, p. 329), and Dralle (*Ber. der D. Chem. Gesell.*, 1884, p. 372), found that no definite and separate compounds were formed by the action of chlorine on hæmatoxylin. After many fruitless experiments, and when all probable means of producing the desired result had been tried, it was determined to make some experiments, using free chlorine added in the form of an aqueous solution, to the solution of the colouring matter. For this purpose a dilute aqueous solution of the extractive matter of cured wood was used. The results were determined by making dyeing tests in the mixed solutions with skeins of woollen yarn mordanted with potassium dichromate and potassium bitartrate. The results were surprising, and showed that the depth of colour increased with the amount of chlorine used, until a maximum quantity was reached, when any further increase in the quantity of chlorine produced a dull and grey shade. After further experiments, it was found that by using a 42° extract of logwood, which had undoubtedly been made from dry cut wood, that is, wood not subjected to the curing process, and chlorine equivalent to about 9 per cent of the weight of the extract, the dyeing power of the colouring matter was increased 150 per cent.

Owing to the difficulties experienced in making and handling large quantities of chlorine-water, it was found necessary to devise some other means of treating the extractive matter with the chlorine. Very good results were obtained by circulating the solution of the extractive matter through any suitable vessel, so arranged as to expose as large a surface of the solution as possible, and into this vessel the chlorine gas was delivered from the generator. The quantity of chlorine used was regulated by the quantity of materials placed in the generator. Later, it was found that if, during the absorption of the chlorine, the temperature of the solution was maintained at about 80° C., less chlorine was required to produce the desired result than when the action took place at the ordinary temperature.

It has been stated that by increasing the colouring power of the logwood by the use of oxidising substances, the colours obtained are not fast on exposure to light and air. In practice, however, it was found that a sample of worsted cloth dyed black on chrominm mordant with logwood extract developed with chlorine, after an exposure of six weeks, had not undergone any more change in shade than a sample dyed with ordinary cured wood.

In order to ascertain the exact chemical change which takes place in the hæmatoxylin in this process, a sample was obtained, manufactured by E. Moerk, and treated in the same manner as the extract. First, to determine the amount of chlorine necessary to yield the greatest dyeing power, samples were treated with varying amounts of chlorine and dye tests made. It was found that the greatest development was obtained when the proportion of chlorine was four atoms to each molecule of hæmatoxylin, which is equal to forty-seven per cent of the hæmatoxylin. This would indicate a more complex reaction than the conversion of hæmatoxylin to hæmatein, as that would require but two atoms of chlorine for each molecule of hæmatoxylin.



Avery, in his patent, calculates the amount of oxidising agents necessary, on the basis of the simple reaction—



This constitutes a marked difference in the two processes. A larger quantity of chlorine renders the shade dull and grey.

* Read at the Chemical Section of the Franklin Institute, January 21, 1890.

It is stated by various authorities, especially by Dralle (*Berichte*, 1884, Feb., p. 372), that no separable compounds are obtainable by the action of chlorine on hæmatoxylin and that hæmatoxylin is not formed in the reaction. An attempt was made to determine the products of this action, and a larger quantity of hæmatoxylin was treated with the proportional amount of chlorine, viz., four atoms of chlorine to each molecule of hæmatoxylin. The method used was to dissolve the hæmatoxylin in hot water, allow it to cool and then treat with chlorine-water containing the calculated amount of chlorine gas. By repeated washing with ether, containing a small portion of alcohol, and distilling off the ether and drying, there was left a brownish resinous mass, completely soluble in alcohol. By treatment of this residue with chloroform, a white crystalline substance was separated. This was soluble in ether, water, chloroform, and acetic acid. However, this was not obtained in sufficient quantity to determine the composition or characteristics. By further treatment of this residue with ether, two bodies were separated; one with a brownish resinous appearance, the other with a bright greenish metallic lustre. By saturation of the original solution with common salt, and again treating with ether, more matter was extracted, but was found to consist mainly of brown resinous matter. Since the method of saturating the solution with salt to separate the products of this reaction appears to have been used in former investigations, it is probably the cause of the statement that only resinous bodies, not admitting of purification, are the result of the action of chlorine on hæmatoxylin.

By carefully distilling the ether from the washing of the solution it is possible to separate most of the bronze substance before the solution is completely evaporated. It then separates in shining scales, which are apparently not crystalline. These contain small amounts of the resinous matter. By washing with ether several times, it is possible to obtain a bright greenish bronze body, with a strong metallic lustre. This gives a red, almost approaching violet, powder. Although seemingly pure, it contains a trace of chlorine, and has not been obtained sufficiently pure to warrant a determination of the composition by combustion. It is insoluble in cold water, somewhat more soluble in hot water, freely soluble in alcohol, almost insoluble in ether and chloroform. It has powerful dyeing properties, 5 per cent on wool giving a blue-black. Therefore, in its physical characteristics and chemical properties, it is identical with hæmatein, and justifies the supposition that it is hæmatein. It is hoped to obtain this in a state sufficiently pure to make a determination of the composition.

The resinous substance is easily soluble in ether, alcohol, and water. It appears to be a chlorine substitution product of either hæmatein or hæmatoxylin, as the amount of chlorine contained in mixtures of this and hæmatein is in proportion to the amount of this substance. It remains in the dye-bath, after the hæmatein has been absorbed by the wool, and probably has no effect on the colour produced. The difficulty in completely separating these bodies lies in the fact that hæmatein is soluble in solutions containing the resinous matter; therefore, it is very difficult to obtain one entirely free from the other.

In order to have some standard of comparison with the colouring-matter of logwood after curing, a well-bronzed sample of wood was treated with alcohol. To this solution, which was brownish yellow, hydrochloric acid was added, and the whole distilled to a small volume. On cooling, there was an abundant separation of colouring-matter, which, after treatment with ether and alcohol, remained as a bronze powder. A combustion of this was made, which gave—

	Erdmann found—
C 62.94	62.66
H 4.31	4.16
O 32.75	33.18

From this it is evident that this is the same as the hæmatein obtained by Erdmann by the oxidation of hæmatoxylin in the presence of ammonia.

On making comparative dye tests of the colouring-matter obtained by the action of chlorine on hæmatoxylin and this extracted from cured wood, the colours obtained were very similar in depth and shade; that of the hæmatein from wood being slightly duller. Both were about double the colour obtained with hæmatoxylin. With the latter it is very doubtful if any deeper shade than a very light blue would be obtained if the air were entirely excluded from the bath; the shade constantly growing deeper in proportion to the time the dyeing is continued, while with hæmatein the bath is exhausted in a comparatively short time, and no further increase of colour occurs.

In practical dyeing there are several methods in use which are practically different; wool dyeing being carried out in a neutral or slightly acid bath at 100° C.; cotton dyeing, commonly in a slightly alkaline solution, and what is known as speck-dyeing, in a strongly alkaline solution containing caustic alkali at a temperature below 15° C. Speck-dye is used to colour the cotton in mixed goods after the wool has been dyed, or to colour the burrs and other vegetable substances which may have become mixed with the wool. The low temperature is employed to prevent the wool absorbing any colour during the operation. From the differing conditions it was considered probable that varying results would be obtained from the use of the same colouring-matter in each of these methods. In the experiment with wool, equal weights of woollen yarn were taken and mordanted with three per cent potassium dichromate and two per cent of potassium bitartrate. These skeins were then dyed with five per cent each of hæmatoxylin, hæmatein from cured wood, and hæmatein obtained with chlorine. The operation was carried on at a boil for one hour. The shade given by the two hæmateins was at least twice as full as that obtained from hæmatoxylin. Next some speck-dye was made of the same substances in the following proportions:—5 per cent colouring-matter, 44 sodium carbonate, 5 sodium hydrate, 1 of sodium sulphite, and 16 of copper sulphate; each dissolved in water, the solutions mixed, made up to equal volumes, boiled, and allowed to cool. The skeins of unmordanted cotton yarn of equal weights were then dyed in these baths. In this case the shade obtained with hæmatoxylin was much darker than with the hæmateins; these being of little practical value. There was a marked difference in the appearance of the baths, that of the hæmatoxylin being of a deep purple colour, with little or no precipitate, the other two of a blue colour, with much precipitate.

Noticing a yellowish colour in this precipitate, which might have been due to the reduction of the copper, the action of each of these substances was tried on Fehling's solution. It was reduced by hæmatoxylin much more slowly than by hæmatein; but it was found that more copper was reduced by the hæmatoxylin than by the hæmatein. 50 m.grms. of hæmatoxylin gave 0.1675 grm. Cu₂O, and the same quantity of hæmatein, 0.1541 grm. Cu₂O. These may not be the constant reduction proportions, as this was not tried under varying conditions; but these figures were obtained by treating the bodies with an excess of Fehling's solution. A farther report will be made on this subject. From these experiments it would appear that when alkaline solutions are used in the application of logwood, the extract or decoction should be made of dry cut wood, while for wool much better results are obtained by the use of cured wood.

On finding that free chlorine in proper proportions would increase the dyeing powers of logwood extract, and that an excess produced dull and grey shades similar to those obtained by the use of bleaching-powder or calcium hypochlorite, the experiment was tried of reducing the amount of the calcium salt to about half the theoretical quantity. When this was done a marked increase of

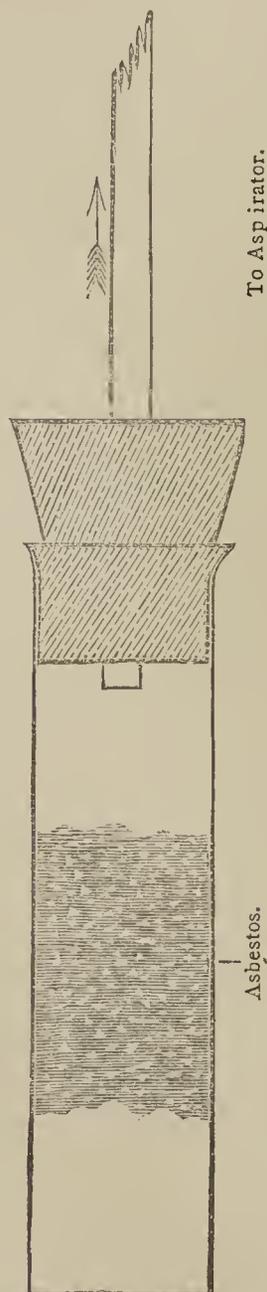
colour was obtained, with no deterioration in shade. It has been shown that the greatest development of the dyeing power of hæmatoxylin results when 47 per cent of free chlorine is used; but when a solution of bleaching-powder is employed, the same effect is produced when the proportion of available chlorine to hæmatoxylin is but 23½ per cent.

MILK ANALYSIS.

By FRANCIS WALLS, F.C.S., Government Analyst, Antigua.

THE following modification of the Adams process of milk analysis has been employed by the writer for some time with good results, and has worked satisfactorily in other hands.

In place of the blotting-paper coil, a tube containing asbestos is employed—a test-tube 18 to 20 m.m. wide with the bottom cut off, leaving a tube about 80 or 90



Drawing of Tube (real size).

m.m. long, is packed with long-fibre asbestos in its middle portion, the asbestos occupying rather more than one-third of the tube; the asbestos being ignited before being used. The tube thus prepared is carefully weighed;

about 5 c.c. of milk are next run on to the asbestos, avoiding soiling the sides of the tube with the milk. The tube and milk are then weighed to ascertain the quantity taken. The tube with its contents are placed in a water-jacketed drying oven, heated to 100° C., into which passes a tube connected with an aspirator, and the milk tube is attached to the aspirator tube by means of a suitable cork. A steady current of air is drawn through the milk, which is thus speedily evaporated to dryness, and when thoroughly dry the tube is weighed to ascertain the total solid matter dried at 100° C.

The total solid matter being ascertained, the tube is transferred to a Soxhlet's extractor, the fat extracted by a suitable solvent and weighed in the usual manner. When the extraction is complete, the tube is again dried in the water-bath and again weighed, thus giving a direct estimation of the non-fatty solids, which can be checked by deducting the weight of the fat from the total solids; the weights thus ascertained will usually agree to about a m.grm. or 0.02 per cent.

This method possesses several advantages over the Adams method, though involving the same principle. The preparation of the tube occupies less time than that of an Adams coil, and requires no previous extraction with solvents to fit it for use. Being of less hygroscopic material, and not liable to loss of substance in handling, it admits of the total and non-fatty solids being determined on the coil itself, thus permitting the whole analysis to be performed on one portion of the milk, affording a direct, instead of differential, determination of the most important constituent—the non-fatty solids—and at the same time enabling the operator to check his results, which is impossible when determining total solids in one portion and fat by the Adams coil, and non-fatty solids by difference.

The following examples are taken as showing results obtained in ordinary practice:—

	I. Grms.	II. Grms.
Weight of tube and milk	12.549	10.7262
„ tube alone	6.293	5.7637
Weight of milk	6.256	4.9625
Weight of tube and dried milk..	7.127	6.2778
„ tube	6.293	5.7637
	0.834	0.5141
Weight of tube and non-fatty solids	6.839	6.0570
Weight of tube	6.293	5.7637
Weight of non-fatty solids	0.546	0.2933
Weight of flask and fat	35.060	34.9920
„ flask	34.771	34.7727
	0.289	0.2193
Weight of non-fatty solids..	0.546	0.2933
„ fat	0.289	0.2193
Sum of non-fatty solids and fat	0.835	0.5126
Weight of non-fatty solids and fat determined di- rectly	0.834	0.5141
Difference	0.001	0.0015

Decomposition of Lead Hyposulphite by Heat. Lead Trithionate.—J. Fogh.—The decomposition of lead hyposulphite by heat gives rise to a thermic phenomenon which is almost null, whilst the ulterior redissolution of the lead salt would absorb - 3 cal.—*Comptes Rendus*, Vol. ex., No. 9.

NEW GENERAL REACTION FOR
 NITROGEN IN ORGANIC SUBSTANCES.

By Prof. E. DONATH.

KJELDAHL'S method for determining the nitrogen in organic bodies has now established itself in nearly all laboratories, since some modifications have rendered it applicable to almost all groups of bodies. The explanations hitherto proposed for the transformation upon which this method is founded are not very satisfactory. The author believes that this transformation may be more easily explained if we regard it with reference to the third thermo-chemical theorem, according to which every chemical change which ensues without the intervention of any foreign power (heat, electricity, light, &c.) always tends to form those bodies which, under the existing circumstances, evolve the greatest quantity of heat.

Every nitrogenous organic substance, on heating with concentrated sulphuric acid, undergoes a more or less thorough decomposition. In consequence, the positions of equilibrium of all the atoms are disturbed, and they are rendered more susceptible of entering into new combinations. If, at the same time, an energetic oxidising agent is present (permanganate, mercuric oxide, &c.), as in Kjeldahl's process, carbon and a part of the hydrogen are burnt, whilst the atoms of nitrogen which may be regarded as in the nascent state combine with a corresponding number of atoms of hydrogen to that system on whose union with the decomposing body (*i.e.*, sulphuric acid) the greatest liberation of heat will ensue. This is ammonia, the simplest compound base. If this inference is correct, then inversely, if the decomposition of a nitrogenous organic body is effected by a powerful base in presence of an oxidising agent, the nitrogen should not pass into combination with hydrogen, but with oxygen, forming an acid, and indeed that acid on whose neutralisation by the decomposing base the maximum of heat is liberated. This must therefore be either nitrous or nitric acid, in which form the nitrogen must appear on the above described decomposition of nitrogenous organic matter.

The neutralisation-heat of nitrous acid with potassa-lye is not to be found in the most competent manual of the subject, Julius Thomsen's "Thermo-chemical Researches." But if we may conclude from an analogy (not in chemical constitution, but in the stage of oxidation) between phosphorous and nitrous acids, the neutralisation-heat of nitrous acid would be rather greater than that of nitric acid. Direct experiments have shown that nitrous acid, although a powerful reducer, does not destroy the colour of permanganate when boiled in an alkaline solution. This corresponds to the behaviour of oxalic acid, which reduces permanganate in an acid but not in an alkaline solution, because the neutralisation-heat of oxalic acid is greater than that of any organic acid which can possibly be formed. In the reduction of organic substances by energetic oxidation in an alkaline solution the nitrogen should appear as nitrous acid.

The experiments which the author has performed with a number of substances belonging to the most different groups have almost completely confirmed this supposition. The substances named below were introduced into small flasks in quantities of from 0.03 to 0.05 grm. (according to the proportion of nitrogen) with 0.5 to 1 grm. powdered permanganate, and from 15 to 20 c.c. of potassa-lye perfectly saturated at the ordinary temperature were added and heated to a boil, adding, if needful, as much more permanganate, until, on further boiling, the liquid remained violet or greenish blue. The flask was then let cool, the liquid moderately diluted with water, which occasions heating; the excess of permanganate is reduced by the addition of a few drops of pure alcohol, and the manganese hydroxide is filtered off. The filtrate is then tested by the admixture of freshly prepared solution of

potassium iodide and acidulation with hydrochloric acid, by means of carbon disulphide or zinc iodide and starch.

In addition, the filtrates were tested for oxy-acids in general by means of diphenylamine in a sulphuric solution, and for nitric acid in particular with brucine and concentrated sulphuric acid.

These experiments showed that in all the substances examined the reactions for nitric acid were produced with the greatest distinctness, but that the brucine and sulphuric reaction for nitric acid did not succeed in all cases. In the case of coal, potassium ferrocyanide, and all bodies of the aromatic group the reaction was more difficult and tedious.

The bodies examined were:—Urea, albumen, potassium ferrocyanide, amygdaline, indigotine, coal, pepsine, quinine sulphate, magenta, binitrobenzol, tropeoline, betaine hydrochlorate, asparagine, ammonium sulphate, casein, Biebrich scarlet, binitronaphthaline, naphthylamine, nitrosonaphthol, and nitrosotoluol.

As these bodies belong to nearly all the most important groups of organic bodies, the conclusion is justified that the above-described oxidation with permanganate and strong potassa-lye, and the consequent formation of nitrous acid, is a new universal reaction for nitrogen in organic compounds.—*Chemiker Zeitung*.

[The reader cannot fail to be struck with this paper. By heating nitrogenous matter with alkaline permanganate, Prof. Donath appears to convert more or less of the organic nitrogen present into nitrous acid. Now, Mr. Wanklyn and the numerous chemists who have used his method of water analysis by the very same treatment, obtain a large proportion of the organic nitrogen in the same substances in the form of ammonia. Prof. Donath does not appear to have made any quantitative determinations, and, on the other hand, we do not find that Mr. Wanklyn has put on record any observations affirming or denying the production of nitrous acid by the action of alkaline permanganate upon nitrogenous bodies. Both Prof. Donath and Mr. Wanklyn find potassium ferrocyanide the most refractory body.—*Ed. C.N.*]

THE VOLUMETRIC DETERMINATION OF
 FREE HALOGENS
 AND THE DETERMINATION OF IODIDES IN
 PRESENCE OF CHLORINE AND BROMINE.

By P. LEBEAU.

For the volumetric determination of iodine in a liquid containing bromine and chlorine the iodine is displaced by dilute nitrous acid in excess and the solution is then poured into carbon disulphide. The violet solution is then decolourised by standard stannous chloride. This method, indicated by Fresenius, is useful, but very tedious, since the iodine must be completely dissolved out by the carbon disulphide, the coloured solution must be transferred to another flask to avoid the action of the nitrous vapours upon the standard solution, and the liquid must finally be washed to remove any traces of nitrous acid.

The author, having to make a great number of exact determinations of the halogens, has sought for a method more precise and more expeditious. To this end he has sought to render visible the limit of the displacement of iodine by bromine, this reaction being the simplest and most certain, and he has finally adopted a procedure based at once upon the colouration of carbon disulphide by iodine and the decolouration of extract of indigo by bromine. There are thus two colour-indications in juxtaposition, easy of comparison, and one of which is annulled at the end of the titration.

Into a flask holding about 200 c.c. there are put 30 to

40 c.c. of carbon disulphide and as much distilled water, and then a known volume of the iodised solution to be examined. A few drops of indigo extract are then added. Standard bromine-water is then dropped in from a burette with a glass tap, stirring briskly. The iodine set free dissolves in the carbon disulphide, which turns violet, and the supernatant liquid remains blue until a drop of bromine-water in excess decolourises the extract of indigo. The end of the reaction is very distinct.

The bromine liquor used is very convenient, but some precautions are necessary to keep its value from varying. Stoppers and joints of caoutchouc must not be used, and the reagent must be transferred directly from the stoppered bottle to a burette with a glass cock. Bromine being very volatile, the strength of bromine-water, when once known, cannot be assumed as permanent. Before each series of assays the relative value of the bromine-water must be established by means of a solution of pure potassium iodide of known strength.

In these determinations the value of the bromine-water was fixed in an independent manner without making use of iodides. The author found it convenient for determining chlorine, bromine, and iodine in solution to convert them into the corresponding zinc salts, and thus to bring their determination to a titration by means of a solution of silver. To this end the liquid containing the free halogen is introduced into a stoppered flask with the addition of a few grms. of pure zinc powder. Almost immediately the halogen disappears, forming neutral zinc bromide, and may be titrated with a silver solution, using neutral potassium chromate as an indicator.—*Comptes Rendus*, cx., p. 520.

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLETT, F.R.S.,
Professor of Chemistry in the University of Virginia.

(Concluded from p. 153).

Calculation of Results.

IN calculating the atomic weight of gold from the data furnished by the experiments which have been described, I have thought it best to conform to the most general usage of those who have been working on questions of this sort of late years, so as to facilitate comparisons with the results of others. Hence, although the atomic weight has been calculated separately from the figures of each experiment reported, the value deduced from each series has not been taken as the arithmetical mean of the separate results, nor has the probable error of these or of the mean been calculated by the method of least squares, as was done in my paper on the atomic weight of aluminium, but instead, the general result for each series has been obtained, as in the calculations of Meyer and Seubert, from the aggregate quantities of the materials employed, though I am by no means convinced that this mode of reckoning is in all cases sound in principle, giving, as it does, weight to each experiment in proportion to the quantity of material employed.

The atomic weights assumed for the other elements involved are those which have been most generally accepted in calculations of this kind, based for the most part on the experiments of Stas, and representing, with greatest probability, the values as at present known to us. They are as follows:—

H = 1.
Ag = 107.66.
Cl = 35.37.
N = 14.01.
C = 11.97.

Calculated Results.

The following are the values obtained for the atomic weight of gold from the different series of experiments:—

First Series.

(Ag₃: Au :: 322.98 : x).

Exper.	Silver. Grm.	Gold. Grm.	Atomic weight of gold.
I.	12.4875	7.6075	196.762
II.	13.8280	8.4212	196.694
III.	11.3973	6.9407	196.688
IV.	5.5286	3.3682	196.770
V.	4.6371	2.8244	196.723
	47.8785	29.1620	196.722

Second Series.

(Ag₃: Au :: 322.98 : x).

Exper.	Silver. Grm.	Gold. Grm.	Atomic weight of gold.
I.	13.5149	8.2345	196.789
II.	12.6251	7.6901	196.731
III.	17.2666	10.5233	196.843
IV.	4.5141	2.7498	196.746
V.	5.8471	3.5620	196.756
VI.	6.4129	3.9081	196.828
	60.1807	36.6678	196.790

Third Series.

(Ag₄: Au :: 430.64 : x).

Exper.	Silver. Grm.	Gold. Grm.	Atomic weight of gold.
I.	12.4851	5.7048	196.772
II.	17.4193	7.9612	196.817
III.	5.3513	2.4455	196.799
IV.	9.1153	4.1632	196.685
	44.3710	20.2747	196.775

Fourth Series.

(N(CH₃)₃HCl₄: Au :: 201.40 : x).

Exper.	Loss by ignition of trimethyl ammonium auri-chloride. Grm.	Gold. Grm.	Atomic weight of gold.
I.	7.5318	7.3754	197.218
II.	7.8432	7.6831	197.289
III.	5.2811	5.1712	197.209
IV.	3.3309	3.2603	197.131
V.	2.8165	2.7579	197.210
	26.8035	26.2479	197.225

Fifth Series.

(Au: Au :: 107.66 : x).

Exper.	Silver. Grm.	Gold. Grm.	Atomic weight of gold.
I.	2.8849	5.2721	196.747
II.	3.4487	6.3088	196.945
III.	2.3393	4.2770	196.837
IV.	1.9223	3.5123	196.709
V.	2.0132	3.6804	196.817
	12.6084	23.0506	196.823

Sixth Series.

(H: Au :: 1 : x).

Exper.	Hydrogen. Grm.	Gold. Grm.	Atomic weight of gold.
I.	0.02053	4.0472	197.136
II.	0.02039	4.0226	197.283
III.	0.02079	4.0955	196.994
	0.06171	12.1653	197.137

Seventh Series.
(H₂: Au :: 3 : x).

Exper.	Hydrogen. Grm.	Gold. Grm.	Atomic weight of gold.
I.	0.15768	10.3512	196.941
II.	0.12574	8.2525	196.894
III.	0.12345	8.1004	196.851
IV.	0.05016	3.2913	196.848 Lowest value.
V.	0.05306	3.4835	196.956 Highest "
VI.	0.05550	3.6421	196.865
	0.56559	37.1210	196.897

General Mean of Results.

If each of the foregoing series of experiments be represented by the result calculated from the aggregates of material used, and if equal weight be attached to the results of all the methods, the general mean derived from the whole of the 34 experiments will be as follows:—

First series	196.722	Lowest value.
Second ,,	196.790	
Third ,,	196.775	
Fourth ,,	197.225	Highest value.
Fifth ,,	196.823	
Sixth ,,	197.137	
Seventh,,	196.897	
General mean	196.910	

The results of the fifth and sixth series, obtained by electrolysis are, I am convinced, much less entitled to confidence than any of the others. If these two be excluded, the general mean of the remaining series will be 196.882, a number differing but little from the mean of all.

The highest value is that derived from the fourth series—ignition of trimethyl ammonium auri-chloride. It has been seen that the individual results of this series agree fairly well with one another, and when examined in connection with the facts as to the different crops of crystals of the salt used, do not seem to present any evidence of want of uniformity in the material. But as it may still be suspected that traces of dimethyl or of monomethyl ammonium auri-chloride may have been present, and have caused the apparent value of the atomic weight of gold to come out higher than the truth, if we exclude also this series, the general mean of the remaining four will be 196.796.

Finally, if for the sake of comparison with the results of Krüss and of Thorpe and Laurie the general mean be taken for the first three series only, in which auric chloride and bromide were examined, the result is 196.762—intermediate between the general means of the two previous researches, but rather nearer to that derived from the work of Thorpe and Laurie than Krüss.

It will be observed that, although there is pretty close agreement among the means of results obtained by altogether different methods, this agreement is not so close as that presented by the results of the nearly similar methods pursued in the first three series. This cannot but suggest the probability of there being still sources of minute errors inherent in the methods themselves, and not dependent upon mere imperfections of manipulation in carrying these methods out. Although there is thus to be noticed a slight tendency on the part of each method to yield high or low figures severally with the exception of the results of the fourth series there does not appear to be any considerable reason to see in the values obtained confirmation of the special suspicions in connection with each method which have been stated. There is no clear evidence of any difference in the results which can be traced to the history of the particular samples of gold used; a larger number of somewhat low results seem to have been yielded by the metal designated as (C)—*i.e.*, obtained from the United States Assay Office

at New York—than by the others, but the difference is not marked or constant enough to warrant any trustworthy conclusions as to the character of this material.

Concluding Remarks.

The atomic weight of gold, as deduced from the experiments reported in this paper, is entirely in accord with the place occupied by the metal in Mendeleeff's "periodic" classification of the elements, but this is equally true of the slightly different values obtained by Krüss, and by Thorpe and Laurie, and the only difficulty at one time apparent as to this point—namely, the relative positions of gold on the one hand and of platinum, iridium, and osmium on the other—has been removed, not by any change in the atomic weight of gold, but by changes affecting the values to be assigned the three other metals, as these values have been determined by Seubert.* It is very desirable that, in order to a fuller and more exact examination of the Mendeleeff table of the elements, there be accomplished as soon as possible a general revision of the atomic weights of *all* the elements of well determined individuality, so many of which are still very imperfectly known.

As to any bearing of the results of the present paper on the so-called hypothesis of Prout,† the general mean of all my results, or even the general mean with exclusion of the values obtained by electrolysis, approaches the integer number 197 rather more nearly than does the final number arrived at by Thorpe and Laurie, and still more nearly than does that considered by Krüss to express the final result of his experiments. If the results of the fourth series be also rejected, my general mean will be nearer the integer than is the Krüss number, but not quite so near as that of Thorpe and Laurie. I feel that somewhat greater confidence may be placed in my own work, simply on the ground of its involving the use of more completely different and independent methods—a principle which I believe to be of the first importance in any attempts at increased accuracy in the determination of atomic weights.

At the same time, as has already been pointed out, this work seems to me to furnish some probable evidence that not all inherent defects of method have been eliminated. Whether or not such defects may exist to an extent sufficient to account for the remaining difference between the value obtained and the integer multiple of the atomic weight of hydrogen there does not seem to be ground on which to express a positive opinion. But this research does not supply any clear evidence contradictory of such a possibility.

On this point, and generally on the attainment of what is sometimes rather too easily spoken of as the greatest possible accuracy in the determination of an atomic weight—particularly of an element for which the value is as high as that for gold—anyone who actually works in a conscientious way at such determinations will be pretty sure to feel more strongly the difficulty of the task, and to express himself with more caution, than do some compilers of results in assuming at any time that the last word has been spoken.

Decrease of the Fermentive Power of Ellipsoidal Yeast in Presence of Salts of Copper.—A. Rommier. —In case of vineyards yielding choice wines, the late application of copper salts as a protection against mildew should be avoided as much as possible.—*Comptes Rendus*, Vol. cx., No. 9.

* *Berichte Deutsch Chem. Gesell.*, vol. xi., p. 1770; vol. xiv., p. 868; vol. xxi., p. 1839.

† Soon after the publication of my paper on the atomic weight of aluminium, I was criticised by a writer of abstracts for the German Chemical Society on account of my use of the expression "Prout's law," amazement being indicated that I should have called the "hypothesis of Prout a law." If this writer had noticed my use of inverted commas, and still more what was said in the course of two or three pages of the paper, he would have seen that the use of the expression "Prout's law" was by no means equivalent to assuming this to be a "law of nature."

ON IODATE OF CALCIUM AS AN
ANTISEPTIC.

By W. DUNNETT SPANTON, F.R.C.S. Ed.

ATTENTION was first called to this substance as a disinfectant and antiseptic by Mr. E. Sonstadt in the year 1872; and in the following year, at this gentleman's suggestion, I used it in various ways for surgical purposes, and have used it more or less ever since. I think it well to make this statement, as I find that reference has been recently made to the use of this calcic iodate in a way which suggests that its properties have only recently been discovered, and its uses known.

In the CHEMICAL NEWS of April 26, 1872, will be found a paper "On the Presence of Iodate of Calcium in Sea-Water," by E. Sonstadt, in which this important inference is mentioned, "that whatever iodine sea-water contains must be in the state of iodate," "and from the results of experiments made upon the iodates, and especially upon iodate of calcium, that iodine must always be set free in sea-water wherever there is putrescent organic matter; and that while this is being oxidised at the expense of oxygen in the iodate, the freed iodine slowly re-forms iodate by the decomposition of water conjointly with that of carbonate of calcium." Mr. Sonstadt further found by direct experiment that sea-water at one time would contain all its iodine as iodate, and at another time free iodine, with scarcely a trace of iodate. Several series of experiments are related which proved, in the opinion of the author of the paper, that "it is only *putrescible* organic matter that is decomposed by and decomposes iodate of calcium; that this substance (the iodate) possesses in a high degree the power of preventing fungoid growths in very putrescible liquids; and that this is to be attributed largely to the unstable equilibrium of the iodate which readily oxidises matter with which it comes in contact, setting free the iodine." In a further article in the CHEMICAL NEWS, vol. xxv., p. 231, the author describes how sea-water taken from the mouth of a river, conveying sewage, contained its iodine in a free state, and after being kept ten days the whole of the iodine had disappeared; and iodate of calcium was present as usual in sea-water taken some miles out from shore. And in another paper on the same matter, Mr. Sonstadt calculates that sea-water contains one part of iodate of calcium in every 250,000 parts by weight. So that whatever influence it may have in tending to keep pure sea-water must be due to the presence of a very minute quantity. After these papers were published the author continued to make experiments with this salt as an antiseptic and disinfecting agent; and in the CHEMICAL NEWS, vol. xxviii., p. 297, in an article "On the Antiseptic and Disinfecting Power of Iodate of Calcium," the results of the experiments are described. The principal putrescible substances experimented upon were urine, albumen, fish, meat, and rain-water. "Equal quantities of fresh urine were put into two test-tubes, and to one portion a small pinch of the solid iodate was added: the specimens were placed close together." After a few days the specimen to which nothing had been added became offensive; but after the addition of a solution of 1-1000th of iodate to about one-fourth of its volume, the offensive odour disappeared, although the odour of urine remained. The specimen to which solid iodate was added never became offensive, and after several weeks could not be recognised for what it was by the smell. White of egg was treated similarly: that to which solid iodate had been added kept sweet about six months, then discoloured and smelled. The other, of course, putrefied quickly. With fish, either by sprinkling, when fresh, with iodate powder, or by immersing in iodate water (containing 0.1 per cent of iodate), it kept good in hot weather about four days.

In the case of meat, the powder only was used, and with it sprinkled over the meat could be kept fresh several days longer than without it. Putrid rain-water became

odourless and agreeable to drink twenty-four hours after the addition to it of one-fourth its volume of 0.1 per cent of iodate water. Then further to ascertain how much might safely be taken in this way, the author took various doses of the salt, the largest being one gramme. This caused no inconvenience beyond after taste, and a slight headache next day. But he adds: "It is in cases of fever, and such diseases as typhus and cholera, propagated by some specific organic poison, that I should expect the exhibition of iodate of calcium to be followed by marked effects."

While these investigations were being carried out I was myself working at the same subject with some of the iodate which my friend Mr. Sonstadt had given to me for the purpose. In 1872 I referred to the uses and value of the salt in an address delivered to the North Staffordshire Medical Society, after I had given it a careful trial as a dressing for wounds, and also for internal administration. The salt was then little known, and I found a difficulty in obtaining it from the chemist, who more than once sent me iodide of calcium in its stead. Fortunately for me and for the subject of my experiment, I knew the difference between them, and discovered the error before using it, for the iodide is a comparatively poisonous salt, and in small doses will produce very unpleasant effects. Of this I had been warned by my friend; and anyone intending to use iodate should make quite certain he does not get iodide instead.

My experiments confirmed to a large extent those described by Mr. Sonstadt, and I have now in my possession several of the specimens I put up seventeen years ago. One, a bottle of fresh urine, to which a small quantity of iodate of calcium was added, has now no odour except that of iodine; whereas the fellow specimen without the iodate is, of course, putrid. Another, containing some boiled meat, is quite devoid of any odour of putridity; its fellow is intolerable. About the same period a patient brought to me a specimen of a lumbricus in water, and to this I added a few grains of iodate and put it aside. After a time it became almost the colour of iodine water; then would become clear again, become dark again, and it is now clear, smelling strongly, and only of iodine. The worm is more or less disintegrated, but the fluid is clear, and has never at any time had the slightest putrid smell.

One curious property the salt has, is that of retaining urine clear when added to it while fresh. Acting upon this knowledge, I employed it in some cases of chronic cystitis, in which the urine was very offensive, with excellent effect, when used for washing out the bladder. And given internally in these cases, it had the effect of clearing the urine and greatly diminishing the fœtor, though I found boracic acid on the whole more efficient, and have generally used it on that account.

As a dressing for wounds of all kinds, for recent amputations and injuries, as well as for suppurating or sloughing wounds, it certainly is useful as an antiseptic. But my experience of it in these cases led me to the conclusion that its insolubility (requiring about 400 parts of water for solution) was a drawback, as that strength is not enough to produce a sufficiently prolonged effect upon the discharges to keep them aseptic. And although one could use the powder itself, suspended or powdered on, I think its action is too slow for its full effect to be realised. I find in some notes I published nine years ago of excision of the tongue, a solution was found to have an excellent effect as a wash for the mouth, and four days after operation no fœtor could be observed in the breath (*Lancet*, 1881, vol. i., p. 911). Given internally, I was never able to convince myself that it had any marked effect, except in cases such as I have referred to, where there was cystitis or a superabundance of lithates in the urine. It occurred to me that its marked effect upon the condition of the urine might render it useful for uric acid calculus, and I gave it in some cases of renal calculus with this view. I am not able, however, to say that any well-

marked effect was observable. Knowing the action of lithium on the uric acid diathesis, it might be found that if an iodate of lithium is procurable, it might prove an active and useful drug for this affection.

So far as my experience has gone, I found the insolubility and the slowness of its action the chief drawbacks to the utility of iodate of calcium as a surgical application; but its innocuous and unirritating properties, and its marked effect upon the renal secretion, indicate a special advantage in its use for such cases as cystitis, nephritic abscess, and for renal operations generally. So many of our best antiseptics are poisonous, or irritate, or stain, that it is useful to have one such as this which is free from those drawbacks. It has at least the merit of being inodorous and almost tasteless, and of not disguising other odours by a still worse one of its own.—*The Provincial Medical Journal*.

NOTICES OF BOOKS.

Some Food Substitutes and Adulterants. (Annual Address of the President, Mr. EDGAR RICHARDS, delivered before the Chemical Society of Washington, January 23rd, 1890). Washington: D.C.

CANDIDLY speaking, we do not like the expression "food substitutes." If a substance is nutritious, digestible, palatable, and free from any injurious properties, let it by all means rank as a food; but let it be sold and used under its own name, and not put forward as a substitute for any formerly known article. Mr. Richards, on more mature reflection, can scarcely deny that the manufacturer and the dealer do not find it "directly contrary to their own interests" to add hurtful matter to food products. There are many injurious bodies used by the adulterator and the substituter, which, though they sap the health, do not promptly cause any marked symptoms of poisoning and are detected perhaps very slowly, perhaps not at all. The list appended by the author, compiled, it is said, from the Reports of the State Boards of Health, the Reports of the British Local Government Board, and those of the Paris Municipal Laboratory, by no means supports Mr. Richards in his contention that "the great majority of substances used for food adulterants or substitutes consist of cheap and harmless substances which are not injurious to health." In this list we find salts of copper, metallic poisons, Prussian blue, alum, mineral acids, antiseptics, gypsum, artificial colouring-matters, poisonous pigments, &c.; in short, a very respectable minority.

The author, further, admits that though a substance, *e.g.*, water, may not be, *per se*, injurious to health, yet if introduced into, say, milk, to the exclusion, in part, of its natural and more nutritious constituents, it may be harmful, or even fatal.

No qualified and competent authority contends that oleomargarine, properly prepared, is hurtful to the consumer. The only feature to be complained of was its sale as butter, or under such delusive names as "butterine." It is worthy of note that the trade feel themselves no little aggrieved that they are now compelled to sell this substance under its own name.

Glucose, or starch-sugar, as prepared from maize in the United States, can have no injurious properties, at least if the acid used in saccharification is free from arsenic. Concerning the glucose manufactured on the Continent from refuse potatoes, we are much less confident. The potato whiskey of Germany is notoriously rich in fusel, and we fear that some substances especially prone on fermentation to generate the higher alcohols must accompany the glucose.

We do not see any chemical objection to the use of cotton oil in food, whether alone or in admixture with

other oils or fats. There is one point which, not belonging to the medical profession, we cannot presume to decide, *i.e.*, will it, being a drying oil, be as easily assimilated as the non-drying olive oil? In any case, it should be sold under its own name.

The author is not mistaken in asserting that on the European Continent the legislation concerning the adulteration of food is much superior to the English Act. There are in the former fewer loopholes for the escape of offenders. "Under the Continental laws every dealer is responsible for the quality of his merchandise; every food material must be sold under its true name; artificial products imitating a natural product must be labelled in a conspicuous and legible manner; all unwholesome foods are confiscated and destroyed without compensation to the owner; and adulterations generally are considered acts of fraud." Some of these points are found in the English law, though not all. In the fearfully mistaken law allowing coffee to be sold mixed with chicory the proportion of the latter should have been stated, and it should have been made impossible to escape by mendaciously calling the mixture "coffee as in France," or "French coffee."

Mr. Richards is not sanguine as to the suppression of adulteration in America. Public opinion is not sufficiently enlightened on this question, no more than it is in Britain.

The Practical Use of the Spectroscope. By J. PARRY, F.C.S.

THE author, in the introductory portion of his treatise, regrets that the spectroscope "has not yet found a permanent place in the laboratory of the ordinary practical chemist." For this neglect he gives several reasons, one of which is that "the instrument has hitherto been mainly in the hands of the physicist." Further, the instruments supplied for ordinary uses are unsuitable, and the directions given in the usual text-books say little of the manipulation of the instrument and of the flame or spark.

All this is perfectly true, but the greatest obstacle to the general use of the spectroscope—other than the absorption instrument—is not formally stated, though it may be inferred from the instructions here given. It lies in the necessary source of light. The Bunsen and the air blowpipe do not give a sufficiently high temperature for the volatilisation of most metals. The oxy-hydrogen blowpipe is justly pronounced very troublesome, though useful in certain special cases. But for general work, Mr. Parry prefers the electric spark derived from a powerful induction coil giving not less than a 6-inch spark. Then, to supply the needful electricity, he prefers a small dynamo driven by a gas-engine. Here, then, is the reason why the ordinary chemist does not make more general use of flame or spark spectroscopy. The expense and the space required for these instruments are the obstacle to the rapid and general extension of spectroscopy.

The author quotes very full and clear directions for adjusting the Hilger spectroscope, the type of instrument which he prefers. Bunsen's one-prism instrument he finds deficient in dispersive power. It is remarked that in Browning's six-prism instrument the adjustment is automatic. The use of photography for recording and checking spectroscopic observations is strongly insisted on. The illustrative diagrams, all of which have appeared in *Industries*, are numerous, and will prove very useful.

Separate chapters treat of the spectra of vapours at different temperatures, the spectrum of iron at varying temperatures, and the spectrum of iron heated *in vacuo*. Absorption spectroscopy does not apparently fall within the author's plan. He evidently inclines towards the theory put forward in Lockyer's "Studies in Spectrum Analysis" that the so-called elements are in reality compound bodies which, under certain conditions, may be

split. We hope and believe that Mr. Parry's work will contribute to that most desirable end, the more extended use of the spectroscope.

The Elements of Laboratory Work: a Course of Natural Science. By A. G. EARL, M.A., F.C.S. London: Longmans, Green, and Co.

THE author of this treatise has in view work in a laboratory not devoted to chemistry mainly or alone, nor to physics, but to all departments of inorganic science. His views on scientific training are very satisfactory. Thus, he concludes his preface with the expression of a hope that the course "may give some training in that habit of directly appealing to nature rather than to theories, which is the root of all scientific progress, though unfortunately it is not always made the basis of scientific education, partly from want of time, and partly from want of appliances." We must here remark that the want of time is mainly due to its profligate expenditure upon subjects of greatly less value.

The cautions on purity of substances addressed to beginners in chemistry are greatly needed. Says Mr. Earl:—"Nothing can be more misleading than those descriptions of chemical changes which omit to state that the reacting substances are not pure and which convey the impression that chemical changes are simple enough to be amply described by an equation. They are often seriously inaccurate in themselves, and conduce to a feeling of certainty when the training of observation has barely commenced. Keeness and faculty of research is thus suppressed, when the aim of even the most elementary work should be to encourage it." A teacher who writes thus may be taken as a trustworthy guide.

The work does not bristle with mathematical formulæ, which with some writers on physical subjects are made not a means, but an end, as if a builder should erect a stately palace not for its own sake but for that of the ladders and scaffolds employed in its construction, and should leave the latter standing.

We notice the occurrence of one novel technical term, "stress," which the author uses as equivalent to "mutual action." He says that "the return of a body to the earth gives rise to the statement that it is caused by the attraction of the earth, or gravitation, but it is more exact to say that a mutual action or a stress exists between the two. If a new term was needed—of which we are not sure—Mr. Earl has done well in proposing one of English origin. The term "weight" is uniformly discarded in favour of "mass." Thus the author speaks of "atomic masses" of the elements of chemistry.

In discussing the theory of the ether, the author admits that new conceptions as to what is truly elementary matter have been gained from spectroscopic investigations. Any discussion on the nature of the supposed simple bodies would, of course, have been out of place in an elementary treatise like the present.

The chief defect which we observe is the lack of an index. But it may be warmly recommended for use in public schools and colleges.

The Trichologists' Pharmacopœia: being a Description of the Drugs used in Diseases of the Hair. By THOMAS GURNEY, M.Df. (?), L.R.C.P., L.R.C.S., Physician to the Hair Hospital, &c. London: Osborne, Garrett, and Co.

To outsiders, like ourselves—non-trichologists—it is a novelty to see the extent of this novel pharmacopœia. In the work itself we see some very satisfactory passages mixed up with occasional errors. Thus, it is going too far to say that vinegar is a liquid "of a brown colour," and that it is "prepared from malt." The brown colour is an accidental feature, often produced artificially, and abundance of vinegar is prepared from other materials.

Acidum boracicum is explained as being "bone acid." This, we think, must be a clerical error: there is no boracic acid present in the bones of animals. An interesting remark is that the use of this acid in preserving milk is decidedly pernicious. "Its addition to milk is a very common source of skin eruptions." This the author concludes from his own observations.

Hydrocyanic acid is mentioned as being applied to kill parasites in the head, with the proviso that it "must be used very carefully!"

The following remark is curious:—"In certain localities in England water exists in liquid, solid, and gaseous states." Sea-water is declared very injurious to the hair, which after a sea bath should always be washed in not less than a gallon of pure water.

Oil of cajeput is said to be imported "from Bavaria and Singapore." We presume Batavia is meant.

The frequent references to syphilitic ulcerations, warts, &c., on the head are sufficiently alarming, and might lead our ethicists to question whether some of their recent movements have not been a mistake.

We are told that a "watery solution of cochineal allowed to stand in a warm spot will develop the *coccus cacti*." Is this an assertion of abiogenesis?

The following is too true:—"Truly in medicine, as in politics, fads are set up and grasped by the ignorant as principles. Miles of speeches are made and written about fads, often in themselves ludicrous, and principles are forgotten!"

We are told that "one part of the cyanide (potassium), two of plaster of Paris, and two and a half of water stirred together and poured, whilst liquid, into a wide-mouthed bottle forms a hard floor, which is constantly giving off a poisonous vapour, which vapour will kill insects without injuring their plumage or structure." The vapour certainly kills many insects, but there are others which it does not affect in the least.

Mr. Gurney is very severe on the soap trade, holding that "money making is more considered in the preparation of soaps than the effect they have on complexions." The author's views on the manufacture of soap are somewhat antiquated. "The usual way of manufacturing common soap," he tells us, "is to boil some low priced oil with the lye of wood ashes." This process would, of course, yield a soft soap only, but the lye of wood ashes has been now laid aside in favour of the pure potash from Stassfurt.

The author gives throughout his work many cautions as to the random and indiscreet use of various agents. In no department is quackery more rampant than in the treatment of the hair, and if he can depose or discredit it he will have performed a good work.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 9, March 10, 1890.

Thermic Researches on the Allotropic States of Arsenic.—MM. Berthelot and Engel.—The author's observations show that the two varieties of arsenic develop almost identical quantities of heat on forming one and the same combination. The difference is even too slight to be guaranteed with certainty.

The Absorption of Atmospheric Ammonia by Vegetable Soil.—H. Schloësing.—Calcareous soils, air-dried, are able to absorb as much as 108 m.grms. of ammoniacal nitrogen per kilo. It is probable that a part of the ammonia absorbed forms, with certain organic matters, compounds stable enough not to reproduce am-

monia under the treatment employed. The author's experiments show that bare vegetable soil, calcareous, acid or neutral, dry or moist, absorbs atmospheric ammonia in important quantities.

Nomination.—The Academy proceeded to nominate a Correspondent for the Physical Section, *vice* Prof. Kirchhoff, deceased. Lord Rayleigh obtained 42 out of 45 possible votes, and was proclaimed elected.

Combination of Hydrogen Phosphide and of Ammonia with Boron Chloride and Silicon Sesquichloride.—A. Besson.—Boron chloride combines directly with hydrogen phosphide at temperatures below +20°, forming a white solid unstable in the air and instantly decomposable by water. The author assigns to this compound the formula BCl_3PH_3 . Dry ammoniacal gas at +8° expels the hydrogen phosphide from this compound, 4 vols. of ammoniacal gas taking the place of 1 vol. PH_3 . The new compound is $2\text{BCl}_3\text{PH}_3$. Silicon sesquichloride combines directly with dry gaseous ammonia, forming a white solid, $\text{Si}_2\text{Cl}_3\cdot 5\text{NH}_3$. The reaction of hydrogen phosphide with silicon sesquichloride is not interesting.

Compounds of the Alkaline Metals with Ammonia. J. Moutier.—A thermo-chemical explanation of the formation of the compounds described by M. Joannis.

Determination of the Free Halogens and of Iodides in Presence of Chlorine and Bromine.—P. Lebeau.—(See p. 163).

Formation of Lead Hyposulphite.—J. Fogh.—The author calculates the formation-heat of this compound at +76 cal.

Researches on the Application of the Measure of Rotatory Power to the Determination of the Compounds resulting from the Action of Malic Acid upon the Neutral Lithium and Magnesium Molybdates.—D. Gernez.—Experiments upon solutions of laevo-rotatory malic acid mixed with gradually increasing quantities of sodium molybdate show, in solutions of similar volume, the formation of successive compounds resulting from the union of 1 equiv. malic acid with quantities of the salt corresponding to 1, 2, 3, 5 equivs., the production of which is characterised by the manner in which the rotatory power of the solutions varies and the maximum values through which it passes.

Volumetric Determination of Tannin.—E. Guenez.—This memoir will be inserted in full.

Determination of Acetone in Methylic Alcohol and in the "Methylenes" of Denaturation.—Leo Vignon.—The method of Kramer is applicable to the determination of very small quantities of acetone in methylic alcohol, but not to its determination in the "methylenes of denaturation," *i.e.*, methylated spirit.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., February, 1890.

Manufacture of Alkali.—B. Hasenclever (*Chem. Industrie*).—Zinc blende is now successfully used in various establishments in Germany for the manufacture of sulphuric acid and liquid sulphurous acid. The author fears that if the Chance process is adopted by all the manufacturers of Leblanc soda the price of sulphur will be seriously reduced.

Chemical Studies on the Ammonia-Soda Process.—H. Schreiber (*Chem. Industrie*).—The author estimates that whilst on the original ammonia-process 200 kilos. of salt were required to produce 100 kilos. sodium carbonate, the recent improvements will reduce this quantity to 115 to 120 kilos.

Historical Notice of Lavoisier.—M. Berthelot.—In this interesting survey the author quotes some of the sayings of the men who overthrew the Academy of Sciences and proscribed Lavoisier. Jean Bon St. André

said that the republic was under no obligation to make *savants* or to bestow upon them any privilege. Bouquier exclaimed in the Convention against the existence of a caste of egotistic and speculative *savants*. Every superiority, even if intellectual, was proclaimed an aristocracy, and as therefore to be suppressed. M. Berthelot remarks that this menacing language in our own time still echoes in the daily press. Guyton de Morveau, Monge, and especially Fourcroy, are blamed for not having even attempted to save Lavoisier. Fourcroy, if he did not, as it has been asserted, intrigue against Lavoisier, made himself very conspicuous in the suppression, or, as it was called, the purification of the "Lycée des Arts."

Metallurgical Review.—This section contains notices on the part played by sulphur in the processes employed in the extraction of zinc, on the hygroscopic property of certain colamines of inferior quality, on a peculiarity of blende in roasting, and on the manufacture of aluminium. These papers are taken from the *Chemiker Zeitung* and the *Zeit. für angewandte Chemie*.

The Action of Water at High Temperatures and at great Pressures upon Wood and Cellulose.—H. Tauss (*Dingler*).—Pure cellulose gives traces of sugar at the ordinary pressure. At higher pressures the quantity of sugar increases, but at 20 atmospheres it is converted into hydrocellulose. Wood is attacked by water at the ordinary pressure, but the action reaches its maximum at 5 atmospheres, when beech wood loses 26.7 per cent of its weight, of which 11 per cent become sugar. There are also produced dextrans, precipitable by alcohol. No vanilline is obtained from the aqueous or ethereal extracts, or from the dried residues. The colour-reactions of Ihl must be due to the transformation of lignine into carbohydrate.

MISCELLANEOUS.

Filtering-Paper from Grycksbo, Sweden.—In his "Treatise on Chemistry," vol. viii., p. 222, Berzelius expresses himself regarding the valuable qualities of this paper as follows:—"The best filtering-paper I know of comes from Grycksbo, in Dalecarlia; the water with which it is made is so pure that it does not give any reaction indicating the presence of foreign substances, nor does it retain any of the earths in solution. The acid and the water extract from this paper and the ash which it leaves when burnt are not more abundant nor of any other nature than those which come from the most unadulterated linen; that is to say, they do not amount to more than 0.006 of its weight. Latterly they have begun to make this paper an article of export, and assuredly there are few localities where nature has combined with so many favourable circumstances as at Grycksbo for the fabrication of an excellent filtering-paper." Fresenius's "Guide to Quantitative Chemical Analysis" (1862, 5th Edit., p. 81), on the subject of filtering-paper, says:—"The best is that known by the name of 'The Swedish Filtering-Paper,' and which bears the water-mark of J. H. Munktel."

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.

Celluloid.—Can any of the scientific readers of your journal give me the formula of a suitable celluloid solvent? If so, I shall feel obliged.—CELLULOID.

Sugar in Carrots.—Will some correspondent be good enough to inform me the percentage of saccharine matter to be found in a carrot, and also if any of our ordinary vegetables (excepting beet) contain more?—A. S.

MEETINGS FOR THE WEEK.

TUESDAY, 8th.—Royal Medical and Chirurgical, 8.30.
Photographic, 8.
WEDNESDAY, 9th.—Microscopical, 8.
Pharmaceutical, 8.
THURSDAY, 10th.—Institute of Electrical Engineers, 8.
FRIDAY, 11th.—Astronomical, 8.
Quekett Club, 8.

TO CORRESPONDENTS.

Torbay.—It would be impossible to answer your questions intelligibly without giving a paper on the subject. You should consult some good work on Volumetric Analysis—Sutton's, for instance.

THE LONDON HOSPITAL MEDICAL COLLEGE. The SUMMER SESSION will COMMENCE on THURSDAY, May 1st.

The Hospital, which is the largest general hospital in the kingdom, contains nearly 800 beds, all in constant use. There are wards for accidents, surgical and medical cases, diseases of women and children, and ophthalmic cases. Special departments for diseases of the eye, ear, throat, skin, and teeth, and for cancer, tumours, diseases of the bladder, piles, and fistula. Number of in-patients last year, 8873; out-patients, 101,548; accidents, 7456.

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N.B. Special arrangements have been made to meet the requirements of the Examining Board in England so as to enable Students entering in May to pass Part I. (Chemistry and Chemical Physics), and Part II. (Materia Medica and Pharmacy) of the First Examination in July.

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THE CHEMICAL NEWS

VOL. LXI. No. 1585.

NOTE ON MANURE DRYERS.

By VINCENT EDWARDS, F.C.S.

THIS being the busy time at manure works, a few words in connection with the above may be of interest. It is of course necessary to add to some manures substances which will not only increase bulk, but at the same time absorb moisture. I have come to the conclusion that there is a good deal of danger of serious error in this matter; in fact, of undoing what has been done at so much expense by adding "dryers" containing iron and alumina; in fact, some manufacturers may be deluded by unscrupulous dealers, as it is almost certain that many of these stuffs are worthless. I have made some experiments with ashes from furnaces, and find that some contain large quantities of iron, which, notwithstanding any new ideas to the contrary, is a very dangerous ingredient to supply without discrimination to plants. It is true that some may be benefited by the use of iron as a manure, but the advantages of its general use are more than doubtful. Manufacturers should see that all substances used for dryers are nearly free from iron. No superphosphate or bone manure should contain more than 0.7 per cent of iron (Fe), which is poison to the plant and injury to the manure.

Dublin, March 28, 1890.

PROFESSOR GRÜNWARD'S MATHEMATICAL SPECTRAL ANALYSIS.

(Continued from p. 159).

DR. KAYSER, when criticising the groups of rays of magnesium, reproaches the author for having included in the third group (embracing the hydrogen rays of magnesium, *i.e.*, those belonging to the primary substance "b" in that chemical condition in which it also occurs in free hydrogen = ba_4), the sharp margins of the bands which Liveing and Dewar have observed in the flame spectrum of magnesium burning in the free air, as he is of opinion that these bands belong, not to magnesium, but to a compound which it may form with hydrogen. But in the demonstration that these margins at 3865, 3860, &c., in the ultra violet (the wave-lengths of which were placed together in a separate column) correspond to the hydrogen rays of magnesium (third group), there lies an important discovery of the writer's, which he has scarcely brought into sufficient prominence, and for which he surely should not receive blame. When magnesium burns in the free air it combines not only with the oxygen of the atmosphere, but it withdraws oxygen from the omnipresent watery vapour and sets the hydrogen at liberty. The latter, in its nascent state, reacts upon the rest of the magnesium vapour, strengthening and rendering visible a portion of the magnesium bands otherwise invisible. This fact is not altered even by assuming that the action of the liberated hydrogen leads to the formation of a magnesium hydride. The latter can have at most the formula MgH , since MgH_2 could not exist in the magnesium flame. But the compound MgH , as a combination of gaseous components in equal volumes, emits only rays belonging in part to free magnesium, in part to free hydrogen, and in part to both in common, the intensities of which are chiefly different from the intensities which they possess in the free components. Entire series of rays which in the latter

are too faint to be noticed become perceptible in the compound MgH , and inversely.

As to the bands, totally distinct from the above, which Liveing and Dewar are really inclined to refer to $Mg+H$, namely (5618-5576 . . .) (5566-5525) (5513, 5512, 5511-5458 . . .) (5210-5185) (see *Proc. Roy. Soc.* 1881, p. 196), the author has only examined them closely after his publication on magnesium and carbon, and finds that their luminous maxima as given by Liveing and Dewar belong to the first or helium group of the magnesium rays. Hence it follows that at least a part of these bands (emitted by magnesium in presence of hydrogen in the electric spark under a pressure of several atmospheres) belong to the group mentioned. Here is another "discovery" hitherto not published, but communicated to Prof. Liveing on September 14th and 20th, 1887, which will, he trusts, survive the criticism of Dr Kayser.

As to the further wave-lengths criticised by Dr. Kayser, it must be remarked that, according to the researches of Liveing and Dewar (*CHEM. NEWS*, 1881, vol. xliii., pp. 261-263, 271-273), magnesium emits rays which are otherwise not observed, but which, nevertheless, like the above-mentioned bands (or luminous maxima of bands), belong to magnesium, and can be without difficulty introduced into the corresponding groups of rays. Their wave-lengths were obtained from the above source, as also from the "Investigations on the Spectrum of Magnesia" (*Proc. Royal Soc.*, vol. xxxii., 189, 203). Thus, λ 4808 was observed by Liveing and Dewar in the blue as a faint line in the electric spark, 4481 strong in the electric spark in presence of hydrogen, but not in the arc; 4350 in the arc-spectrum only; 4586 in the spark spectrum; 4703 in both; 4165, in place of 4166, is a clerical error, since 4166 agrees better with the criteria. That the respectively adjacent wave-lengths, 3330 of Liveing and Dewar, and 3329.1 of Hartley and Adeney (Abney?), are drawn together in the conspectus on page 11 of the memoir on magnesium and carbon is an oversight. In the tables they are kept distinct.

Finally, it must be mentioned that the author obtained a series of wave-lengths (which were not to be found in the original memoirs then at his disposal) from a well-known compilation, the "Text-book of Spectral Analysis," by Dr. Kayser (1883), with the unfortunate result that several of the numbers given, *e.g.*, 4456, 4705, 3896, and 3894, are inaccurate! The author has learnt the sparing trustworthiness of the numerical data of this manual on obtaining from England and Ireland the original treatises and the "Reports of the British Association." Dr. Kayser's work should be used with great caution by those who have not *all* the original documents at command.

The correct values of the two last-mentioned wave-lengths, 3895 and 3893 (instead of 3896 and 3894), as well as the wave-lengths of various other magnesium lines, were re-determined by Liveing and Dewar, in 1888 (*Proc. Royal Soc.*, vol. xlv.), and, of course, could not be utilised in 1887.

I call attention to the fact that if a rhythmic relation exists between two wave-lengths $\lambda \lambda'$ of the spectrum, or of two different spectra, this relation may be recognised and deduced even from rather defective measurements. For if $\lambda + \delta \lambda + \delta'$ are two faulty values of the true wave-lengths—

$$\lambda \lambda' \text{ and } \frac{\lambda'}{\lambda} = \frac{m}{p},$$

where $m p$ represent whole numbers, the error of—

$$\frac{\lambda' + \delta'}{\lambda + \delta} : \frac{\lambda' = \delta'}{\lambda + \delta} - \frac{\lambda}{\lambda'} = \frac{\lambda \delta' - \lambda \delta}{\lambda^2} = \frac{m}{p} \left\{ \frac{\delta'}{\lambda'} - \frac{\delta}{\lambda} \right\}$$

is very small, especially when $\lambda \lambda'$ are considerable. This is the cause why the Balmer's rhythmic relations among a portion of the hydrogen lines (which belong to the primary element a of $H=ba_4$) may be deduced even from Angström's measurements. Further, the mere

accidental character of a rhythmic relation among a large number of the corresponding wave-lengths of the two spectra is much less probable than it would be the case with a constant but non-rational relation.

The author, therefore, did not scruple three to four years ago to attempt the verification of his theory, and in connection therewith to search for any existing rhythmic relations between two groups of lines of different spectra. This was done, notwithstanding the then very incomplete and, in some cases, rather faulty data. Along with the more recent determinations by Liveing and Dewar, Hartley and Adeney (Abney?), Thalén and Cornu, he utilised the former results of such men as Kirchhoff, Plücker, Huggins, H. W. and W. C. Vogel, especially when more later measurements were wanting.

It should never be forgotten that Rowland's new method of measuring wave-lengths by means of concave gratings, which admits of a degree of accuracy previously unknown, has found entrance into England and the rest of Europe only within the last few years. The increased precision thus attained will be to the advantage of the author's theory and of the comparisons which it requires. At present there is especial need of new accurate measurements of the lines of oxygen and of the luminous maxima of its bands, both alone and under the influence of the aqueous vapour of the oxyhydrogen flame. The collocation of different data compelled by external circumstances has led J. S. Ames (*Amer. Chem. Journ.*, 1889, vol. x., p. 138) to a supposed fundamental objection to the theory. The wave-lengths 6742 (Kirchhoff) and 6740 (Huggins) are two distinct data, in consequence of errors of observations, for one and the same cadmium line which in the author's spectral analysis of cadmium appear mentioned in the first group of the cadmium rays, the former (Kirchhoff's) being in especial type to signify that it displays all the criteria of the group in a particularly satisfactory manner. Ames assumes that, according to the author's theory, two lines should be present, though one only is visible, and, in common with Dr. Kayser, he sees here a fundamental objection to the theory! Here it must be remarked that even if accidentally both wave-lengths should fulfil all the criteria of the first group (which is here not the case), it would merely follow that both must belong to the same form of condensation of the primary element "c," but not necessarily the actual equal visibility of the corresponding rays in the spectra of all substances which contain "c" in this form of condensation, because its intensity is variously modified by the influence of the other constituents of such substances which may intensify the ray in one and in another enfeeble it down to disappearance. These and similar criticisms are not valid against the author's theory.

(To be continued).

EXAMPLES OF "SOLUTION COMPOUNDS."*

By G. GORE, LL.D., F.R.S.

THE term "solution compounds" has been applied chiefly to those substances which exist only whilst dissolved in water, &c., and are decomposed on evaporating or crystallising the liquids. A method of detecting those bodies and of ascertaining the combining proportions of their ingredients by means of the "voltaic balance" has already been published (see *Roy. Soc. Proc.*, vol. xlv., p. 265).

The formula of each "solution compound" in the following series of examples is the one yielding the smallest amount of voltaic energy, and is indicated by a star (*). The act of chemical union is usually attended by a great loss of such energy, and the relative amount of

voltaic energy of the new compound is usually very much smaller than that of the mean of its constituents. Each "solution compound" is recognised by a depression of such energy. In each of the following cases only a sufficient number of measurements are given to show a portion of the depression of energy caused by chemical union of the ingredients of the compound. One example only is given of each class of compounds, and only average amounts of available voltaic energy are stated; the proportions of such energy given do not include the amounts lost by "local action." Zinc platinum couples and aqueous solutions were employed in all cases.

EXAMPLES.

1.—Element with Element.

Chemical equivalents.		Average energy.
4Br+5Cl	at 20° C.	1,934,496
4,, +4,,*	"	1,817,901
4,, +3,,	"	1,981,035

2.—Element with Monobasic Acid.

4HCl+5Cl	at 21° C.	863,774
4,, +4,,*	"	739,922
5,, +4,,	"	876,300

3.—Element with Bibasic Acid.

2H ₂ SO ₄ +5I	at 18° C.	320,460
2,, +4I*	"	267,958
2,, +3I	"	312,815

4.—Element with Tribasic Acid.

Citric acid+4Br	at 20° C.	775,944
" +3,,*	"	636,956
" +2,,	"	706,506

5.—Element with Tetrabasic Acid.

H ₄ P ₂ O ₇ +5Br	at 20° C.	716,768
" +4,,*	"	586,785
" +3,,	"	614,269

6.—Element with Monobasic Salt.

4AmCl+5Br	at 17° C.	355,698
4,, +4,,*	"	308,699
3,, +4,,	"	326,081

7.—Element with Bibasic Salt.

2K ₂ SO ₄ +5Cl	at 20° C.	74,368
2,, +4,,*	"	50,648
2,, +3,,	"	54,536

8.—Element with Tribasic Salt.

2Na ₂ HPO ₄ +7I	at 21° C.	30,869
2,, +6I*	"	26,556
2,, +5I	"	28,703

9.—Element with Tetrabasic Salt.

Na ₄ P ₂ O ₇ +5Br	at 21° C.	104,387
" +4,,*	"	82,289
" +3,,	"	86,377

10.—Monobasic Acid with Monobasic Acid.

4HF+5HCl	at 19° C.	162,078
4,, +4,,*	"	151,760
4,, +3,,	"	170,678

11.—Monobasic Acid with Bibasic Acid.

2H ₂ CrO ₄ +5HCl	at 17° C.	72,445
2,, +4,,*	"	62,056
2,, +3,,	"	68,746

12.—Monobasic Acid with Tribasic Acid.

Citric Acid+4HF	at 20° C.	107,223
" +3,,*	"	102,319
" +2,,	"	107,223

13.—Monobasic Acid with Tetrabasic Acid.

H ₄ P ₂ O ₇ +5HNO ₃	at 20° C.	26,795
" +4,,*	"	23,731
" +3,,	"	25,969

* Read before the Birmingham Philosophical Society, Nov. 12, 1889.

14.—Bibasic Acid with Bibasic Acid.		Average energy.	30.—Tribasic Acid with Tetrabasic Salt.		Average energy.
Chemical equivalents.			Chemical equivalents.		
3Oxalic Acid + 4H ₂ SO ₄ at 20° C.	81,232	3(KCr ₂ SO ₄) + 5Citric Acid at 23° C.	25,969
4 " + 4 " * "	63,851	3 " + 4 " * "	24,035
5 " + 4 " * "	78,304	3 " + 3 " * "	25,559
15.—Bibasic Acid with Tribasic Acid.			31.—Tetrabasic Acid with Monobasic Salt.		
2Citric Acid + 4H ₂ CrO ₄ at 18° C.	924,835	5KNO ₃ + H ₄ P ₂ O ₇ at 28° C.	2,726
2 " + 3 " * "	779,734	4 " + " * "	2,253
2 " + 2 " * "	927,682	3 " + " * "	2,659
16.—Bibasic Acid with Tetrabasic Acid.			32.—Tetrabasic Acid with Bibasic Salt.		
2H ₄ P ₂ O ₇ + 5H ₂ SO ₄ at 20° C.	25,587	5Na ₂ SO ₄ + 2H ₄ P ₂ O ₇ at 25° C.	1,755
2 " + 4 " * "	21,648	4 " + 2 " * "	1,577
2 " + 3 " * "	23,542	3 " + 2 " * "	1,841
17.—Tribasic Acid with Tribasic Acid.			33.—Tetrabasic Acid with Tribasic Salt.		
5Citric Acid + 4H ₃ PO ₄ at 25° C.	3,900	5Na ₂ HPO ₄ + 3H ₄ P ₂ O ₇ at 21° C.	936
4 " + 4 " * "	3,495	4 " + 3 " * "	842
3 " + 4 " * "	3,823	3 " + 3 " * "	962
18.—Tribasic Acid with Tetrabasic Acid.			34.—Tetrabasic Acid with Tetrabasic Salt.		
3H ₄ P ₂ O ₇ + 5Citric Acid at 20° C.	13,119	5Na ₄ P ₂ O ₇ + 4H ₄ P ₂ O ₇ at 21° C.	171
3 " + 4 " * "	11,637	4 " + 4 " * "	136
3 " + 3 " * "	13,231	3 " + 4 " * "	165
19.—Monobasic Acid with Monobasic Salt.			35.—Monobasic Salt with Monobasic Salt.		
4KCl + 5HF at 17° C.	12,241	4KNO ₃ + 5KCl at 15° C.	275
4 " + 4 " * "	11,063	4 " + 4 " * "	211
4 " + 3 " * "	12,241	4 " + 3 " * "	259
20.—Monobasic Acid with Bibasic Salt.			36.—Monobasic Salt with Bibasic Salt.		
2Na ₂ SO ₄ + 5HNO ₃ at 18° C.	86,377	2(Ba ₂ NO ₃) + 5NaCl at 15° C.	61'4
2 " + 4 " * "	77,446	2 " + 4 " * "	54'3
2 " + 3 " * "	88,480	2 " + 3 " * "	61'4
21.—Monobasic Acid with Tribasic Salt.			37.—Monobasic Salt with Tribasic Salt.†		
Na ₂ HPO ₄ + 4HCl at 19° C.	78,754	2LCI + Na ₂ HPO ₄ at 13° C.	-1,390
" + 3 " * "	70,959	3 " + " * "	-1,558
" + 2 " * "	81,805	4 " + " * "	-1,295
22.—Monobasic Acid with Tetrabasic Salt.			38.—Monobasic Salt with Tetrabasic Salt.		
Na ₄ P ₂ O ₇ + 5HCl at 18° C.	8,637	Na ₄ P ₂ O ₇ + 5KCl at 16° C.	-7,657
" + 4 " * "	8,123	" + 4 " * "	-9,623
" + 3 " * "	8,880	" + 3 " * "	-7,951
23.—Bibasic Acid with Monobasic Salt.			39.—Bibasic Salt with Bibasic Salt.		
5KCl + 2H ₂ SO ₄ at 15° C.	10,765	4Na ₂ CO ₃ + 5K ₂ Cr ₂ O ₇ at 17° C.	-23,785
4 " + 2 " * "	9,867	4 " + 4 " * "	-28,574
3 " + 2 " * "	11,637	4 " + 3 " * "	-26,615
24.—Bibasic Acid with Bibasic Salt.			40.—Bibasic Salt with Tribasic Salt.		
4K ₂ SO ₄ + 5H ₂ CrO ₄ at 18° C.	52,438	4Na ₂ SO ₄ + 3Na ₂ HPO ₄ at 20° C.	779
4 " + 4 " * "	41,413	3 " + 2 " * "	727
4 " + 3 " * "	46,049	2 " + 3 " * "	818
25.—Bibasic Acid with Tribasic Salt.			41.—Bibasic Salt with Tetrabasic Salt.		
4Na ₂ HPO ₄ + 7H ₂ SO ₄ at 21° C.	37,706	5Am ₂ SO ₄ + 2Na ₄ P ₂ O ₇ at 25° C.	-1,134
4 " + 6 " * "	30,931	4 " + 2 " * "	-1,346
4 " + 5 " * "	33,215	3 " + 2 " * "	-1,163
25.—Bibasic Acid with Tetrabasic Salt.			42.—Tribasic Salt with Tribasic Salt.		
2Na ₄ P ₂ O ₇ + 5H ₂ SO ₄ at 21° C.	14,004	4Na Citrate + 5Na ₂ HPO ₄ at 22° C.	381
2 " + 4 " * "	12,145	4 " + 4 " * "	365
2 " + 3 " * "	13,008	4 " + 3 " * "	400
27.—Tribasic Acid with Monobasic Salt.			43.—Tribasic Salt with Tetrabasic Salt.		
4NaCl + Citric Acid at 18° C.	10,526	5Na ₂ HPO ₄ + 3Na ₄ P ₂ O ₇ at 21° C.	-1,715
3 " + " * "	8,707	4 " + 3 " * "	-1,894
2 " + " * "	8,912	3 " + 3 " * "	-1,723
28.—Tribasic Acid with Bibasic Salt.			44.—Tetrabasic Salt with Tetrabasic Salt.		
7BaBr ₂ + 4Citric Acid at 21° C.	2,172	5Am ₄ P ₂ O ₇ + 4Na ₄ P ₂ O ₇ at 23° C.	-351
6 " + 4 " * "	2,044	4 " + 4 " * "	-379
5 " + 4 " * "	2,324	3 " + 4 " * "	-337
29.—Tribasic Acid with Tibasic Salt.			45.—Sugar + Common Salt.		
3Na ₂ HPO ₄ + 4Citric Acid at 19° C.	4,330	2Cane sugar + 5NaCl at 11° C.	-43'6
4 " + 4 " * "	3,900	2 " + 4 " * "	-47
5 " + 4 " * "	4,461	2 " + 3 " * "	-44'5

† The loss of voltaic energy in this case and several others is indicated by a maximum minus number, instead of a minimum plus one.

It is evident in all these cases, from the proportions of substances required to reduce the energy to the smallest number, that the two uniting substances must be chemically equivalent to each other.

The foregoing series of examples show that all kinds of soluble elements, acids, acid, neutral, and alkaline salts, &c., whilst in aqueous solution together, unite with each other indiscriminately in the definite proportions by weight of their ordinary chemical equivalents.

As in every one of these cases, either one of the two ingredients may be replaced by almost any other soluble ingredient of equal chemical value, and as each of these instances is only a solitary example of a large number of the same class of compounds, and each compound is capable of uniting with nearly every other compound individually whilst in solution, and these more complex ones are similarly capable of uniting with others of equal chemical value almost without limit, except in cases where separation by precipitation or evolution of gas occurs (see *Roy. Soc. Proc.*, vol. xlv., p. 266; also "Loss of Voltaic Energy by Chemical Union," *Proc. Birm. Phil. Soc.*, 1888, vol. vi., Part 2), it is evident that the total number of possible "solution-compounds" is exceedingly great—certainly thousands.

The fact, which has been so largely disclosed by means of the voltaic balance, that *all kinds of chemical substances, when in mutual solution, unite with each other indiscriminately and irrespective of the chemical nature of the substances*, has an important bearing upon chemical action, and throws great light upon the cause of chemical union.

The following are the average amounts of available voltaic energy of the ingredients employed in making the above compounds, and from these numbers and the foregoing ones the amounts of loss of such energy which occurred during the formation of the compounds can be ascertained:—

	Degrees Centigrade.	Average voltaic energy.
Cl.. .. .	at 11	1,282,000,000
Br	13.7	81,022,500
HCl	16.5	9,344,092
H ₂ SO ₄	19	3,900,941
I	13.5	3,310,985
HNO ₃	19	3,204,395
H ₂ CrO ₄	18	1,611,111
HF	18	1,151,363
KCl	8	69,803
NaCl	15	207,589
Citric acid	22	36,597
KCr ₂ SO ₄	19	35,902
H ₃ PO ₄	26	34,952
H ₄ P ₂ O ₇	17	20,336
AmCl	13.5	15,069
KNO ₃	20	10,841
Oxalic acid.. .. .	15	9,450
K ₂ Cr ₂ O ₇	13	7,156
Am ₂ SO ₄	20	2,634
K ₂ SO ₄	12	2,274
Na ₂ HPO ₄	15	2,057
Na ₂ SO ₄	13	2,020
Na Citrate	22	1,466
Am ₄ P ₂ O ₇ (variable) ..	23	327
LCl	16	204
Water	16	0
Cane sugar.. .. .	15	-67.8
Ba ₂ NO ₃	19	-163
BaBr ₂	17	-163
Na ₄ P ₂ O ₇	18	-232
Na ₂ CO ₃	19	-14,795

The amounts of voltaic energy with zinc-platinum couples of more than three hundred "solution-compounds" are given in a paper on "Relative Amounts of available Voltaic Energy of Aqueous Solutions" (*Ibid.*, 1889, vol. vii., Part 1).

EXAMINATION OF CORPSES FOR ALKALOIDS AND OTHER NITROGENOUS BASES.*

Dr. ANTON SEYDA.

THE examination of the organs of a corpse for alkaloids is one of the most difficult chemical problems, as every chemist will admit, the more distinctly the longer experience he has had in this sphere. Our fragmentary knowledge of the ptomaines and of the conditions in which they are formed and again disappear, involves much uncertainty of judgment on the alkaloidal nature of a substance. So much has been already written on ptomaconines, ptomastrychnines, &c., that we could not wonder if a publication were to appear "On a Strychnine or Morphine obtained from Putrid Albumen."

It has been rightly said:—"A nitrogenous base obtained from a corpse can only be pronounced identical with a well-known vegetable alkaloid when the two agree together physically, chemically, and physiologically. In this case the confusion of a ptomaine with an alkaloid is almost out of the question. On the other hand, in such a position of things it cannot be denied that a really existing vegetable alkaloid may easily be overlooked, especially if we consider that we have to do with only very small quantities. In reading the accounts of ptomaines the author has not been able to avoid a suspicion that the chemist concerned had been almost too cautious, and on the faith of a few not very decided reactions has been induced to pronounce in favour of the presence of ptomaines.

In the present state of science it is, under certain circumstances, easier to prove the presence of a ptomaine than of a vegetable or artificial alkaloid. To consider the proof of the absence of an alkaloid or of the presence of a ptomaine in amorphous residues, as furnished on the faith of doubtful or defaulting colour-reactions, is an equally hazardous affair, as when the solution of a residue gives with the general reagents for alkaloids a more or less intensely coloured precipitation, or none at all. The physical, chemical, and physiological behaviour of the alkaloids in a pure state is tolerably known, but not in an impure state, or better, in a not quite pure state, and such occur for the most part in the examination of the organs of a corpse.

Extracts from such organs are best obtained by treatment with tartaric alcohol. The fat separated along with the water requires no further treatment. It is not, indeed, absolutely impossible that it may act as a solvent for some organic poison, *e.g.*, nitroglycerin. For isolating and determining this poison in matter free from fat the author recommends the following method:—The air-dry substance is shaken out with chloroform and from the filtrate the chloroform is chiefly distilled off in a retort, the residue is then cautiously evaporated in a moderately warm water-bath in a beaker glass previously tared, dried over concentrated sulphuric acid, and then weighed again.

If the fat is saponified and the soap is dissolved in water and shaken up with ether, the latter is covered intensely yellow; on evaporation there is obtained a yellowish crystalline residue, insoluble in water, which may be obtained pure by repeated crystallisation, and proves to be cholesterine.

The extracts obtained from the stomach are mostly light yellow; the colour being more intense in cases when the bile has poured out into the stomach. Extracts of a more dark brown colour are obtained from the large abdominal glands which are filled with blood, and this colour passes more or less strongly into all the liquids which have been obtained by shaking out the residues. This evil can be decreased by freeing the organs as far as possible from blood.

The solutions of the extracts may often be cleared in

* *Chemiker Zeitung.*

the following manner:—To the alcoholic solution an alcoholic solution of tartaric acid is added as long as a precipitate is formed (the substance obtained being always tested for the presence of an alkaloid); it is filtered off and drained, the filtrate is evaporated, the residue is taken up in water, the filtered clear solution is neutralised with potassa, concentrated, and mixed with alcohol. The potassium tartrate is thus separated out, and carries down with it a part of the colouring-matter. The watery solutions of the extracts finally resulting (an absolutely neutral solution cannot be obtained in any case, so that both red and blue litmus-paper remain unaffected, hence the solutions must be set so that blue litmus-paper is very slightly reddened) and they are then tested with the general reagents for alkaloids; more or less decided precipitates are obtained in most cases.

Before proceeding to a closer examination, the liquids should always be tested for their behaviour with iodic acid and also for the presence of meconic acid. A reduction of iodic acid will often occur (the acidulation must be effected with tartaric acid and not with hydrochloric acid, since an excess of this latter may decompose the iodic acid), and is not always due to morphine. Occasionally this reducing substance is met with in the ethereal extract obtained from an acid solution. Sometimes it cannot be detected after extraction either in the amylic or in any other of the residues from extraction, nor, remarkable to say, the original watery extract. This substance seems to be decomposed by the supersaturation with potassa-lye or the treatment with the different solvents.

If iodic acid is not reduced, the specific search for morphine becomes unnecessary.

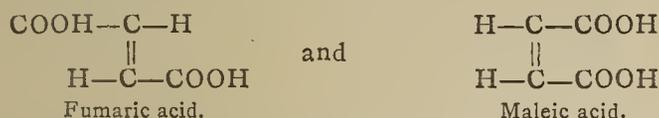
(To be continued).

ON THE SYNTHESIS OF FUMARIC ACID.*

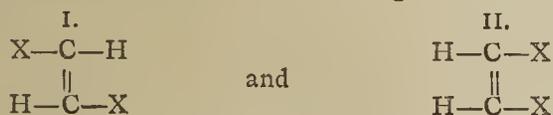
By E. H. KEISER.

(PRELIMINARY COMMUNICATION).

VAN'T HOFF† has proposed the following stereometric formulæ for fumaric and maleic acids:—



Johannes Wislicenus‡ has shown in a series of important papers that it is possible to determine experimentally the stereometric formulæ of certain isomeric compounds. A consideration of the hypothesis put forward by him, suggested the idea that it ought to be possible to prepare both fumaric and maleic acids synthetically from acetylene. In accordance with Van't Hoff and Wislicenus's theory, the di-halogen additive compounds of acetylene can exist in two isomeric forms having the formulæ:—

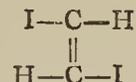


in which X represents any halogen atom. And, further, compounds having the constitution represented by formula I. are more stable than those having the structure represented by the second formula. Fumaric acid would then appear to be closely related to the halogen derivatives of the first class, and maleic acid to those of the second.

It occurred to me that it might, perhaps, be of interest in this connection to start with acetylene, and prepare, in the first place, two isomeric di-halogen additive compounds, and then endeavour to transform these into fumaric and maleic acid. The investigation is not yet completed, but one of the acids, namely, fumaric acid, has been prepared in this way from acetylene.

Acetylene was prepared by the action of alcoholic potash upon ethylene bromide, and the purified gas was passed through a series of wash-bottles containing crystals of iodine covered with a layer of absolute alcohol. After a time, the iodine disappeared, and from the liquid two isomeric acetylene di-iodides were separated. One of these compounds is a solid at ordinary temperatures; the other is a liquid. The solid di-iodide is much more stable than the liquid variety. It does not decompose on standing, and can be sublimed without suffering change. On the other hand, the liquid di-iodide undergoes decomposition when heated, and cannot be distilled with steam without being decomposed. These compounds have been prepared by Sabanejeff,* who has analysed them and found them to have the composition represented by the formula $\text{C}_2\text{H}_2\text{I}_2$. No attempt was made by him to determine their constitution.

In accordance with the Van't Hoff hypothesis, the solid acetylene di-iodide, which is much more stable than the liquid di-iodide would have the constitution represented by the formula—



and would, therefore, belong to the same general class of acetylene derivatives to which fumaric acid belongs. Now, experiment shows that this solid acetylene di-iodide can be transformed into fumaric acid.

Nine grms. of the acetylene di-iodide crystals (m.p. 73°) were dissolved in alcohol, and 5 grms. (two molecules) of potassium cyanide added, and the solution was boiled for thirty-six hours in a flask with an inverted condenser. Caustic potash was thereupon added, and the boiling continued for two hours longer. On cooling the contents of the flask, a considerable quantity of needle-shaped crystals separated from the liquid. They were removed from the solution, and on examination proved to be the potassium salt of fumaric acid, which crystallises in the form of needles, insoluble in cold alcohol. More of the salt was obtained from the mother-liquor. The aqueous solution of the potassium salt was treated with silver nitrate, and a white precipitate consisting of the silver salt was obtained. The silver salt was purified by dissolving it in nitric acid and re-precipitating it by carefully neutralising the solution with ammonia. The silver salt of fumaric acid is characterised by its great insolubility in water, and by the fact that when it is heated it deflagrates like gunpowder. Both of these properties were exhibited by the silver salt of the acid made by synthesis.

A quantitative determination of the percentage of silver gave the following result:—

0.2039 grm. of the salt, dried at 100°, gave
0.1786 grm. of AgCl = 65.97 per cent Ag.

	Calculated for $\text{Ag}_2\text{C}_4\text{H}_2\text{O}_4$.	Found.
Ag.. ..	65.43	65.97

The free acid itself was recognised by its insolubility in water; it was precipitated from moderately concentrated solutions of its salt by the addition of strong acids. It will be analysed as soon as larger quantities of it have been obtained in pure condition.

In 1882, Sabanejeff‡ studied the action of potassium cyanide upon acetylene di-bromide and obtained an acid

* Read at the Meeting of the Chemical Section of the Franklin Institute, February 20, 1890.

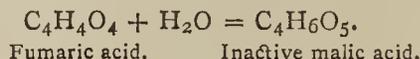
† "Lagerung der Atome im Raume," p. 21.

‡ "Räumliche Anordnung der Atome in organischen Molekülen," *Ann. Chem.* (Liebig), cxxlvi., 53.

* *Ann. Chem.* (Liebig), clxxviii., 118.

† *Ann. Chem.* (Liebig), cxxvi., 275.

having the formula $C_4H_6O_5$. It is probable that fumaric or maleic acid was first formed in his experiments, which afterwards, by the prolonged action of boiling caustic alkali, was converted into the acid $C_4H_6O_5$. It has been shown by Linnemann and Loydl* that when fumaric acid is heated with caustic alkalies, it is gradually changed into an inactive malic acid, thus:—



A more detailed study of the reactions, which give rise to the formation of the two acetylene di-iodides, as well as the attempt to prepare maleic acid from acetylene, is reserved for future work.

THE SPONTANEOUS IGNITION OF COAL CARGOES.†

By Professor VIVIAN B. LEWES,

Associate of the Institution of Naval Architects, F.C.S., F.I.C.

FIFTEEN years ago the loss of life and property caused by the spontaneous ignition of coal cargoes became so serious that the Board of Trade, acting in unison with the Committee of Lloyds', urged upon the Government the necessity for appointing a Royal Commission to inquire into and report upon the possibility of preventing a class of disaster as appalling in nature as it is destructive in result. The Commission, which was appointed in April, 1875, had the good fortune to be aided in their inquiry by the scientific knowledge of Dr. Percy and Mr., now Sir Frederick, Abel, and after collecting and collating all the evidence which could be obtained, they, in the following year, published their report upon the subject. In this report much valuable evidence is passed in review, and much sound advice is given for the guidance of those employed in the shipment of coals; but whether it is that the sight of a blue-book scares the ordinary reader, or that the circulation of such literature, often of the most valuable character, is of necessity very limited, the fact remains that the conditions at present existing are as nearly bad as they were before the publication of the report.

In the nine years immediately following the report, viz., 1875 to 1883, 57 coal-laden vessels are known to have been lost from spontaneous ignition of their cargoes, whilst during the same period 328 were missing from unknown causes, a large percentage of these losses being undoubtedly due to the same cause; and these, again, form but a very small percentage of the cases in which cargoes have heated and fired, but in which the vessel has been saved; and now, within the last few years, the statement has gained ground that with the general increase of temperature in steam-ships, due to the introduction of triple expansion engines and high-pressure boilers, spontaneous firing in the coal-bunkers and coal cargoes is very much increased, and that many accidents arise from this cause.

Under these circumstances, Mr. Martell suggested to me some time ago that an inquiry into the causes and possible prevention of this very serious evil would be work, not only likely to be acceptable to the members of this Institute, but also one that was needed in the Service, as well as in the mercantile marine; and I have now much pleasure in bringing before you the results obtained in a long series of experiments, and which, taken in conjunction with the work done by others on the subject, throws a somewhat clearer light upon the causes of this particular class of phenomenon, and enables suggestions to be made for its prevention.

* *Ann. Chem.* (Liebig), cxcii., 80.

† Read at the Thirty-first Session of the Institution of Naval Architects, March 28, 1890; the Earl of Ravensworth in the Chair.

Coal is a substance of purely vegetable origin, formed out of contact with air by long exposure to heat and pressure, from the woody fibre and resinous constituents of a monster vegetation which flourished long before the earth was inhabited by man: and coal may therefore be looked upon as a form of charcoal which, having been formed at a temperature lower than that of the charcoal burner's heap and under great pressure, is very dense, and still retains a quantity of those constituents, which, in the latter case, are driven off, as tar, wood naphtha, &c.; and these bodies consist essentially of compounds containing carbon and hydrogen, together with a little oxygen and nitrogen, and form the volatile matter and hydrocarbons of the coal.

Besides the carbon and hydrocarbons, coal also contains certain mineral bodies which were mostly present in the sap and fibre of the original vegetation, and which give the ash which is left behind when the coal is burnt.

These substances consist chiefly of sulphate of lime or gypsum, silica, and alumina, whilst in nearly all kinds of coal is to be found a substance called disulphide of iron, coal brasses, or pyrites, which has been formed by the gradual reduction of the sulphates by carbonaceous matter in the presence of iron salts, and which, during the combustion of the coal, is decomposed, giving off sulphur compounds, and leaving behind oxide of iron, which gives the reddish brown colour to the ash left by many kinds of coal.

Of these constituents of coal, the only ones which play no part in the phenomena attending heating and spontaneous ignition are the mineral constituents other than the pyrites, and we have therefore to deal with the chemical actions which take place when the carbon, hydrocarbons, and brasses contained in newly-won coal come in contact with air and moisture.

(a) *The Influence of Carbon in Producing Heating.*

Carbon is one of those substances which possess to an extraordinary degree the power of attracting and condensing gases upon their surface, this power varying with the state of division and density of the particular form of carbon used. The charcoal obtained from dense forms of wood, such as box, exhibit this property to a high degree, one cubic inch of such charcoal absorbing*—

Ammonia gas	90	cubic inches.
Sulphuretted hydrogen	55	"
Carbon dioxide	35	"
Ethylene (olefiant gas)	35	"
Oxygen	9.25	"
Nitrogen	6.5	"

whilst certain kinds of coal also exhibit the same power, although to a less degree.

The absorptive power of newly-won coal due to this surface attraction varies, but the least absorbent will take up $1\frac{1}{4}$ times its own volume of oxygen, whilst in some coals more than three times their volume of the gas is absorbed. This absorption is very rapid at first, but gradually decreases, and is, moreover, influenced very much by temperature, for reasons which will be explained later.

The absorption is at first purely mechanical, and itself causes a rise of temperature, which, in the case of charcoal formed in closed retorts, as in preparing alder, willow, and logwood charcoal for powder-making, would produce spontaneous ignition if it were not placed in sealed cooling vessels for some days before exposure to air.

The rate of absorption varies with the amount of surface exposed, and therefore able to take part in this condensing action, so that when coal or charcoal is finely powdered, the exposed surface being much greater, absorption becomes more rapid, and rise of temperature at once takes place. If charcoal is kept for a day after it

* Saussure.

has been made, out of contact with air, and is then ground down into a powder, it will frequently fire after exposure to the air for thirty-eight hours; whilst a heap of charcoal powder, of 100 bushels or more, will always ignite. It is for this reason that, in making the charcoal for powder, it is always kept, after burning, for three or four days in air-tight cylinders before picking over, and ten days to a fortnight before it is ground.

In the case of coal, this rise in temperature all tends to increase the rate of the action which is going on; but is rarely sufficient to bring about spontaneous ignition, as only about one-third the amount of oxygen being absorbed by coal that is taken up by charcoal, and the action being much slower, tends to prevent the temperature reaching the high ignition-point of the coal. Air-dry coal absorbs oxygen more quickly than wet coal.

(b). *The Action of the Bituminous Constituents of the Coal in Spontaneous Ignition.*

All coal contains a certain percentage of hydrogen, which is in combination with some of the carbon, and also with the nitrogen and oxygen, and forms with them the volatile matter in the coal, and the amount present in this condition varies very largely, being very small in anthracite and very great in cannel and shale. When the carbon of the coal absorbs oxygen, the compressed gas becomes very chemically active, and very soon commences to combine with the carbon and hydrogen of the bituminous portions, converting them into carbon, dioxide, and water vapour. This chemical activity increases rapidly with rise of temperature, so that the heat generated by the absorption of the oxygen causes it to rapidly enter into chemical combination. Chemical combination of this kind—*i.e.*, oxidation—is always accompanied by evolution of heat, and this further rise of temperature again increases rapidity of oxidation, so that a steady rise of temperature is set up, and this taking place in the centre of a heap of small coal, which, from the air and other gases enclosed in its interstices, is an admirable non-conductor of heat, will often cause such heating of the mass, that if air can percolate slowly into the heap in sufficient quantity to supply the necessary percentage of oxygen for the continuance of the action, the igniting-point of the coal would be soon reached.

The effect of rise of temperature in increasing the rapidity of chemical actions of this kind can be realised from the effect which it has in the spontaneous ignition of oily waste or rag.

If a substance like cotton-waste be rendered oily with anything except the mineral oils, it acquires the power of taking up oxygen from the air, and this oxidising the oil gives rise to heat. At ordinary temperatures this oxidation is slow, and, consequently, it may be days before the rise in temperature becomes sensible, but when this point is reached the oxidation proceeds with remarkable rapidity, and in a few hours the point of ignition is reached and the mass bursts into flame, whilst if the oily waste be placed in a warm place at first, spontaneous ignition is only a question of hours, or sometimes even minutes.

Galletley found that oily cotton at ordinary temperatures took some days to heat and ignite, whilst placed in a chamber warmed to 130° to 170° F. (54° to 76° C.), the cotton greasy with boiled linseed ignited in one hour fifteen minutes, and olive oil on cotton in five hours, and in a chamber heated to 180° to 200° F. (82° to 93° C.) olive oil on cotton ignited in two hours.

It has been suggested that very bituminous coal, such as cannel, shale, and coals containing schist, is liable to spontaneous ignition from the fact that a rise in temperature would cause heavy oils to exude from them, which, by undergoing oxidation, might cause rapid heating. But experiment not only shows that this is not the case, but that the heavy mineral oils have a remarkable influence in retarding heating, cotton waste, oily with easily oxidisable

oils mixed with 20 per cent of heavy mineral oil, being exempt from heating.

(c). *The Action of Iron Disulphide, Pyrites, or Coal Brasses in Promoting Spontaneous Ignition.*

Ever since Berzelius first expressed the opinion that the heat given out by the oxidation of iron disulphide into sulphates of iron might have an important bearing on the heating and ignition of coal, it has been adopted as the popular explanation of that phenomenon; and although the work of Dr. Richters clearly proves this not to be the case, the old explanation is still given, a notable exception, however, being in the case of our great metallurgist, Dr. Percy, who, as early as 1864, pointed out that probably oxidation of the coal had also something to do with spontaneous combustion, a prediction amply verified by Dr. Richters' researches some six years later.

This disulphide of iron is found in coal in several different forms, sometimes as a dark powder distributed throughout the mass of the coal, and scarcely to be distinguished from coal itself. In larger quantities it is often found forming thin golden-looking layers in the cleavage of the coal, whilst it sometimes occurs as large masses and veins, often an inch to two inches in thickness, but inasmuch as these masses of pyrites are very heavy, they rarely find their way into the screened coal for shipment, many hundreds of tons of these "brasses" being annually picked out from the coal at the pit's mouth, and utilised in various manufacturing processes. If the air is dry the pyrites undergo but little change at ordinary temperatures; but in moist air they rapidly oxidise when in a finely-divided condition, the first action being the formation of ferrous sulphate and sulphur dioxide, together with the liberation of sulphur, the relative amounts of the two latter being regulated by the temperature and the supply of air, whilst longer contact with moist air converts the ferrous sulphate into a basic ferric sulphate generally termed "misy."

It is during this process of oxidation that the heat supposed to cause the ignition is evolved. But when it is considered that some of the coals most prone to spontaneous combustion contain only eight-tenths of a per cent of iron pyrites, and rarely more than 1½ per cent, the absurdity of imagining this to be the only cause of ignition becomes manifest. If 100 lbs. of coal were taken, and the whole of the pyrites in it concentrated in one spot and rapidly oxidised to sulphate, the temperature would barely be raised to 100° C., if all loss of heat could be avoided. Besides which, in certain manufactures pure iron pyrites are largely used, and, when free from carbonaceous matter, may be kept in a state approaching to powder in heaps containing many hundred tons; and although undergoing continual oxidation, I have been unable to trace a single case of heating, much less a rise of temperature which would approach the igniting-point of coal. When, however, it is mixed with finely-divided carbonaceous matter, then heating and ignition is a frequent occurrence in even moderate sized heaps.

I have carefully determined the igniting-point of various kinds of coal, and find that—

Cannel coal	ignites at 698° F. = 370° C.
Hartlepool coal	" 766 = 408
Lignite	" 842 = 450
Welsh steam coal	" 870.5 = 477

So that no stretch of imagination could endow the small trace of pyrites scattered through a large mass of coal, and undergoing slow oxidation, with the power of reaching the needful temperature.

Dr. Richters fully realises this point, and discards the idea of the pyrites doing anything more than adding their mite to the causes which bring about rise of temperature. In this, however, I think he is mistaken, my experiments, which will be published when complete, pointing to the fact that they may increase the liability to ignition when

present in large quantities, and do so by liberating sulphur under certain conditions. Now, sulphur has an igniting-point of 482° F. or 250° C., so that the presence of free sulphur would lower the ignition-point of the coal by considerably over 100 degrees Centigrade, the sulphur in this case playing exactly the same part that it does in gunpowder, in which it lowers the point of ignition, and increases the rapidity of combustion. A still more important part played by the pyrites is that as they become oxidised to ferrous sulphate they swell in size, and so tend to split up the coal into small pieces, and by exposing a large extent of fresh surface to the air cause increase of temperature and energetic chemical action.

We can now trace the actions which cumulate in ignition. The newly-won coal is brought to the mouth of the pit, and at once commences by virtue of its surface action to absorb oxygen from the air, but unless piled in unusually large heaps, and a good deal broken, it does not, as a rule, show signs of heating, as the exposed surface is comparatively small, and the air finding its way freely between the lumps keeps down the temperature. The coal is now screened, and the obtrusively large lumps of brasses picked out; it is then put in the trucks and enjoys the disintegrating processes of joltings and shuntings innumerable, every jar adding to the percentage of small coal present, and a corresponding increase in the size of the surface exposed to the air. Arrived at the docks, it has to be transferred from the truck to the ship, which is done by one of the numerous forms of tips, shoots, or spouts employed for the purpose, and it is during this operation that more harm is done than at any other period. The coal first shot into the vessel by reason of the distance which it has to fall is broken down into small lumps, and having to bear the impact of the succeeding load falling upon it from a height, rapidly becomes powdered into slack, whilst the succeeding loads falling in on the cone so formed get more or less broken down, so that by the time the cargo is all taken in, a dense mass of small coal is to be found under the hatchway, and it is invariably at this point that heating takes place, as the large surface exposed fresh to the air by the breaking down of the coal causes rapid absorption of oxygen, and consequent rise of temperature. This sets up chemical combination between the oxygen absorbed by the coal and the hydrocarbons and coal brasses.

The combination of the brasses with oxygen causes the swelling of the oxidised mass and splitting up of the coal; fresh surfaces are exposed, and more absorption of oxygen takes place, and the igniting-point of the sulphur vapour and sulphur compounds distilled out of the pyrites is reached, and rapidly raises the temperature to the ignition-point of the coal. It is only in cases where large quantities of dense coal brasses are present that this action can take place, as in the ordinary case, where 1 or 2 per cent only of pyrites are present, the sulphur vapour distilled out from the pyrites is oxidised to sulphur dioxide at temperatures far below the point of ignition of sulphur vapour; and in such cases the heat of absorption and oxidation of the bituminous portions of the coal is amply sufficient to raise the temperature to the requisite 752° to 932° F. (400° to 500° C.).

(To be continued).

Action of Sulphuric Acid upon Aluminium.—A. Ditte.—Cold dilute sulphuric acid seems to have no action upon aluminium, yet, as the formation of aluminium hydroxide evolves 195·8 calories, this metal should at ordinary temperatures decompose water and *a fortiori* dilute acids. The author in this paper demonstrates that such is the case, and that if a plate of aluminium immersed in dilute sulphuric acid seems not to be attacked, the cause is that it becomes coated with a continuous layer of hydrogen which prevents all direct contact with the liquid.—*Comptes Rendus*, cx., No. 11.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

ON the 27th ultimo, the first Anniversary Dinner of the Chemical Society took place at the Hôtel Métropole, under the presidency of Dr. W. J. Russell, F.R.S. About 150 sat down to dinner, including the President of the Royal Society, the President of the Pharmaceutical Society, the President of the Society of Chemical Industry, the President of the Institute of Chemistry, the President of the Physical Society, the President of the Institute of Civil Engineers, the President of the Society of Electrical Engineers, the Director of the Royal Gardens (Kew), the Master of the Drapers' Company, Sir F. A. Abel, Sir H. Roscoe, Sir F. Bramwell, Sir Owen Roberts, Dr. M. Foster, Dr. H. Müller, Dr. J. H. Gladstone, Mr. A. H. Allen, Mr. W. Anderson, Dr. H. E. Armstrong, Dr. E. Atkinson, Dr. Attfield, Mr. W. Roberts-Austen, Mr. H. Bauerman, Mr. H. Bassett, Mr. F. W. Bayley, Mr. W. P. Beale, Mr. M. Bechler, Mr. W. J. Bell, Mr. E. Best, Mr. E. J. Bevan, Mr. B. Blount, Mr. E. R. Blundstone, Dr. H. Borns, Mr. P. Braham, Mr. B. Brough, Dr. L. Brunton, Mr. J. Y. Buchanan, Mr. A. Carpmael, Mr. A. Cooper, Mr. W. Crookes, Mr. C. F. Cross, Mr. R. H. Davies, Prof. J. Dewar, Mr. W. H. Dixon, Mr. F. Down, Mr. W. R. Dunstan, Mr. C. Ekin, Mr. T. Fairley, Prof. G. C. Foster, Mr. W. Foster, Mr. G. B. Francis, Dr. J. H. Gilbert, Mr. M. C. Godson, Mr. J. G. Gordon, Mr. Friese Green, Mr. A. J. Greenaway, Mr. C. E. Groves, Mr. R. Harrison, Dr. G. Harley, Mr. E. S. Harris, Mr. C. W. Heaton, Mr. W. Hills, Herr V. Hofmann, Dr. J. Hopkinson, Mr. D. Howard, Mr. W. L. Howie, Prof. J. J. Hummel, Dr. W. Ince, Dr. F. R. Japp, Prof. Judd, Dr. W. Kellner, Mr. T. A. Lawson, Mr. J. B. Lyon, Mr. G. H. Makins, Mr. Edward Matthey, Mr. B. McNeil, Mr. G. Mellin, Dr. Merz, Dr. G. Moody, Mr. E. R. Moritz, Mr. F. Moul, Mr. W. Naylor, Mr. W. Newton, Prof. W. Odling, Mr. J. F. Page, Mr. P. R. Parsons, Dr. B. Paul, Dr. W. H. Perkin, Mr. S. U. Pickering, Mr. J. J. Pilley, Mr. M. Prentice, Mr. W. Prideaux, Dr. A. Pullar, Mr. R. D. Pullar, Mr. L. O. M. Pyke, Prof. W. Ramsay, Prof. E. Reynolds, Dr. Ruhemann, M. A. G. Salamon, Mr. J. H. Sellon, Dr. Senier, Mr. H. R. Smith, Mr. F. Smith, Mr. A. Smithells, Mr. C. W. Stewart, Dr. L. Thorne, Mr. W. Thorp, Prof. T. E. Thorpe, Mr. J. M. Thomson, Dr. Tidy, Dr. W. A. Tilden, Mr. C. Tookey, Mr. E. W. Voelcker, Mr. R. Warington, Rev. Henry White, Mr. W. M. Williams, Mr. W. P. Wynne.

After the usual loyal toasts, the President, Dr. W. J. RUSSELL proposed "Prosperity to the Chemical Society," in the following words:—

I am afraid that some may think that the Chemical Society is becoming frivolous as it grows old, for to-day it arrives at the mature age of forty-nine, and for the first time gives a party on its birthday. Before I ask you to toast it on this festive occasion, let me say a few words concerning its birth and early history. For the moment, I stand as a sort of father to the Society, and to-day allow me to use a father's right of telling what a wonderful child it has been even from its birth, and how strong and active it is at the present time. My remarks shall not, however, extend to such a length as parents' remarks sometimes do when speaking of favourite children.

On the 23rd of February, 1841, some twenty-five or so chemists, who had been summoned by Mr. Warington, met at the rooms of the Society of Arts to consider whether it was desirable to found a Chemical Society. They seem all to have been of one mind, and unanimously to have declared that it was advisable to found such a society. Three, I believe, of those present at this preliminary meeting are still with us. They are Sir W. Grove, Sir L. Playfair, and Mr. Heisch. The

provisional committee then formed suggest an outline of what they think should be the constitution of the Society, and on the 30th of March of the same year a general meeting is held, the Society is definitely founded, Thomas Graham is elected President, and Sir W. Grove a member of Council.

The Society seems at its formation to have numbered some 77 members, and of these original members six are still upon our list. The reading and discussion of papers, and the publishing of a journal seems at once to have followed the formation of the Society, and the work done by the Fellows of our Society in those early days is recorded in the three volumes of *Memoirs and Abstracts of the Chemical Society*. These appeared in small parts and at very irregular intervals.

If we might measure the age of our Society, not by years, but by the changes which it has seen in the science which it represents, and the progress which it has registered, then it becomes a Society of high antiquity.

On glancing through these three volumes of *Memoirs*, one is struck not only by the simplicity of the facts and formulæ there described, but above all by the immense development of our science since that time.

It seems to take one back to a very primitive time when we find recorded in the first of these volumes, that Dr. Clark exhibited to the Society his method of ascertaining quantitatively the comparative hardness of water by means of a tincture of soap, and promises further details at a future meeting. In the same volume Fownes describes how CO can best be prepared from ferrocyanide of potassium, and Mr. Croft, it is stated, on April 19, 1842, exhibited and described Dr. Bunsen's new galvanic arrangement. The original work done by the Fellows in those days has stood well, and in criticising their work we must remember how inferior the tools they had to work with were to those at our command.

In addition to the original papers in these early volumes are translations in full or abstracts of foreign papers; thus, from the first, was begun a practice which has been so successfully carried on till the present day. Our past president, Dr. Gilbert, translates for the first volume of these *Memoirs* a long paper by Redtenbacher and Liebig, on the atomic weight of carbon, and we find also in this volume Bunsen's paper on the "Radical of the Cacodyl Series," and we find Will and Varentrapp describing and defending the accuracy of their soda-lime process.

In the second volume is an important paper by Drs. Muspratt and Hofmann, describing the preparation of aniline from nitro-benzene, and shortly afterwards these same chemists describe a new base; it is called toluidine. In the same volume are also important papers by Joule and Playfair on atomic weights and specific gravities, and one by R. Hunt, interesting as showing how different and distinct light, heat, and chemical force were supposed at that time to be.

Volume three proclaims the discovery of gun-cotton, and Teschemacher and Porrett, and afterwards Gladstone, examine its composition.

These three volumes carry the history of the Society to the end of 1847. The Society now numbers between 200 and 300 members, and they, it appears, were no longer satisfied with a journal which appeared only at irregular and often long intervals, and determined to replace it at the end of this year by a quarterly journal. Great stress was laid when this form of journal was established on its containing not only original papers, but also carefully drawn up abstracts of important chemical papers published in other journals, a practice which has, with so much advantage, been continued to the present day, but in addition to the abstract was appended to each annual volume what it would trouble us at the present day to furnish a list of, all the chemical papers published during the year in British and foreign journals. In the volume for 1848 this list occupies nineteen pages.

The establishment of this Quarterly Journal gave life and vigour to the Society, and chemistry was now being most vigorously studied on the Continent. Giessen was at the height of its fame, and the influence of Liebig was being strongly felt, even in this country. Laboratories were being founded, and in the Anniversary Address of the President, in 1847, he announces the establishment in London of three chemical laboratories designed to further the prosecution of original research; one, the College of Chemistry, and the two others at the older colleges of the University of London.

This first volume of the *Quarterly Journal* is full of matter which has kept its interest to the present day. I am not going to give you even an epitome of its contents, but we are all happy to see here the joint author of two of the papers which it contains, Sir F. Abel. He, in conjunction with Prof. Rowney, give very elaborate and careful analyses of the Trafalgar Square water and the Cheltenham mineral waters. Among the many good papers in this volume there is one other I cannot pass over without mentioning; it is the one by Mansfield "On Coal-Tar," a paper which, on account of its own intrinsic merits, would have a lasting importance, but, as indicating clearly the scientific and practical value of coal-tar, which till then had been looked upon as an objectionable article, is of special and remarkable interest. The simple way in which he describes "some of the useful properties of benzole" is like reading a novel of the last century, only much more interesting, or reading an account of a body described as new which one had looked upon as having existed from the earliest times.

This volume also records the fact that Hofmann had begun to work upon the organic bases. I do not intend, you will be glad to hear, even rapidly going through the remaining five and forty volumes of our *Journal*, but I think there is an interest at the present moment in briefly noting what was being done when our Society was first formed.

The beneficial influence which our Society has exercised in the bringing together of people of like tastes and pursuits no doubt has been great, but the publication of its *Journal* has probably done most towards extending a knowledge of chemical science.

In 1847 the original memoirs had to give way to the *Quarterly Journal*, and thirteen years later the *Quarterly Journal* has to give way to a monthly *Journal*, for the fellows again clamour for the more rapid publication of their papers. A graphic history of the *Journal* is given by Dr. Hofmann in his Presidential Address in 1862, when the *Monthly Journal* was established. He says that after "the year 1860 it was found convenient to discontinue the alphabetical list of the heads of chemical papers. In fact this list, which, when first published, occupied not more than 19 or 20 pages, had gradually expanded beyond legitimate proportions, filling, in the last volume, 79 pages, or one-fourth of the whole volume. By its discontinuance a considerable amount of additional space was thus given for original communications and for abstracts, but it proved inadequate for the requirements of the Society, and consequently, he goes on to say, the *Monthly Journal* was established, and he concludes by adding these words, which time has shown to be true to the letter:—"The rank a Society holds will always depend upon the number, value, and rapidity of its publications. I believe, therefore, that the transition from a *Quarterly* to a *Monthly Journal* will be received with general approbation. "Not only does this change secure to our contributors almost immediate publication, but it will enable us henceforth to publish abstracts of all valuable chemical papers which are dispersed in the *Proceedings* and *Transactions* of the several learned societies, in which they are not always easily accessible, and to make our *Journal* a sort of *Comptes Rendus* of all the work done in chemical science throughout the country.

We all must feel how wise these words were, and how at the present time we are attempting to do exactly what

Hofmann describes nearly thirty years ago, and the result is as I said this afternoon. I think no Society can boast of a Journal more complete, more useful, and more up to date than ours.

Turning for a moment from the theoretical and literary side of the development of chemistry to the practical and instrumental, the change during the last half century is not less striking nor less important. At the present time it is really difficult for us to realise how incomplete were the laboratories and how clumsy was the apparatus which was then in use. Even the refined process of organic analysis illustrates this. In 1841, Liebig had only lately described this process, which will ever be so nearly associated with his name, and which really made the analysis of organic bodies possible; compare how the process, although essentially the same, was then and now carried on. I can remember the use of charcoal for heating the tube, the use of sheet india-rubber for joining the tubes, which it did in a way which gave the greatest anxiety to the operator when he had, with a hot coal, to test the tightness of the apparatus; and how often the test gave an unsatisfactory result. Then, with regard to the use of charcoal, what an amount of fanning it did require, and what an amount of dust and ashes it did give rise to, and altogether what a hot and dirty operation it was—no laboratory at the present day would tolerate it. Now the tightness of the apparatus is easily assured, and the whole heating of the tube regulated by turning a gas-tap. Surely mechanical ingenuity and dexterity have done much to aid in the development of our science. Even the founders of our Society, men who but the other day were with us, would be astonished at the gigantic and elaborately fitted laboratories of the present day—astonished to see how electricity, gas, and steam are now forced into the service of the chemist, and how operations and experiments in general have been shortened in time and increased in accuracy.

In 1847, the President, in his Anniversary Address, calls attention, as I before mentioned, to the establishment in London of three laboratories for original research. I know not how many exist in this country at the present time, but beside the university cities, every large town has its well-equipped laboratory, and in London the number still increases; and if, among the latest additions, the large laboratories now being built by the conjoint Board of the Medical Colleges are not for strictly chemical purposes, the work carried on there, if it be real and useful, as I doubt not it will be, must to a large extent be dependent on chemical science; and of a more purely chemical character are the large research laboratories lately established by the Pharmaceutical Society.

What our Society has done in the past to aid and extend chemical science is clearly written and fully acknowledged, and the question now is what will it do in the future? The answer, I doubt not, is that it will do even more in the future for the progress of the science than it has done in the past.

Sir F. A. ABEL then proposed "The Kindred Societies and Institutions," to which Sir GABRIEL STOKES and Sir LOWTHIAN BELL replied.

Professor MICHAEL FOSTER then proposed the health of the Visitors, which was responded to by Sir F. BRAMWELL and Dr. THISELTON DYER.

The health of the Chairman was proposed by Sir HENRY ROSCOE, and the proceedings then terminated.

Corresponding Reactions of Carbazol and Pyrrol.—S. C. Hooker (*Berichte Deutsch. Chem. Gesell.*) mentions that both carbazol and pyrrol give the pine-wood reaction, give a deep blue compound with isatin and sulphuric acid, both give two distinct compounds with benzoquinone, one of a violet-red, soluble in ether, and the other green, insoluble in ether. Both pyrrol and carbazol give, with picric acid, a compound which crystallises in red needles.

NOTICES OF BOOKS.

Chemical Laboratory Labels. Second Edition, Part III. Compiled by W. H. SYMONS, F.R.M.S., F.C.S., &c. London: Gallenkamp and Co.

THESE labels are clear, sufficiently large, and not encumbered with needless matter, such as formulæ. The nomenclature is very "advanced," the old familiar acids have disappeared, and in their room we find such names as hydrogen chloride, hydrogen nitrate, &c. Hydrogen citrate, however, is wanting. Many of the labels, such as "test-tubes," "retorts," "retort-stand fittings," &c., are, of course, intended, not for bottles, but for drawers, presses, or the like. "Hydrogen," "oxygen," and "carbon dioxide" are destined for gas-holders. A feature of practical value is that the labels are exceedingly well-gummed.

CORRESPONDENCE.

LARD.

To the Editor of the *Chemical News*.

SIR,—Kindly allow me to make an addendum to my letters on the above subject. I have read Dr. Swindell's letter in your last week's issue.

In the year 1885 I found $1\frac{1}{2}$ to $2\frac{3}{4}$ per cent of water in several samples of lard. Since then I have, at times, found more. The publicity given to these examinations proved, I think, of beneficial result, inasmuch as latterly I have found the samples of the various brands of lard which I have examined almost free even of moisture. Lard, however, is melted and cooled in jacketed pans, containing steam and cold water. Should a leakage take place in the internal jacket of either, water is bound to show itself in the lard. If such leakage can be proved, and it can be shown that immediate action, upon discovery, was taken to stop it, I do not think a magistrate would be justified in inflicting a penalty for *wilful adulteration*. But this opens out a great field of enquiry, which I shall not enter upon. The magistrate has only to deal with the subject at issue, in this case water, and to inflict a fine to show the world that the public insists upon having dry lard. If it can be shown that it was by accident the water became incorporated with the lard, the magistrate can, of course, use his discretion as to the amount of the fine, but convict he must.

If anyone buys lard knowing that it contains cotton-seed oil, he must sell it as a compound. If he does not, Dr. Swindell and myself can only be of one opinion, viz., that his action is illegal, and, of course, must be punished, for the law must be obeyed.

With respect to the addition of other matter to lard, viz., stearin, I think Dr. Swindell's "light" is of a refractive rather than a reflective nature. I notice that he has toned down his "doctored dripping" to "pork dripping." When he writes again on lard his common sense will probably take the place of his theoretical opinion, and he will call the fat of swine, when rendered down and "larded," or improved, by stearin, "Lard," like the rest of the world.—I am, &c.,

WILLIAM BROWN.

3, Hereford Road, Seaforth,
near Liverpool, April 2, 1890.

The Camphorates of the Dextro- and Lævo- α -Borneols.—A. Haller.—The author finds that the total etherification of camphoric acid is not effected until a relatively high temperature has been reached, and only with the anhydride. Under these conditions the production of isomers is certain. One of the functions of camphoric acid in the acid ethers approximates to that of the phenols.—*Comptes Rendus*, Vol. cx., No. 11.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 11, March 17, 1890.

Reactions between Vegetable Soil and the Atmospheric Ammonia.—M. Berthelot.—A portion of soil may be made at pleasure either to absorb almost all the ammonia contained in a given atmosphere, or to give off a part of its nitrogen in the form of ammonia. All intermediate and even contrary results may be realised by experiments systematically directed, but without being applicable, except to the special circumstances of the observation.

Researches on Phenomena produced during the Condensation of Gaseous Carbides under the Influence of the Effluve.—P. Schützenberger.—The gases studied have been carbon monoxide, cyanogen, ethylene, and acetylene. In operating upon carbon monoxide the author obtained a brown matter of the composition:—

Carbon	45·6
Hydrogen	0·6
Oxygen	53·8
	—————
	100·0

These figures would lead to a formula between $C_{12}H_2O_{10}$ and $C_{12}H_2O_{11}$. The sum of the weights of the products formed (brown solid, water, and carbon dioxide) exceeds the weight of the carbon monoxide utilised by 0·046 gm. Water and oxygen must therefore have been introduced from without, through the glass, as the author purposes demonstrating in a future memoir.

Double Lead and Sodium Hyposulphites.—J. Fogh.—The salt of Lenz, $PbS_2O_3 + 2NaS_2O_3$, is not a simple mixture, but a true double hyposulphite, probably the only one existing.

A New Crystalline Form of Ammonium Chloride.—G. Geisenheimer and F. Leteur.—The crystals in question contain about 1·5 per cent of ruthenium subchloride. They were obtained from the washing waters left on preparing pure iridium by the method of Deville and Debray.

The Monobenzoic and Dibenzoyl Acetals of Sorbite.—J. Meunier.—Monobenzylsorbite has the composition $C_6H_{13}O_5(C_7H_5O)$. Dibenzylsorbite is represented by $C_6H_{12}O(C_7H_5O)_2$.

On Oxytetric Acid.—Ch. Cloez.—Not adapted for useful abridgment.

The Value of the Heat of Hydratation of Maleic Anhydride.—Iw. Ossipoff.—The hydratation-heat of malic anhydride when forming maleic acid is 9·6 cal. If it yields fumaric acid, 11·1 cal.

Dissociation of the Hydrochlorates of Amines and of the Salts of Dissolved Fatty Acids.—J. Müller.—This dissociation can be demonstrated by means of phenolphthalein.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., February, 1890.

Fluorescent Colouring-Matters derived from Resorcine (Weselsky's Colours).—E. Noelting.—A description of the preparation and properties of resazurine (diazoresorcine) and of resorufine (diazoresorufine) with a notice of hystazarine, an isomer of alizarine. In a comparative table are given the reactions of hystazarine, alizarine, quinizarine, xanthopurpurine, anthrarufine,

chrysazine, anthraflavic acid, metabenzene dioxyanthraquinone, isoanthraflavic acid, and isochrysazine.

Fire-proof Compositions.—Tissues can be rendered unflammable at about 30 centimes per square metre, and retain this property for several months, in one experiment for three years. Wood can be still better secured if the protective salts are allowed to penetrate into its substance.

Determination of Ferrocyanides in Spent Purifying Mass.—O. Knublauch.

Analysis of Spent Purifying Mass.—C. Moldenhauer and W. Leybold.

Extraction of Sulphocyanides and Ferrocyanides from Spent Purifying Mass.—J. V. Esop.—The substance of these papers, which are taken from *Dingler* and from the *Zeit. f. Angewand. Chemie*, has been already noticed.

Determination of Ferric Oxide and Alumina in Phosphates.—E. Glaser (*Zeit. Angewand. Chemie*).—5 grms. of the sample are dissolved in the ordinary manner in 25 c.c. of nitric acid at 1·2 sp. gr. and about 12 c.c. of hydrochloric acid of sp. gr. 1·12, and the whole is made up to 500 c.c. Of the filtered liquid 100 c.c. are put in a $\frac{1}{4}$ litre flask and 25 c.c. of sulphuric acid of sp. gr. 1·84 are added. The flask is let stand for about five minutes, it is shaken several times, about 100 c.c. of alcohol at 95° are added, the flask is cooled and filled up to the mark with alcohol, and shaken briskly. There is produced a contraction. The stopper is withdrawn, more alcohol added, and the flask is again shaken. It is let stand for half an hour and filtered; 100 c.c. of the filtrate (representing 0·4 gm. of the sample) are evaporated in a platinum capsule until all the alcohol is expelled. To the liquid thus freed from alcohol 50 c.c. of water are added in a cylindrical glass and heated to boiling. Ammonia is added until an alkaline reaction appears (not during the boiling). The excess of ammonia is expelled at a boil, the liquid is let cool, filtered, the precipitate washed with hot water, ignited, and the ferric and aluminium phosphates are weighed.

New Use of Oxygenated Water in Analysis.—C. Hiepe (*Chemiker Zeitung*).—Already noticed.

Use of Oxygen in Quantitative Analysis.—M. M. Minor (*Zeit. Angewandte Chemie*).—The author incinerates organic substances in currents of oxygen.

Detection of Small Quantities of Nitrous Acid.—G. Lunge (*Zeit. Angewandte Chemie*).—Already noticed.

Examination of a Common Method for the Determination of Tartar, Tartaric Acid, and Malic Acid.—R. Gans.—From the *Zeit. Angewandte Chemie*.—Not adapted for useful abstraction.

Citric Acid in the Milk of Cows.—F. Soxhlet (*Weiner Land. Zeitung*).—Normal milk contains about 1·1000th of citric acid.

Analysis of Commercial Saccharine.—Ira Remsen and W. M. Burton (*American Chemical Journal*).

Reply to the Above.—Dr. C. Fahlberg (*Chemiker Zeitung*).—A dispute of little general interest.

Detection of Saccharine in Aliments.—B. Fischer (*Neuen Arzneimittel*).—Tests for saccharine in a variety of admixtures.

Chemical Section of the Industrial Society of Mulhouse.—The business done consisted chiefly in opening "sealed papers," one of which, deposited by M. Jules Persoz, September 12th, 1875 (!), describes a process for dyeing aniline blacks.

Apparatus for Checking the Purification of Gas.—M. Ledig (*Chemiker Zeitung*).—A band of paper saturated with lead acetate is caused to be unrolled in a current of the gas. The paper travels at such a rate that 2 c.m. of length pass hourly into the bell containing the gas.

MEETINGS FOR THE WEEK.

- MONDAY, 14th.—Medical, 8.30.
 TUESDAY, 15th.—Society of Arts, 8. "Modern Indian Art," by C. Purdon Clarke, C.I.E.
 — Institute of Civil Engineers, 8.
 — Pathological, 8.30.
 — Royal Institution, 3. "The Place of Oxford University in English History," by George C. Brodrick, D.C.L.
 WEDNESDAY, 16th.—Society of Arts, 8. "Old and New Fashions in Typography," by Talbot B. Reed,
 — Meteorological, 7.
 — Geological, 8.
 THURSDAY, 17th.—Royal, 4.30.
 — Royal Society Club, 6.30.
 — Chemical, 8. "Phosphorus Oxide," by Prof. T. E. Thorpe, F.R.S., and Mr. T. E. Fuller.
 — Royal Institution, 3. "The Heat of the Moon and Stars," by Prof. C. V. Boys, A.R.S.M., F.R.S.
 FRIDAY, 18th.—Royal Institution, 9. "Welding by Electricity," by Sir Frederick Bramwell, Bart., D.C.L., F.R.S.
 — Physical, 5.
 SATURDAY, 19.—Royal Institution, 3. "Colour and its Chemical Action," by Captain W. de W. Abney, R.E., C.B., F.R.S.

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THE CHEMICAL NEWS.

Vol. LXI. No. 1586.

THE VOLUMETRIC ANALYSIS OF COPPER.

By REGINALD A. FESSENDEN,
Chemist, Edison Laboratory, Llewellyn Park, Orange, N.J.

It is well known that the ordinary method of titrating ammoniacal copper solutions by cyanide of potassium contains several sources of error which cannot be entirely removed without considerable waste of time. After a particularly irritating example of this the following experiments were made:—

I. 2 c.c. of copper solution (nitrate with no free acid) taken. Cyanide run in till liquid decolourised. Amount of cyanide solution used, 1.95 c.c.

II. 2 c.c. of same solution taken, made moderately alkaline with ammonia. Amount of cyanide solution used, 2.0 c.c.

III. 2 c.c. of copper solution taken. Large excess of ammonia added. Amount of cyanide solution used, 4.25 c.c.

IV. and V. showed that ammonium nitrate and other ammoniacal salts (as carbonate, &c.), have a similarly disturbing influence.

These experiments showed that it was hopeless to expect accuracy when ammonia was used as a neutraliser. Sodium carbonate suggested itself, and proved exactly what was desired.

VI. 2 c.c. of copper solution taken. 5 c.c. nitric acid added. Made alkaline with sodium carbonate. The clear blue solution was then titrated in the ordinary manner. Amount of cyanide used, 1.90 c.c.

VII. 4 c.c. of copper solution taken. 25 c.c. nitric acid added, sod. carb. added, and titrated. Amount of cyanide used, 3.80 c.c.

VIII. and IX. showed that neither sulphuric nor a mixture of nitric and sulphuric acids have any effect on the result. Analyses were then made of several copper ores, and the results obtained were in the highest degree satisfactory, no matter what variations were made in the amounts of the reagents, provided always that a slight excess of nitric acid is present above that necessary to dissolve the copper sulphide. This condition, however, always obtains in practice.

The end of the reaction is very much more sharp and decided than is the case when ammonia is used, and takes place immediately, so that the tedious waiting at the end of every drop towards the end of the titration is unnecessary.

ON THE
EFFECTS OF RETARDED DISSOLUTION.

By H. N. WARREN, Research Analyst.

THE speedy dissolution of a zinc rod, when suspended in contact with such a menstruum as solution of lead acetate, cupric sulphate, or any readily precipitable metal, is always attended more or less by the copious development of a dense spongy metallic mass, which almost instantaneously incrusts the precipitant employed. In the case of a lead salt thus acted upon, which is frequently practised by amateurs with a view of obtaining what is known as the lead tree, the incrustation that is formed, remaining in close proximity to the zinc, is never very striking as regards metallic lustre, and it not unfrequently happens that a considerable course of time has elapsed before the purer quality, which is characterised by its feathery ap-

pearance, begins to develop. If round the zinc rod, however, is wrapped a few coils of asbestos paper before applying the same, on now introducing the zinc into the solution a most interesting modified action accompanies the lead being slowly precipitated upon the outer surface of the asbestos. Notwithstanding it being a non-metallic surface, it continues to increase in size, gradually assuming large and perfect octahedrons of metallic lead, the asbestos covering thus acting in much the same manner as the first precipitated or porous quality. If a solution of cupric sulphate be substituted for that of the lead, and the same raised and maintained for some time at the boiling-point, the whole of the copper is precipitated in regular crystals; in short, all the more easily reducible metals may, by the retarding action of the asbestos covering, be obtained in a crystalline form.

Amongst one of the most curious exceptions may be mentioned that of antimony. If to a solution of antimony chloride containing a sufficiency of a tartrate to prevent re-precipitation of basic salts, is introduced the so prepared zinc, part of the antimony is set free, attaching itself in the usual form of crystals to the asbestos covering, whilst a second portion falls in the state of an amorphous black powder, resembling in appearance ordinary lamp-black. This, when raised to an elevated temperature, is oxidised with explosion, being what is known as explosive antimony.

For a further and more complete study of retarded action may be mentioned the withdrawal of the zinc and the replacement of magnesium for the same. By this means zinc was crystallised in a perfectly metallic state, and communicating to the same an arborescent form. Iron, manganese, and even zirconium, were gradually reduced.

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

PROFESSOR GRÜNWARD'S MATHEMATICAL
SPECTRAL ANALYSIS.

(Concluded from p. 172).

THE view of Dr. Kayser that the comparison with hydrogen and oxygen is used by the author to escape a comparison with the vapour of water is erroneous. As soon as the rhythmic relations of the spectra of hydrogen and oxygen to the spectrum of watery vapour have been established, the rhythmic relations of the groups of rays of one element, *e.g.*, magnesium, to the spectrum of water suffice to indicate its rhythmic relations to hydrogen and oxygen, whether the rays of the latter, ascertained in this manner, can be observed or not. But in the single cases in which the results of sufficiently accurate measurements, *e.g.*, those of the oxygen rays, by Dr. Schuster, agree with the calculated lines, this does not prevent us from seeing in such coincidences a confirmation of the results of the comparison with the vapour of water, or a kind of additional criterion. If in addition along with the predicted wave-lengths, *e.g.*, of oxygen, the author has noted down the less accurate values of Salet and others, he cannot be justifiably held blameworthy on that account. The calculated lines of oxygen and hydrogen are essentially predictions, which are affected by the errors springing from the faults of the material of observation, and thus may be doubted until their accuracy is confirmed by direct or indirect observations.

Of especial importance are those calculated oxygen and hydrogen lines which agree with the corresponding least refrangible lines in the spectrum of the oxy-hydrogen flame, as given by Liveing and Dewar. They can be already tested experimentally, whether they are really oxygen or hydrogen lines, by passing into the oxy-hydrogen flame a gentle current of oxygen or hydrogen, previously ignited, and observing which lines undergo an

intensification. Such lines will probably belong to oxygen or respectively to hydrogen.

The comparison of the calculated hydrogen lines with the solar spectrum of Rowland, or of Müller and Kempf, is of great importance, notwithstanding its unequal accuracy. For even if one of these hydrogen lines was affected with an error of 0.5 Angström unit in either direction, it would indicate a very small region of the solar spectrum, 1 Angström unit in breadth, in which there is situate a hydrogen line not yet recognised as such. Very probably the relatively strongest of the few Fraunhofer lines (2, 3 to 10) situate in this region will be the hydrogen line thus indicated, since enormous masses of ignited hydrogen are contained in the external atmosphere of the sun. If these lines can be experimentally proved to be actual hydrogen lines it will be a new confirmation of the theory.

5. The entire physical and chemical behaviour of a substance is determined by the transverse and longitudinal ether-waves, which, under certain circumstances, combine to form vortex waves, by the fluctuations in pressure and the accompanying currents of the ether. The waves proceeding from two substances, *e.g.*, hydrogen and oxygen, determine, under certain exceptional circumstances, their chemical combination, and thus the waves of a different kind which the compound (*i.e.*, the atomic particles of the components after the establishment of a new dynamic condition among themselves and with the surrounding ether) emit. In consequence the total complex of the waves emitted by a compound (*e.g.*, watery vapour) must be a function of the wave complexes of the two components (*e.g.*, hydrogen and oxygen) in their free condition, and the first complex must be capable of mathematical deduction from the two latter complexes.

The main question which the author has proposed to himself is to ascertain the necessary mathematical connection between the waves which the free constituents emit previous to combination and the waves of a different kind which the compound emits.

The author finds that in the simplest possible cases, in which the primary elements of the constituents undergo an equal or approximately equal condensation, the wave-lengths of the rays produced by their atomic particles undergo a rational modification, and by multiplication into the corresponding factor of condensation they pass into the corresponding wave-lengths *within* the compounds: the fundamental *theorem!* Here we have especially to consider only the single rays, the luminous maxima, and the sharp margins of the so-called bands, which the atomic particles of the constituents produce before and after combination. The very manner of putting the question, and the precise definition of the mathematical and dynamical problem, here to be solved is a half discovery.

Here also Dr. Kayser completely misunderstands the real position of matters, and the scope of the thoughts briefly sketched above. He imagines that the author aims at explaining the band-spectra of compounds as such merely by a collocation of certain line spectra, after the latter have been multiplied by rational numbers. He does not consider that our present so-called elements possess, under certain circumstances, visible band spectra, and that the particles which produce such, under other circumstances, in which there appear no visible band-spectrum, do not remain motionless or cease to act upon the ether, though these effects in the latter case have become too feeble to be recognised without especial arrangements, perhaps not yet known.

The author's present position is that of a scientific pioneer and pathfinder, who with imperfect—though constantly improving—arms and instruments, seeks to open up new ways in unknown regions. His position is in this respect very similar to that of Kepler, when he sought to ascertain the laws of the planetary orbits from the observations of his day. His fundamental theorem given above is exactly analogous to the law of Kepler on the ratio of the squares of the time of rotation of the planets

and the cubes of the major axes of their orbits, whilst the plane propositions of the central movements of the stellar world find here their counterparts in linear equations among the reciprocal values of entire groups of the wave-lengths of a substance.

He hopes that the results of his labours may once be better understood, and that in particular he may succeed in making more probable the structure of hydrogen and oxygen as spectrologically determined. The compound nature of oxygen—though unsuspected by many—has already found an indirect but very weighty confirmation from the discovery of Jansen, verified by Liveing and Dewar, that oxygen possesses two groups of rays, which undergo various laws of absorption in condensed oxygen. This fact is of the higher importance as it is a simple consequence of the remarkable structure of oxygen ascertained by the author, and as other bodies of similar composition must possess analogous properties of absorption.—*Chemiker Zeitung*.

EXAMINATION OF CORPSES FOR ALKALOIDS AND OTHER NITROGENOUS BASES.

By Dr. ANTON SEYDA.

(Continued from p. 175).

THE solution of the extract is then divided into three portions. A check test for the possible presence of metallic salts soluble in alcohol must not be omitted.

The first portion is rendered alkaline with potassa-lye, and distilled with the aid of steam. Sometimes it may be needful to distil it in a current of hydrogen. The distillate must be specially examined for nicotine, coniine, and aniline, but it generally yields but little material, consisting of the aminic bases of the fatty series. To this end the distillate is shaken out with ether, the latter is separated and evaporated at a low temperature, preferably in the following manner:—

The flask containing the ethereal extract is placed in water at 70–80° and into it there is passed a moderate current of air. The ether evaporates rapidly at a temperature of about 25°. As soon as its volume is brought to 10 or 20 c.c. the forced evaporation is interrupted, the ethereal solution is poured into a small beaker and allowed to evaporate spontaneously in a warm place.

A constant temperature of 25–40° may be secured as follows:—An air-bath is made by covering a porcelain capsule with a small plate, placing it upon a boiling water-bath, and immersing it more or less deeply according to the temperature required.

The residue after the evaporation of the ether is dried over undiluted sulphuric acid, and ultimately in a partially exhausted receiver. For a closer determination the residue is converted into a neutral hydrochlorate. Above all, the presence or absence of nicotine, coniine, and aniline must be determined. If these bases are absent the attempt is made to obtain the residue in a crystalline form, by preparing, according to well-known methods, double salts with platinum chloride or gold chloride, by dissolving or evaporating in an aqueous or alcoholic liquid at ordinary or at reduced temperatures, or in a vacuum over sulphuric acid. If this succeeds, a determination of the platinum and of the nitrogen, indeed, a complete elementary analysis, followed by a crystallographic determination, will be indispensable.

If no volatile bases are present in the solution, the second portion is shaken out successively with the following liquids:—

1. Ether in a neutral or acid solution.
2. Ether in an alkaline solution.
3. Chloroform.
4. Amylic alcohol in an ammoniacal solution, if in the preliminary examination iodic acid was reduced.

Before passing from one of these shakings-out to the next, the watery solution must be heated and treated with a current of air, to eliminate any residues of the former solvent.

If reactions are obtained which indicate the presence of any alkaloid, the reserved portion of the solution is used for a special examination. The procedure is here modified according to the properties of the alkaloid in question. The solution is mixed with mercuric chloride, and in this general manner the precipitation of the nitrogenous bases is effected. After the lapse of twenty-four hours—not earlier—the precipitate is filtered, washed with sublimate water, and treated further, in known manners, with regard to the demonstration of the special alkaloid.

The residues left after the evaporation of the ethereal, chloroformic, and amylic extracts, are always dried over sulphuric acid. They are sometimes amorphous, sometimes crystalline, and either colourless, yellowish, or brown. They often reduce Frøehde's reagent energetically, with the production of a blue colour, a reaction generally of little importance. The solution of ammonium metavanadate is also reduced, but with a dirty colour. The green colour which generally appears on adding the substance is mostly unimportant.

The ethereal residue obtained from an alkaline solution if heated on the water-bath with officinal (?) phosphoric acid will generally take a more or less distinct reddish violet. This circumstance is important, being regarded as a characteristic of aconitine.

Vitali's reaction with fuming nitric acid and alcoholic potassa, though it occurs beautifully with pure atropine, is in many cases quite worthless. We often obtain residues which show the well-known xanthoproteine reaction more or less plainly, thus quite masking the beautiful violet colour. The pleasant odour so readily obtained with pure atropine cannot be obtained from extractive residues.

Ammonium vanadate, which has of late been warmly recommended as a test for strychnine, is very suitable. The reaction may be effected in a twofold manner. A drop of the vanadic solution may be cautiously mixed with the sulphuric solution of the residue, diluted, if needful, with strong sulphuric acid, and the dry ammonium vanadate is then sprinkled over another portion of the solution as it is done with potassium dichromate.

The advantages of the reaction with ammonium metavanadate, as compared with that obtained with potassium dichromate, are especially distinct with sulphuric solutions of imperfectly pure strychnine. A direct introduction of particles of the residue into the sulphuric solution of ammonium metavanadate, as is done with Frøehde's reagent, is never admissible, since the colour-reactions then come out indistinctly, or not at all, especially in presence of substances which are readily decomposed by strong sulphuric acid. In such cases there often occurs a reduction accompanied with the evolution of sulphurous gas, and thus a coloured reaction may readily be destroyed. In such case the sulphurous acid must be expelled by gently heating the capsule before any further reagent is added.

It must be added that colocynthine gives, both with chromic and vanadic acid, a reaction very similar to that of strychnine, and, as the author believes, not yet publicly known. To produce this reaction a few particles of the extract of colocynth are placed at the edge of the lid of a porcelain crucible and intimately mixed with an equal quantity of pulverised potassium dichromate, but only for a very short time, with the addition of a drop of dilute sulphuric acid (1 vol. acid and 2 vols. water). Strong sulphuric acid is dropped at the opposite margin of the lid, and a narrow streak of the paste is led over to the acid with a thin glass rod. On the contact of both, there appears a fine violet-red colour, gradually increasing in intensity if the mixture of extract is gradually let pass over to the sulphuric acid. This reaction must be initiated very

cautiously, and the strong sulphuric acid must be in excess. If ammonium vanadate is used, the colour produced is at first blue and then reddish.

The amylic residue is often obtained in abundance, colourless, or brown amorphous, or sometimes finely crystalline. Purification by solution in alcohol recommended. The shaking-out in amylic alcohol should always be effected in heat, and the separation of the two strata is promoted by placing the flask in hot water. The amylic alcohol must not be drawn off until completely cold, and evaporation must only be applied to the clear solution after filtration. In this manner, the troublesome property of hot amylic alcohol of taking up not only bases and pigments but water containing various substances will be found less annoying.

The reaction for morphine is best carried out by dissolving the residue in water containing tartaric acid, and adding a solution of iodic acid. As a further reaction may be applied the method for apomorphine. The amylic residues are generally distinguished by their strong reductive action with Frøehde's reagent, which often gives a splendid corn-flower blue.

The watery solution of the extract is tested in the known manner for narceine and curarine.

An examination for the possible presence of metallic salts soluble in alcohol (mercuric chloride, silver nitrate, lead acetate, &c.), though mostly superfluous, should be effected for complete satisfaction.

(To be continued).

AN EXAMINATION OF FUSEL OIL.*

By J. H. LONG and C. E. LINEBARGER.

A FEW analyses of fusel oil are given in the literature, but of these none, as far as we know, have been made of samples of American origin.

The analysis most frequently quoted is that by Rabuteau, while less complete results are given by others. We have attempted to determine, approximately, the composition of a sample of fusel oil obtained at a Chicago distillery, and give the results below:

Most of our American distillers use corn as the chief substance to be converted into mash, with smaller amounts of other grains, and it would therefore naturally be expected that a somewhat different product would be obtained from that produced from a mash of potatoes or beets.

For the purpose of our investigation, several gallons were secured and submitted to distillation, and the other tests given below. This oil has been separated from alcohol fermented during the spring season, by the longer or seventy-two hour period allowed by law. When brought to the laboratory, it was saturated with water and held some in suspension. This was allowed to settle out, leaving a perfectly clear liquid, of which the specific gravity was found to be 0.810 at 20° C. For one series of tests, two litres of this clear oil was dried as thoroughly as possible by shaking it with anhydrous copper sulphate. It was found that all of the water could not be removed in this way. The liquid poured from the sulphate was then treated with dry potassium carbonate, the mixture being kept at a temperature of 40—50° C. for two hours on several successive days. The supernatant liquid was then poured off and distilled nearly to dryness from a retort. Of the distillate thus freed from the water and purified, a litre was taken for a preliminary fractionation. After three complete fractionations the following approximate results were obtained from this sample:—

* From the *Journal of Analytical Chemistry*, vol. iv., Part, 1, January, 1890.

80—90°	17 c.c.
90—95	8
95—105	15
105—115	30
115—120	55
120—125	95
125—130	240
130—133	515
Loss and residue ..	25

The general character of the liquid being shown in this way, larger quantities were operated upon, from which we finally secured several litres boiling above 130°, and correspondingly smaller amounts at the lower temperatures.

Attention was first turned to the portions with higher boiling-points, and at the outset the specific rotation was found for several different samples. For the fractions boiling at the given temperatures, we found in a 400 m.m. tube (Smith and Haensch, large model instrument) at 25° C.—

Fraction.	a_D	d_{25}	$[\alpha]$
120—125°	-3°37'	0·8075	-1°043
125—128	-3°94'	0·8092	-1°217
128—130	-3°86'	0·8110	-1°189
130—133	-3°59'	0·8115	-1°106

From this it is evident that, notwithstanding all our precautions, a considerable portion of the active amyl alcohol passed over below 125° C., with other portions, and this was observed in samples distilled at several different times. An attempt was made to separate the active and inactive alcohols in two of the portions. For this purpose, over a litre of the portion boiling above 130° was treated with sulphuric acid according to the Pasteur method, the mixture of acid and alcohol being allowed to stand for a week, with an occasional gentle heating on the water-bath. The barium amyl sulphate was formed in the usual manner, and crystallised repeatedly in fractions, the less soluble portion being finally reserved. This was converted into the sodium salt by treatment with sodium carbonate. The sodium salt was distilled with sulphuric acid, producing an alcohol which after washing and drying showed a constant boiling-point of 131° and a specific gravity of 0·8116 at 25°. Only 30 c.c. of the alcohol was obtained in the process. When examined in a 100 m.m. polarisation tube, it showed a rotation of $a_D = -0°18'$, from which the specific rotation $[\alpha] = -0°222'$. This is a smaller value than usually given, suggesting, probably, comparative freedom from the active alcohol. An equal degree of success was not obtained in the separation of the latter in a state of purity. For this a litre boiling below 128° was treated in the same manner as before, but only a small amount of alcohol was secured from the more soluble barium amyl sulphate. When washed and dried, the volume amounted to about 20 c.c., and showed a boiling-point 128—129° C. In the 100 m.m. tube this gave a rotation $a_D = -3°50'$, which is a much smaller rotation than reported by Ley, Le Bel, and others.

The preparation of this alcohol from the more soluble barium amyl sulphate is practically a very tedious matter, and it is evident that in our experiments the crystallisations were not carried far enough. But enough was done to show that both alcohols were present in quantity in the fusel oil. From a preliminary examination of the oils obtained from other sources, it appears that the amount of the active alcohol present must in some cases be quite small, as the specific rotations of fractions boiling from 128—133° were often less than $[\alpha] = -0°75'$.

In the distillation of the dried crude oil in quantity, numerous small fractions could be separated between 85—105°, and a considerable portion below 85°.

150 c.c. of this was converted into bromine compounds in the usual manner, by treatment with red phosphorus and bromine, and the product obtained, amounting to

nearly 100 c.c., was washed, dried, and carefully fractionated. We found in this way over 50 c.c. boiling near 40° C. This fraction by subsequent tests was found to consist essentially of ethyl bromide.

35 c.c. was obtained boiling from 61—62° C., which pointed to the presence of isopropyl alcohol in the liquid brominated. Practically nothing was found boiling above these limits.

From the boiling-points of the alcohols taken, it would be possible for butyl alcohol to be present, and this has been reported as a constituent of fusel oils. But we did not succeed in isolating a bromine fraction corresponding to it. The bromide is said to boil at 72° C., but only a very minute quantity was obtained about 62°.

It appears, therefore, that the lower alcohol fractions consist essentially of the ethyl and isopropyl compounds.

It was stated above that no large fraction of alcohol was obtained between 85° and 105°. We took the fraction boiling between 95—105°, and converted it into bromide as before. If normal propyl alcohol existed in the oil, it should be found in the fraction taken, and as it is readily converted into a bromide, we should expect to find some of the latter compound boiling about 71°. In the distillation of the mixed bromides resulting from the reaction, it at first sight appeared that only a trace boiled as low as 71°, but after some little difficulty, we found that the mixture could be resolved into two portions, boiling between 70—73° and 90—94°. That the lower portion actually consisted of normal propyl alcohol was shown by the behaviour of the product on saponification.

The presence of a product boiling between 90—94°, would suggest that in the alcohol fraction brominated, along with the propyl compound, some isobutyl alcohol boiling normally at 108—109° must have been present. In order to gain more accurate information regarding the isobutyl alcohol apparently present, 150 c.c. of the fraction boiling at 105—110° was taken and brominated.

The product obtained after washing and drying amounted to 60 c.c., of which over 50 c.c. boiled at 90—93°. An abundance of the isobutyl alcohol was therefore present in this fraction. It was suspected that the higher fractions, 110—120°, might also contain a not inconsiderable portion. They were subjected to treatment with phosphorus and iodine, the latter being added very gradually, so as to avoid the loss complained of by Chapman and Smith (*Journ. Chem. Soc.*, xxii., 153). 100 c.c. boiling at 110—120°, and 100 c.c. boiling at 120—125°, were treated in this way. The yield was satisfactory. On purifying and fractionating the products, we found 65 c.c. boiling at 121—122°, 20 c.c. boiling at 128—130°, and over 50 c.c. boiling between 140° and 145° C. Below 120° and between 122° and 128° only very small amounts were found. On further fractionating the portion boiling at 140—145°, we found that most of it boiled at 143°, while a little boiled continually higher. It would appear, therefore, judging from the boiling-points alone, that the fractions converted into iodides consisted chiefly of active amyl alcohol and primary isobutyl alcohol, with a smaller amount of normal butyl alcohol.

It may appear singular that so large an amount of iodide with high boiling-point was obtained from the alcohol boiling below 125°, but it must be remembered that this fraction showed also a marked rotary polarisation; in fact, almost as great as with the fraction 125—130°. It is also possible that methylpropylcarbinol was present in the fraction 120—125°, as its boiling-point is only slightly below 120°, and the boiling-point of the iodide 145—146°, but no attempt was made to separate it.

The alcohols of high boiling-point seem to pass over readily with those of lower, but from an experiment carried out by us, it appears plain that the fractions boiling above 125° are but slightly, if at all, mixed with lower alcohols. We converted about 200 c.c. of the fraction 125—130° into iodides, and found that of the purified product only a very inconsiderable portion passed over below 140°.

We have made no attempt to find alcohols or other bodies, present in minute quantity only, in the fusel oil examined, but have sought, rather, to show the characteristic features of the oil. From the foregoing, it appears that it consists chiefly of the active and inactive amyl alcohols, probably three-fourths being made up of these bodies. The next most important substance appears to be isobutyl alcohol, and after that isopropyl and ethyl alcohols, with traces of normal propyl and normal butyl alcohols.

Only a very inconsiderable portion of the original fusel oil possessed a higher boiling-point than 133°. Part of this residue consisted of alcohols, and a part of bodies of an ethereal nature, as shown by simple saponification tests, but the amounts concerned were too small for identification.

THE SPONTANEOUS IGNITION OF COAL CARGOES.*

By Professor VIVIAN B. LEWES,

Associate of the Institution of Naval Architects, F.C.S., F.I.C.

(Continued from p. 178).

ON examining the evidence to be obtained as to the conditions under which spontaneous ignition of coal in ships usually takes place, it is found that liability to ignition increases with—

(1) The increase in tonnage of cargoes.

Thus, in cargoes of under 500 tons the cases reported amount to a little under $\frac{1}{4}$ per cent for shipments out of Europe; from 500 to 1000 tons, to over 1 per cent; from 1000 to 1500 tons, to 3.5 per cent; 1500 to 2000 tons, to 4.5 per cent; and over 2000 tons to no less than 9 per cent.

The evidence demonstrating this very remarkable result is to be found in the "Report of the Royal Commission" for 1875, p. 8, and clearly shows the influence of mass upon this action which acts in two ways—

(a) The larger the cargo, the more non-conducting material will there be between the spot at which heating is taking place and the cooling influence of the outer air.

(b) The larger the cargo, the greater will be the breaking-down action of the impact of coal coming down the shoot upon the portions first loaded into the ship, and the larger therefore the fresh surface exposed to the action of the air.

(2) The ports to which shipments are made, 26,631 shipments to European ports in 1873 only resulting in 10 casualties, whilst 4485 shipments to Asia, Africa, and America gave no less than 60.

This startling result is partly due to the length of time the cargo is in the vessel, the absorption and oxidation being a comparatively long action, but a far more active cause is the increase in the action brought about by the increase of temperature in the tropics, which converts a slow action into a rapid one, and if statistics had been taken, most of the ships would have been found to have developed active combustion somewhere about the neighbourhood of the Cape, the active action developed in the tropics having raised the temperature to the igniting-point of the coal by that time.

(3) The kind of coal of which the cargo consists, some coals being specially liable to spontaneous heating and ignition.

This is a point on which great diversity of opinion exists, but I think it will be pretty generally admitted that cases of heating and ignition are more frequent in coals shipped from East Coast ports than in shipments of the South Wales coals. As has been pointed out, however, so much depends on the amount of small coal present

that a well-loaded cargo of any coal would be safer than a cargo of Welsh steam coal in which a quantity of dust had been produced during loading.

The idea that the percentage of pyrites present is any indication of the liability to spontaneous combustion must be entirely discarded, as experiment shows that many coals poor in pyrites frequently ignite, whilst others rich in them are perfectly safe.

A much surer guide is to be found in the quantity of moisture present in an air-dried sample of coal, which is a sure index to the absorptive power; the higher the amount of moisture held by the coal after exposure for some time to dry air, the greater will be its power of absorption for oxygen, and the greater therefore its liability to spontaneous heating and ignition.

This is beautifully shown by a table which follows, in which the percentage of pyrites and moisture present in some coals are contrasted with their liability to self-ignition.

(4) The size of the coal, small coal being much more liable to spontaneous ignition than large.

This, as has been pointed out, being entirely due to the increase in active absorbent surface exposed to the air, a fact which is verified by the experience of large consumers of coal on land; gas-managers recognising the fact that coal which has been stamped down or shaken down during storage being more liable to heat than if it has been more tenderly handled, the extra breakage causing the extra risk.

(5) Shipping coals rich in pyrites whilst wet.

Liability to spontaneous ignition.	Pyrites per cent.	Moisture per cent.
Very slight	{ 1.13	2.54
	{ 1.01 to 3.04	2.75
	{ 1.51	3.90
Medium	{ 1.20	4.50
	{ 1.08	4.55
	{ 1.15	4.75
	{ 1.12	4.85
Great	{ 0.83	5.30
	{ 0.84	5.52
	{ 1.00	9.01

The effect of external wetting on coal is to retard at first the absorption of oxygen and so to check the action, but it also increases the rate of oxidation of the pyrites, and so causes disintegration of the coal, with consequent crumbling and heating due to exposure of fresh dry surfaces.

(6) Ventilation of the cargo.

The so-called ventilation, which has from time to time been introduced into coal ships, is undoubtedly one of the most prolific causes of spontaneous ignition.

For ventilation to do any good, cool air would have to sweep continuously and freely through every part of the cargo, a condition impossible to attain, whilst anything short of that only increases the danger, the ordinary methods of ventilation supplying just about the right amount of air to create the maximum amount of heating. The reason of this is clear. A steam coal absorbs about twice its own volume of oxygen, and takes about ten days to do it under favourable conditions, and it is this oxygen which in the next phase of the action enters into chemical combination and causes the serious heating.

A ton of steam coal occupies 42 to 43 cubic feet, and if properly loaded contains between the lumps as nearly as possible 12 cubic feet of air space, that is to say, of the 42 cubic feet, 12 cubic feet is air and 30 cubic feet is coal.

Thirty cubic feet of coal, with its fresh absorbing surfaces laid bare by the crushing incidental to loading, will, in the first ten days after being taken on board, absorb 60 cubic feet of oxygen, if it can get it. Now, air contains only, roughly, one-fifth of its volume of oxygen, so that 60 cubic feet represent 300 cubic feet of air, or twenty-five times as much as is present; so that it is evident that

* Read at the Thirty-first Session of the Institution of Naval Architects, March 28, 1890; the Earl of Ravensworth in the Chair.

if air could be excluded there would be only one twenty-fifth the quantity of oxygen present which is needed for complete action, and any heating would, in consequence, be very slight; whilst to produce the greatest heating it would be necessary to change the entire air in the cargo twenty-five times in the first ten days, and this is just about what the ordinary method of taking a box shaft along the keelson with Venetian lattice upshafts from it would give.

The most forcible illustration of the evil of such ventilation is to be found in the case of the four colliers, *Euxine*, *Oliver Cromwell*, *Calcutta*, and *Corah*, which were loaded at Newcastle under the same tips, at the same time, with the same coal, from the same seam. The first three were bound for Aden, and were all ventilated. The *Corah* was bound for Bombay, and was not ventilated. The three thoroughly ventilated ships were totally lost from spontaneous ignition of their cargo, whilst the *Corah* reached Bombay in perfect safety.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

March 20, 1890.

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

MESSRS. Bertram Blount, S. Home Collins, F. H. Perry Coste, T. S. Dymond, and W. Charles Sayers were admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Dixon, 3, Belle Vue Park, Sunderland; Thomas Flower Ellis, Widmore, Bromley, Kent; Frederick John Hambly, 13, Osborne Place, Dundee, N.B.; Charles Terry Holloway, 188, Lewisham High Road, S.E.; John Stewart MacArthur, 46, Melville Street, Pollokshields; Harold Picton, 80, Regent's Park Road, N.W.; Alexander Smith, 4, West Castle Road, Edinburgh.

The following lecture was delivered:—

"The Evidence Afforded by Petrographical Research of the Occurrence of Chemical Change under Great Pressure." By Professor J. W. JUDD, F.R.S., F.G.S., &c.

The materials constituting the deeper parts of the earth's crust must sustain great *statical* pressure, due to the weight of superincumbent rock masses; some of these materials, too, have from time to time been subjected to enormous *dynamical* pressures resulting from the stresses which arise during mountain-making and other earth-movements. Hence it is found that the rocks and minerals which have at any time formed the deeper parts of the earth's crust show many striking evidences of the action of these pressures: among these may be mentioned the cavities filled with various supersaturated solutions, carbon dioxide, and other materials; there are also remarkable indications of strain, distortion, and fracture presented by the minerals when their optical properties are studied.

The question was discussed how far the phenomena observed by the geologist in his study of rocks under the microscope can be explained by the laws that have been experimentally determined by the physicist and chemist; and it was pointed out that the conclusions to which both the experiments of physicists and chemists and the observations of mineralogists and geologists point are as follows:—

1. In all those cases in which crystallisation is accompanied by *contraction*, the tendency of pressure is to promote the change from an amorphous to a crystalline condition.

2. Crystallised minerals developed in a magma under

pressure may lose their stability, and be dissolved by the same magma when the pressure is removed.

3. In all those cases in which solvent action is accompanied by *contraction*, dissolution is promoted by pressure.

4. Under great statical pressures the whole substance of solid bodies may be permeated by fluids (liquids and gases alike), and chemical action between these and the solids is thus greatly facilitated.

5. By the intimate admixture, under great statical pressures, of solids with fluids, the properties of the former are remarkably modified.

6. Mechanical stresses, which tend to overcome the attraction between the particles of a solid, promote chemical action at those parts of the mass which are in a condition of intense strain.

7. Pressure may supply the conditions required for the renewal of the growth of crystals when their development has been arrested for an indefinite period, and even after they have suffered mechanical injuries.

8. When dissolution under pressure is going on in a crystalline substance, the action is controlled and modified by its molecular structure; this structure having been produced in the process of crystallisation, or having been acquired by the crystal subsequently, owing to the action of mechanical and other forces upon it.

9. Under great pressures, paramorphic changes take place in crystalline substances without change in their chemical composition.

10. Both the dissolution of existing compounds and the formation of new crystallised minerals may result from pressure; and these two operations frequently going on together, pseudomorphs are produced, the action sometimes affecting great rock masses.

11. When, as the result of *dynamical* pressures, the crystalline constituents of rocks are brought into close contact, chemical affinities come into play between them, and new mineral species result from the interactions. This operation is facilitated when, as the result of internal strains, differential movements are set up in a rock mass, and rubbing or sliding contacts between the particles are brought about.

12. When internal strains and differential movements affect a mass in which the process of crystallisation is going on, the forms and positions of the crystals may be modified. The structures known to geologists as "granulitic" and "foliated," which characterise the crystalline schists, have been produced in this way, as was shown by Scrope, Dana, Darwin, Sharpe, and Naumann, and confirmed by many subsequent investigators.

In arriving at these conclusions recourse has been had only to proved causes of change, and hypothetical causes have been avoided. Some of them may seem insignificant, but, affecting, as they have done, vast masses of material during enormous periods of time, the results accomplished by such apparently insignificant causes have been very great.

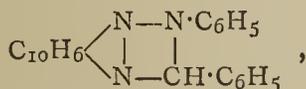
Although *dynamical* pressures may be converted into heat, as shown by Mallet, or into chemical action, as argued by Sorby, no very distinct evidence of great effects having been produced by these methods has been discovered.

The following papers were read:—

21. "The Formation of Triazine Derivatives." By R. MELDOLA, F.R.S.

In consequence of a recent paper by Goldschmidt and Rosell (*B.*, 1890, 487), which to some extent anticipates an investigation upon which the author and C. Tyrer have been at work for some time, the method adopted for the synthesis of triazine derivatives is briefly described in this communication. The method consists in acting on a benzyldine derivative of an amine with a diazo-salt so as in the first place to form an orthazo-compound; on heating a solution of the azo-compound, preferably in

glacial acetic acid, the benzylidene and azo-groups then undergo condensation, forming a triazine ring. In this way diphenyl- $\alpha\beta$ -naphthotriazine, having the formula



has been prepared from benzylidene- β -naphthylamine and diazobenzene chloride. It is a feeble base forming dense flat white needles melting at 193—194°, dissolving with difficulty in benzene and but very sparingly soluble in alcohol. Other triazine derivatives prepared by this method are in course of investigation.

22. "Contributions to the Knowledge of Mucic Acid. Part I., Hydromucic Acid." By S. RUHEMANN, Ph.D.

Chloromuconic acid, prepared from mucic acid in accordance with Bode's directions (*Annalen*, cxxxii., 195), is very stable, as indeed Limpricht has already stated; its chlorine is not displaced by the action of boiling alcoholic potash or ammonia; aniline acts very readily on its alcoholic solution, but the product is simply the aniline salt. Its ethylic salt is converted by ammonia into chloromuconamide.

The authors find that chloromuconic acid is most conveniently converted into hydromucic acid by treatment with tin and chlorhydric acid. Of the two possible formulæ of this acid, $\text{COOH} \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ and $\text{COOH} \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \cdot \text{COOH}$, there can be no doubt that the former is to be regarded as correct, as v. Baeyer has shown that hydromucic acid is obtained on reducing the dicarboxylic acid, $\text{COOH} \cdot \text{C} : \text{C} \cdot \text{C} : \text{C} \cdot \text{COOH}$.

It appears that, contrary to Limpricht's statement, the same dibromadipic acid is obtained by the action of bromine on hydromucic acid when acetic acid is taken as solvent as when water is used. The acid melts at 185—207°, according to the rate of heating. Ethylic dibromadipate, prepared either directly from the acid or by brominating ethylic hydromuconate, crystallises in long needles melting at 64°; by the action of ammonia, this salt is converted into the amide of an acid isomeric with muconic acid. This *isomuconic* acid, $\text{C}_6\text{H}_6\text{O}_4$, can be easily obtained by heating ethylic dibromadipate with alcoholic potash; it crystallises in white fine needles, very sparingly soluble in water and alcohol. The barium, lead, potassium, silver, and ethylic salts of this acid are described. On oxidation with permanganate, isomuconic acid yields oxalic and succinic acids, and there can be no doubt, therefore, that its formula is—



23. "The Molecular Weights of Metals when in Solution." By C. T. HEYCOCK, M.A., and F. H. NEVILLE, M.A.

In a previous communication (*Proc. Chem. Soc.*, 1889, p. 41) the authors have given a preliminary account of their observations on the effect of metals on the solidifying point of tin, and they subsequently described similar experiments using sodium as the solvent (*Chem. Soc. Trans.*, 1889, 666). They now give the details of the investigation of solutions in tin.

Tables of results are given showing the effect of various proportions of the following metals:—Silver, gold, copper, nickel, sodium, palladium, magnesium, zinc, lead, cadmium, mercury, bismuth, calcium, indium, aluminium, and antimony. Of all these metals, antimony alone behaves abnormally, producing a rise instead of a depression in the solidifying point.

An example will illustrate the method of calculating the "atomic depression." In an experiment with silver, 4.3085 grms. were dissolved in 400 grms. of tin, *i.e.*, $\frac{4.3085}{108}$ of an atomic proportion; and therefore there was present per 100 proportions of tin—

$$\frac{4.3085 \times 118 \times 100}{108 \times 400} + 1.177$$

atomic proportions of silver. The observed solidifying point of tin was 231.68°, and of the solution 228.29, a depression of $231.68 - 228.29 = 3.39^\circ$; hence the atomic depression was—

$$\frac{3.39}{0.177} = 2.875.$$

In the majority of cases, the atomic depression is a number not far removed from 3. If Raoult's generalisation be true, that the depression produced by a molecular proportion of any substance in the solidifying point of the same solvent is the same whatever the substance, it would therefore seem probable that the molecules of most metals are of the same type, M_n , where n is the number of atoms in the molecule; and if it be supposed that the molecules of, say, zinc, when dissolved in tin, are monatomic, as in the gaseous state, it would follow that n is unity in the case of many other metals. The theoretical depression calculated from Van't Hoff's formula is 3, and a similar value may be deduced from a formula suggested by Professor J. J. Thomson. In the case of aluminium, the atomic depression is so nearly half the average value that it seems probable that the molecule is diatomic. Indium resembles aluminium in producing an abnormally low depression; and it is noteworthy that the value for mercury is distinctly low: in fact, the data recorded show that there are many interesting points of difference to be noted between the various metals.

Annual General Meeting, March 27th, 1890.

The President delivered an address, of which the following is an abstract:—

There are at present 1733 Fellows of the Society of whom 34 are honorary foreign members; at the same period last year there were 1650, including 36 honorary foreign members.

145 Fellows have been elected during the year.

16 Fellows have died during the year:—Richard Anderson, M. T. Buchanan, M. Chevreul (foreign member), John Dale, Dr. Warren de la Rue, Ernest H. Francis, Prof. A. Geuther (foreign member), James Hindle, J. P. Joule, Benjamin Nickels, Henry Pollock, Owen Prosser, Dr. R. Romanes, Dr. Edmund Ronalds, Joseph Stapleton, Dr. David Waldie.

12 Fellows have withdrawn:—S. F. Burford, E. B. Clarke, N. M. Falkiner, Alex. Galt, John Innes, Alfred Neild, W. F. Pankhurst, Forbes Rickard, Newton Samuelson, Rev. S. D. Titmas, Wm. Weston, G. H. With, Charles Williams.

34 Fellows have been removed from the Society's list on account of arrears:—G. W. Arnott, A. B. Avarne, W. Alabaster, W. A. Bradbury, F. W. Drinkwater, Joseph Fletcher, F. W. Fleming, T. H. Judson, Chas. A. R. Jowett, T. N. Kirkham, John W. King, R. W. E. MacIvor, E. C. L. Muspratt, K. D. Naegamvala, W. O. Nicholson, Rev. P. R. Ogle, J. B. Orr, C. H. Piesse, A. N. Pearson, Victor E. Perez, A. E. Robinson, Alfred Southall, J. Schwarts, Frederick Sear, F. W. Simpson, J. H. Thompson, John A. Tate, Caleb Terry, John D. Veira, Peter H. Walsh, R. N. Wolfenden, H. P. White, Edward Willmore, and Chas. F. Young.

100 papers have been communicated to the Society during the session; a considerable number of these have, at their authors' request, been published in the *Proceedings*, now in the sixth year of its existence, and which has become a most valuable adjunct to the Journal, serving to give as wide and as important a publicity to a paper as the *Transactions*, and at the same time affording a rapidity of publication not exceeded by any other scientific journal.

In the year 1889, 71 papers, occupying 773 pages, have been published in the *Transactions*; 75 papers, occupying 895 pages, having been published in the year 1888. The number of abstracts published during 1889 is 2131, which

occupy 1252 pages; the number is considerably smaller than in the previous year, when it was exceptionally large, viz., 2470, occupying 1351 pages.

After speaking with approval of the work done by the Publication Committee and the Editors, the President said that it was intended to give more attention in future to the abstracts of analytical papers, and to illustrate these when necessary; and referring to the fact that next year the Society will have been in existence fifty years, he said that it had been suggested that the issue of a complete subject catalogue of the Society's original publications would be a fitting memorial of the occasion; such a work was practicable, and the Society had the means of carrying it out.

Not only had the Library Committee procured a considerable number of new books during the year, but by the generosity of several Fellows and others, and by purchase, a very important addition had been made to the Library of old books. The importance to the Society of a complete collection of historical works could not be overrated: the Committee lose no opportunity of securing such works, but they trust that Fellows will, whenever possible, assist their efforts in this direction, and he would remind them how much the value and interest of an old book is increased when it becomes an integral part of a series of historical works such as the Society already possesses. The present state of the Library shelves is shown in the following table:—

	March 31st, 1889.	Additions in 1889-90.	Present state.
Volumes of systematic works	2,922	160	3,082
Volumes of journals ..	5,474	193	5,667
Volumes of duplicate journals for circulation	1,084	51	1,135
Pamphlets	1,426	24	1,450
	<u>10,906</u>	<u>428</u>	<u>11,334</u>

The expenditure under this head during the year had been £270 18s. 11d.

During the year the Royal Society had awarded both the Davy and a Royal medal to Fellows of the Society, and he felt sure, said the President, that all rejoice that the important investigations of Dr. Perkin and of their Treasurer, Prof. Thorpe, had met with such well deserved recognition of their value.

Referring to the alteration which had been made in the time of the anniversary meeting, and to the dinner which was to take place in the evening, the President said that it had been thought that it would be of advantage to the Society in general to follow the example of other societies and to have an anniversary dinner; and it was hoped that the change would have the effect of bringing a large number of Fellows together, and that those not resident in London would feel it to be a duty as well as a pleasure to attend at least the annual evening meeting of the Society.

The recent important lecture for which the Society was indebted to Professor Judd was referred to. Attention was then drawn to the special meeting for the exhibition of apparatus to be held on May 8th next; in every active laboratory there is to be found apparatus devised to meet some special requirement which has not been made known, which can be appropriately shown at such a meeting.

The President then proceeded to discuss the teaching of chemistry to medical students. It was too seldom recognised that the fundamental action of medicines—the origin of their power—is a chemical change, and hidden and complicated as are the changes produced by medicines, they must ever retain their chemical character; if an understanding and appreciation of their effects is to be sought for, the first step must be to learn the laws which govern chemical action, and the chemical nature of the substances employed. But in addition to furnishing

so many of the elementary facts on which the rational practice of medicine rests, chemists may claim that a better schooling cannot be devised for the student of medicine than that afforded by the study of these facts in their simplest form. Reference was made to the Reports of the British Association Committee on the Teaching of Chemistry in Schools, and to the influence exercised by the Science and Art Department on the teaching of chemistry throughout the country, in proof that, however imperfect the system of teaching has been, attention is now drawn to the importance of effecting an improvement, and that it is to be expected that the number of students will rapidly increase, and that the quality of the teaching will advance.

While protesting most emphatically against the exclusion of chemistry from the medical curriculum, the President said that chemists had, he thought, unduly urged an extensive knowledge of their science as necessary to the medical man; he would willingly relinquish the idea of making him a chemist, but he most pertinaciously adhered to the statement that he must be well trained in elementary chemistry. If students were encouraged to regard elementary knowledge as of no use and the methods by which knowledge is gained from experiment as of no avail to them, we should be educating them to become empiricists instead of fitting them to become observant and reasoning human beings. He thought that chemistry should be placed in the same category as the recognised subjects of general education, and made obligatory in the preliminary examination; all students on commencing their career at the medical school would then have some knowledge of the subject: the teacher there would commence his instruction at a higher level than at present, and would be able to enforce his teaching by preference by means of illustrations having a technical bias. The Examining Board of the two Colleges insists in the case of anatomy, medicine, and physiology that the student shall have studied at a recognised medical school, thus recognising most wisely the importance of study under efficient instructors and at places properly equipped; he desired to protest most strenuously against the exclusion of chemistry from this healthy regulation. At present the candidate, on presenting himself for examination in chemistry, has but to produce a certificate stating that he has received chemical instruction; if only qualified persons gave certificates these would be of value; as it is, he failed to see the use of the certificates. A strong feeling is growing up that a most valuable, if not indispensable, adjunct to examinations is the knowledge where the student has studied, and the guarantee that he not only has had proper and sufficient opportunities, but also that he has made use of them. If all restrictions be waived in the case of chemistry, and everything be allowed to depend on an examination, the examination must be made far more searching than at present, and in place of hours must last for days.

It would be of great advantage to the medical student to direct his attention to chemistry at two distinct periods; and, in addition to the elementary class, there should be in every medical school a higher class for students who have time and inclination for the more thorough study of the subject. The teacher of physiology and the teacher of chemistry should work together far more than is now the case; at present the student regards the chemistry of the chemical teacher as something distinct from and not nearly so necessary as the chemistry of the physiologist.

The Fellows of the Society could best realise the advantages to be derived from the careful and accurate study of chemistry, and it must devolve on them, while not blind to the importance of other studies, to advocate that chemistry should be assigned its proper place, and should be efficiently taught, not only to the medical student, but as a branch of a liberal and general education to all other students.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 12, March 24, 1890.

Condensations of Carbon Monoxide and the Penetrability of Glass by Water.—M. Berthelot.—The author calls attention to the aptitude of carbon monoxide to form condensed and polymerised compounds stable only at temperatures below redness. The condensed product is brownish with a white portion on its edges. It attracts moisture from the air with extreme rapidity. The penetrability of glass by water under electric influence, if it can be conceived of as possible with certain exceptional glasses, does not appear to constitute a general phenomenon.

Remarks on M. Berthelot's Observations on the Reactions between Vegetable Mould and Atmospheric Ammonia.—Th. Schloësing.—All the discussions in the world are not worth a fact well observed. The fact of the absorption of aerial ammonia by vegetable soil is now well observed and is a general fact.

New Preparation of the Betaines.—E. Du villier.—The author has arrived at very good results by causing a hydriodic ether to act upon a zinc salt of the amidic acids in presence of zinc oxide, a process analogous to that which enabled M. Schützenberger to obtain the leucines synthetically.

Determination of Acetone by Iodoform.—G. Arachequesne.—The author recommends that Krämer's method, as it stands, should be employed only for pure methylic ether. For methylated spirit containing from 1.5 to 30 per cent of acetone he uses the same method, but takes a relatively smaller volume. For spirit of 20 to 30 per cent he takes 5 c.c. and dilutes with water to 500 c.c. Of this mixture he takes 5 c.c. and multiplies the result by 20.

On Callose, a New Fundamental Vegetable Substance Existing in Membrane.—Louis Mangin.—The author has not yet obtained this substance in a state of purity, so as to determine its composition. It is colourless, amorphous, insoluble in water, in alcohol, and in Schweitzer's reagent; very soluble in caustic alkali at 1 per cent, soluble in the cold in sulphuric acid, calcium chloride, and strong stannic chloride; insoluble in cold alkaline carbonates and ammonia, which gelatinise it. It is coloured by aniline blue and rosolic acid and certain azo-colours.

Determination of Fatty Matter in Milk.—M. Lezé.—The author takes a glass flask with a long neck graduated in c.c. and tenths of a c.c. He pours into it a mixture, already prepared and agitated, of 100 parts of the milk and 200 to 250 parts of pure strong hydrochloric acid, and heats until the liquid turns brown. He then adds dilute ammonia until the liquid becomes clear, and lastly hot water until the level reaches the height of the graduation. He then reads off the number of divisions occupied by the fatty matter. This butter has a sp. gr. close upon 0.90, and by multiplying the volume observed by this factor we have the weight.

No. 13, March 31, 1890.

Observations on the Foregoing Communication and on the Desiccation of Gases.—M. Berthelot.—The author still entertains doubts on the origin of the moisture observed by M. Schützenberger. He does not think the penetrability of ordinary glass by water proved, and supposes that the interior of the glass tubes and the mercury may have been slightly damp.

Sir F. A. ABEL proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed; Professor EMERSON REYNOLDS seconded the motion; Mr. CASSAL then spoke on behalf of the motion, in order to give expression to his views as to the status of Fellows of the Society. The motion was carried by acclamation. The President having acknowledged the vote,

Professor THORPE, the Treasurer, gave an account of the financial position of the Society. The receipts by admission fees and subscriptions had been £3637; by sale of the Journal, £377 3s.; and by dividends on invested capital, £340 10s. 9d. The expenses on account of the Journal had been £2310 18s. 3d.; on account of the Proceedings, £177 4s. 7d.; on account of the Library, £420 8s. 11d.; the total expenditure being £3578 18s. 8d. £530 had been invested in Metropolitan Board of Works 3½ per cent stock, and the balance in hand was £2036 2s. 7d., as against £1833 13s. 6d. for the corresponding period last year.

Dr. H. MÜLLER proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; the motion was seconded by Professor DUNSTAN.

Professor THORPE, after replying, proposed a vote of thanks to the Auditors, Messrs. R. H. Davies, Bernard Dyer, and R. J. Friswell; this was seconded by Mr. F. J. M. PAGE and acknowledged by Mr. DAVIES.

A vote of thanks to the Officers and Council, having been proposed by Mr. CARTEIGHE and seconded by Professor RAMSAY, was acknowledged by Professor THOMSON.

Mr. WARINGTON moved that thanks be tendered to the Editors, Abstractors, and Librarian; Mr. PICKERING seconded the motion; Mr. GROVES replied.

Mr. T. Fairley and Mr. Wm. Thorp having been appointed scrutators, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session:—

President—W. J. Russell, Ph.D., F.R.S.

Vice-Presidents who have filled the Office of President.

—Sir F. A. Abel, C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—Dr. A. Crum Brown, F.R.S.; G. Carey Foster, F.R.S.; W. N. Hartley, F.R.S.; J. W. Mallet, M.D., F.R.S.; J. Emerson Reynolds, M.D., F.R.S.; Robert Warington, F.R.S.

Secretaries—H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary—F. R. Japp, LL.D., F.R.S.

Treasurer—T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council—Henry Bassett; Norman Collie, Ph.D.; C. F. Cross; Wyndham Dunstan; John Ferguson, M.A.; E. Kinch; Raphael Meldola, F.R.S.; M. M. P. Muir; F. J. M. Page; S. U. Pickering, M.A.; R. T. Plimpton, Ph.D.; Thomas Purdie, B.Sc.

Society of Arts.—The papers for the Wednesday evening meetings after Easter to the end of the session have been fixed as follows:—On April 16, "Old and New Fashions in Typography," by Talbot B. Reed; April 23, "Coal in the South-East of England," by William Whitaker, F.R.S.; April 30, "Photographic Lenses," by T. R. Dallmeyer; May 7, "The Aim and Scope of Higher Technical Teaching," by Dr. Percy F. Frankland; May 14, "Professor Elihu Thomson's Electro-Magnetic Induction Experiments," by Dr. J. A. Fleming; May 21, "The Mannesmann Process for making Seamless Tubes," by J. G. Gordon.

Condensation of Carbon Monoxide.—P. Schützenberger.—In reply to M. Berthelot the author maintains that the two chief conclusions in his paper of March 17 are not contradicted by the experiment described by the latter.

Conductivities of Phenols and Oxybenzoic Acids.—Daniel Berthelot.—The three isomeric oxybenzoic acids have quite distinct conductivities, decreasing in the order ortho-, meta-, para-, the conductivity of the latter approaching that of benzoic acid.

Refraction-Indices of Saline Solutions.—B. Walter.—The author objects to the conclusion of M. Doumer that the molecular refractive powers of the salts are functions of the number of valencies of the metallic element which enters into the composition of the salts. He holds, on the contrary, that the molecular refringent power of copper and iron sulphates is triple that of potassium and sodium chlorides and $\frac{2}{3}$ that of potassium and sodium sulphates.

Action of Sodium Thiosulphite upon the Salts of Silver.—J. Fogh.—The author maintains that on thermo-chemical principles the solution of silver iodide in thiosulphite is not possible without the assistance of some extraneous energy. This result is confirmed by experiment. A solution of the double silver and sodium thiosulphite is precipitated by potassium iodide, whilst it is not affected by the addition of a solution of a chloride or a bromide.

Pre-Columbian Metallurgy in Venezuela.—V. Marcano.—An analysis of three metal trinkets recently found near Caracas in some earthen sarcophagi containing bones. One of these has probably been formed by the hammer from native gold, very rich in silver and containing copper. The other two are alloys of argentiferous gold with a product of the reduction of an ore of copper and iron. Near the site there occurs a vein of copper carbonate intimately mixed with iron oxide, but containing neither gold nor silver.

Influence of the Chemical Constitution of the Derivatives of Carbon upon the Direction and the Variations of their Rotatory Power.—P. A. Guye.—The author draws the following conclusions:—Whenever, in consequence of the substitution of an element or radicle by another, the centre of gravity of the molecule remains on the same sides of the planes of symmetry of the carbon, the rotatory power of the substituted derivative thus obtained must retain the same sign. If, in consequence of a substitution, the centre of gravity of the molecule is removed from the planes of symmetry, the rotatory power of the substitution-product must be greater than that of the original substance. On the contrary, it will be smaller if the centre of gravity approaches the planes of symmetry. If, in consequence of substitution, the centre of gravity is displaced from one side to the other of one of the planes of symmetry, the rotatory power of the new product changes its sign.

Preparation and Properties of Fluoroform.—M. Meslans.—The gas is colourless; it burns with difficulty, giving off much hydrofluoric acid and colouring the flame blue. Its odour resembles that of chloroform. It is sparingly soluble in water, chloroform, and benzene; alcohol dissolves about 5 vols. The sp. gr. is between 2.48 and 2.53; theoretically it would be 2.44. It liquefies at 20° under a pressure of 40 atmospheres, and solidifies at higher pressures. If heated to 160° in a sealed tube with alcoholic potassa it is split up into potassium fluoride and formiate. The composition of the gas is CHF_3 .

Sulpho-Conjugated Phenols derived from Ordinary Camphor.—P. Cazeneuve.—Concentrated sulphuric acid in the cold gives, with monochlorocamphor, a mixture of sulpho-conjugated compounds having a phenolic function. This formation proves that the terebenic series contains the benzene nucleus, and is merely a branch of the aromatic series.

Zeitschrift für Analytische Chemie.
Vol. xxviii., Part 6.

Method for Determining Quinine in Quinine Tannate.—Dr. Sig. Neumann.—The author weighs out exactly 2 grms. of pulverised quinine tannate, and introduces it into a glass cylinder holding about 300 c.c., and having a well-fitted stopper, previously charged with 20—25 c.c. potassa-lye (sp. gr. 1.240), and shakes the whole well up. Care must be taken that the tannate does not adhere to the sides of the glass, as it is there not easily removed by the potassa-lye. The whole is then made up to 60—80 c.c. and 100 c.c. ether, accurately measured, are added, the stopper is rapidly inserted, and the whole is shaken well together. After a few minutes, there appear two separate layers of liquid, the colourless ether above and below the potassa-lye coloured brown by the tannin. No solid particles should be floating about in either. If the potassa is so dark as to be opaque, it is diluted or the cylinder is laid horizontally and observed from above. After the two strata have completely separated, the cylinder is unstopped, 50 c.c. of the ether are quickly measured off with the pipette, and poured into a weighed beaker. The ether is allowed to evaporate slowly at a temperature of 50—60°, and the residue (quinine anhydride) is dried at 100°. When cold, it is weighed, and if two grms. of the substance were originally taken, we have at once the percentage. The residue can be examined for other alkaloids. It should be perfectly soluble in dilute hydrochloric or sulphuric acid, otherwise either the ether was impure or fats or resins were present in the sample.

Detection and Determination of Chlorine in Alkaline Sulphocyanides.—C. Mann.—If an alkaline sulphocyanide is mixed with a solution of copper sulphate and treated with sulphuretted hydrogen, there falls at first only white copper sulphocyanide, which on prolonged action passes into copper sulphocyanide. If more copper is present than suffices for the formation of copper sulphocyanide, and if the current is interrupted at the moment when the liquid becomes brown, and if a corresponding quantity of fresh solution of copper is added to take up the free sulphuretted hydrogen and precipitate any hydro-sulphocyanic acid which may have become free, the filtrate no longer gives the sulphocyanide reaction. If, therefore, there was in the sulphocyanides used only a very trifling quantity of chlorine or bromine, it can be easily detected by the addition of a little nitric acid and a few drops of dilute silver nitrate. The mixture of copper sulphocyanide and sulphide can be easily filtered, and the filtrate never runs through turbid on washing. In practice, 5 grms. of the sample at most are taken, and require 20 grms. pure copper sulphate, which may be kept ready in solution of the strength 20 : 100 aq. Both salts, each dissolved in 100 c.c. of cold water, are poured together, sulphuretted hydrogen is passed in and 8 grms. copper sulphate, 40 c.c. water are added, well stirred, and the precipitate is filtered off. The chlorine in the filtrate is determined in the ordinary way as silver chloride.

New Extraction Apparatus.—Dr. O. Knöfler.—This paper requires the accompanying cut.

New Porcelain Capsules for Quantitative Work.—Dr. O. Knöfler.—The author's improvement consists in introducing a dark green or black lining-colour underneath the glaze, so that light-coloured—especially amorphous—precipitates may be seen more readily.

Distinction between Propylic and Butylic Alcohol. Normal propylic alcohol has the sp. gr. 0.813, boils at 97°, is readily soluble in water, and if rubbed on the hands has a pleasant fruity smell. If its solution in 30 per cent spirit is shaken with chloroform it is not taken up. Butylic alcohol (fermentation) has the sp. gr. 0.805; it boils at 108—109°, dissolves with difficulty in water, floating on the surface like oil; it has an unpleasant oily fusel smell if rubbed in the hands, and is taken up by

Chloroform with increase of volume. If crude spirit diluted to 30 per cent is shaken up with chloroform, amylic alcohol, acetal, aldehyd, and (fermentation) butylic alcohol are extracted, whilst ethylic alcohol, acetic acid, and tertiary butylic alcohol remain in the supernatant liquid.

Apparatus for Fractionated Distillation at Reduced Pressure.—E. Valenta.—This paper requires the five accompanying figures.

Laboratory Apparatus.—Dr. A. Burgemeister.—These appliances consist of a gas-generating apparatus, a filter-bell, and a sulphuretted hydrogen apparatus, all figured.

Apparatus for Emptying Gas-Generators.—A. C. Hertzog.—This paper requires the two accompanying cuts.

New Potash Apparatus.—S. Schiff.—This paper cannot be reproduced without two woodcuts.

Determination of Copper by Converting the Sulphide into Oxide.—C. Holthof.—On working with precipitates of 0.18—0.22 grm., the author observes that precipitated copper sulphide, filtered in a suction-pump, introduced, while still moist, into the crucible, and treated exactly according to Bunsen's directions, smoulders at a moderate temperature of the crucible, and passes readily into copper oxide, so that, on subsequent ignition over a good burner for seven to ten minutes, there is no further loss of weight on re-ignition, nor can any trace of sulphuric acid be found in a solution of the residue. Dried precipitates of copper sulphide, even after ignition for hours, still retain traces of sulphuric acid.

Hygrometric Methods.—W. N. Shaw.—From the *Philosophical Transactions*.

Determination of the Specific Gravity of Pulverised Substances.—W. F. Smeeh.—From the *Scientific Proceedings of the Dublin Society*.

Determination of Specific Gravity of Fluids.—A. B. Taylor.—From *American Journal of Pharmacy*, per CHEMICAL NEWS.

Absorption of Gases in Liquid Mixtures.—O. Müller and O. Lubarsch (*Annalen der Physik und Chemie*).

Absorption and Condensation of Carbonic Acid on Clean Surfaces of Glass.—H. Krause (*Acad. des Sciences, Petersburg*).—In the absence of water there occurs no condensation or absorption of the gas. If water is present, condensation takes place more abundantly if the surface of the glass is rich in alkali.

Tension of Watery Vapour over an Aqueous Solution of Caustic Potassa.—G. Errera (*Gazetta Chimica*).—Merely mentioned.

Separation of Precipitates difficult to Filter from the Liquid.—E. Bauer (*Chemiker Zeitung*).—The author removes the liquid by diffusion. He takes a funnel without neck, ground off below rather broad so that the point of a filter may project out downwards. If the funnel thus prepared is set on a vessel of water into which the point of the filter dips, and the precipitate and mother-liquor are introduced, the solution will diffuse into the water, and can be entirely removed by the use of successive quantities of water.

Apparatus for the Rapid and Correct Measurement of Liquids.—G. P. Vanier (*Journal of Analytical Chemistry*) and B. Gerdes (*Chemiker Zeitung*).—For the description of these appliances we must refer to the originals.

Filtering Arrangements.—An account of the apparatus of G. Neumann (*Journal für Prakt. Chemie*), G. C. Stone (*Journal of Analyt. Chemistry*), and L. L. de Koninck (*Zeitschrift Angewandte Chemie*). The last proposes that the filtration of precipitates which require to be dried and weighed on the papers should be effected in small light funnels capable of being weighed.

Colorimeters.—A brief mention of Lovibond's tintometer, from the *Journ. Soc. Chem. Industry*, and also of M. Müller's colorimeter for Nesslerising water (*Dingler's Journal*), and of Ad. Jolle's colorimeter. The two latter depend on well-known principles.

A Normal Barometer.—P. N. Raikow (*Chemiker Zeitung*).—A syphon barometer with a mercury level which can be displaced, as in Fortin's barometer.

A New Barometer with an Air Thermometer.—F. C. G. Müller (*Annalen der Physik*).—For the description of this instrument we must refer to the original.

Vaporimeter for Determining the Tension of Vapours at the Temperature of Boiling Water.—G. Th. Gerlach (*Chemische Industrie*).—This instrument differs chiefly from one formerly described by the same author by the method of heating which takes place in two concentric tubes filled with steam.

MISCELLANEOUS.

Determination of "Total Residue" in Water Analysis.—Wm. P. Mason.—Water residues, particularly those from mineral waters, are often so hygroscopic as to be exceedingly difficult to weigh, if the evaporation be performed in an open platinum dish. It has been my custom, for some time past, to substitute for the dish a large broad weighing bottle, of ordinary form, holding somewhat more than 100 c.c. The vessel being closed after dryness is obtained, the weighing may be done at leisure. Results are more satisfactory, but great difficulty is found in afterwards removing the stopper of the bottle, owing to the high temperature at which it was closed. To overcome this objection, I have had bottles made with a small stop-cock in place of the usual handle on the cover, and am thus able to control the inside pressure. Such bottles may be obtained of Eimer and Amend, New York.—*The Journal of Analytical Chemistry*, January, 1890.

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.

Schäffer's Betanaphthol - betasulphonic Acid—As no answer has appeared to the query in the issue for March 14th, as to the mode of preparing this substance, I may quote the following passages from "Commercial Organic Analysis," vol. iii., p. 194:—"When betanaphthol is heated with twice its weight of strong sulphuric acid (sp. gr. 1.845) to about 90° C., until completely sulphonated, the chief product is a monosulphonic acid, known as 'Schäffer's acid.' When betanaphthol is added gradually to twice its weight of strong sulphuric acid (sp. gr. 1.845), taking care that the temperature does not rise above 50° to 60° C., Schäffer's acid, and an isomeric acid, betanaphthol-alphasulphonic acid, often known as Bayer's acid, are formed in about equal quantity. The use of a temperature of 20° C. for preparing Bayer's acid has been patented. Schäffer's and Bayer's acids may be separated by converting them into sodium salts and treating the dry product with alcohol, in which liquid the salt of betanaphthol-alphasulphonic is by far the most readily soluble. Another method of separating Bayer's acid from Schäffer's and another isomeric acid said to be present, is based on the different facility with which the three acids act on certain azo-compounds. Thus, by treating the alkaline solution of the mixed sulphonic acids with a properly regulated quantity of tetra-azo-diphenyl, the unnamed acid and Schäffer's acid are precipitated as claret-coloured dyes, while Bayer's acid remains in solution in the requisite purity for the manufacture of crocein scarlet, for which purpose the isomeric acids are not available. A naphthol-sulphonic acid distinct from, and giving shades redder than either of the above acids, is said to be obtainable by a process described in patent No. 15,781, of 1885." The sulphonic acids of alphanaphthol have been recently described by F. Bender (*Ber.*, xxii., 993).—ALFRED H. ALLEN.

ERRATUM.—P. 169, in the paragraph headed "Filtering-Paper from Grycksbo, Sweden," for "The acid and the water extract from this paper," &c., read "The acid and the water extract nothing from this paper," &c.

MEETINGS FOR THE WEEK.

- MONDAY 21st.—Medical, 8.30.
— Society of Chemical Industry, 8. "On the Expulsion of Ammoniacal Compounds from Sulphuric Acid used in Kjeldahl Determinations," by Dr. Moritz. "The Petroleum Fields of India," by Boretton Redwood.
- TUESDAY, 22nd.—Society of Arts, 5. "The Danube and its Trade," by Sir John Stokes, K.C.B.
— Royal Institution, 3. "The Place of Oxford University in English History," by The Hon. George C. Brodrick, D.C.L.
— Royal Medical and Chirurgical, 8.30.
— Institute of Civil Engineers, 8.
- WEDNESDAY, 23rd.—Society of Arts, 8. "Coal in the South-East of England," by William Whitaker, F.R.S.
- THURSDAY, 24th.—Royal Institution, 3. "The Heat of the Moon and Stars" (the Tyndall Lectures), by Prof. C. V. Boys, A.R.S.M., F.R.S.
— Royal, 4.30.
— Institute of Electrical Engineers, 8.
- FRIDAY, 25th.—Royal Institution, 9. "The Shape of Leaves and Cotyledons," by Sir John Lubbock, D.C.L., F.R.S.
— Quekett Club, 8.
- SATURDAY, 26th.—Royal Institution, 3. "Colour and its Chemical Action," by Captain W. de W. Abney, F.R.S., &c.

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THE LONDON HOSPITAL MEDICAL COLLEGE. The SUMMER SESSION will COMMENCE on THURSDAY, May 1st.

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N.B. Special arrangements have been made to meet the requirements of the Examining Board in England so as to enable Students entering in May to pass Part I. (Chemistry and Chemical Physics), and Part II. (Materia Medica and Pharmacy) of the First Examination in July.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1587.

ANALYTICAL TOUTS.

THE *City Leader* has lately been calling attention most emphatically to a scandal in the analytical profession. It appears that letters are being sent out to manufacturers, offering to submit their products to a careful analysis, and to embody the results in a "pithy and concise report," which, the recipient is told, "if printed on your circulars, labels, and show-cards," will be found "productive of excellent business results."

The issue of such letters by a person calling himself "F.C.S." our contemporary thinks scarcely in keeping with the dignity of a scientific body, and he is undoubtedly right.

But he asks further, in a later issue, whether the writer is really a Fellow of the Chemical Society or not, adding that "if he is, he should certainly take steps to have his name included in the list." He also expresses himself "somewhat surprised that the Chemical Society has not taken some notice of the matter." Here our contemporary is at fault. The silence of the Society is due, not to approval or indifference, but to want of powers. If Tom, Dick, or "Arry" thinks proper falsely to call himself a Fellow of the Chemical Society, there appears to be no remedy! The other chartered societies are in the same position. Hence it is suggested that they should join hands and endeavour to obtain the power to restrain any illicit assumption of their distinguishing titles.

The same bodies are also, it appears, in want of the power to eliminate any Fellow who acts in a manner calculated to bring the Society to which he belongs into contempt. A Fellow of the Chemical Society, indeed, on his reception, formally pledges himself to uphold the dignity of the Society. But it is very doubtful if this provision would enable the Council to get rid of an undesirable Fellow.

We must further point out that the Chemical Society, unlike the Institute of Chemistry, the Pharmaceutical Society, or the Royal College of Surgeons, &c., is not a professional organisation. This difference materially affects its powers of dealing with undesirable subjects. If any man calls himself, falsely, a member of the Pharmaceutical Society, the Courts make short work of him. But before bogus Fellows of any non-professional Society, such as the Royal, the Linnean, the Chemical, or the Geological, can be made to lay aside their borrowed plumes the law will have to be altered.

Dr. H. E. Armstrong, F.R.S., and Mr. J. M. Thomson, F.R.S.E., the Secretaries of the Chemical Society, have both written to the editor of the *City Leader*, assuring him that the person referred to in the articles of March 29 and April 12 is not a Fellow of the Chemical Society. An official letter has also been sent to the individual in question, informing him that, not being a Fellow of the Society, he is not justified in appending to his name the letters F.C.S. This caution, it is important to note, was given prior to the date of his circular quoted in the *City Leader*. Hence he can scarcely be supposed to have assumed the title in mistake.

As he declares himself to be also a Fellow of the German Chemical Society, it might be well to address an inquiry to the Secretary of that distinguished body at 35, Georgenstrasse, Berlin, N.W.

Preparation of Litmus-Paper.—E. Utescher (*Apotheker Zeit. per Chem. Industrie*) recommends hydrochloric acid instead of phosphoric acid.

VOLUMETRIC DETERMINATION OF TANNIN.

By E. GUENEZ.

THE process of Löwenthal, modified by Neubauer, the most important of the volumetric methods, is applicable only in certain cases. It is founded upon the oxidation of tannin by permanganate, and it can be accurate only if applied to a solution of pure tannin. The presence of organic matters which accompany tannin in industrial extracts becomes a grave source of error.

The author finds a rapid process for the determination of tannin upon the following reactions:—

1. If into a boiling solution of potassium-antimony tartrate, mixed with a suitable aniline colour, there is poured a solution of tannin, there is formed a precipitate of antimony tartrate, which carries down the colouring-matter, forming a true lake. If the proportion of tannin is sufficient, the supernatant liquid becomes colourless. The antimony salt must be in excess in reference to the colouring-matter.

2. The volume of the coloured solution of the antimony salt, and the volume of the solution of tannin which must be added, are always proportional. Dilution does not affect the results.

3. A given quantity of antimony tannate always fixes the same quantity of colouring-matter.

4. If a solution of gallic acid is poured into a boiling solution of the antimony salt, no immediate precipitate of antimony gallate is formed. Under the same conditions, the antimony tannate is produced immediately. Hence it is permissible to suppose that the presence of gallic acid does not interfere.

The method of operating is as follows:—

A solution is prepared of—

Antimony salt	12 grms.
Poirier's green, 4JE	1 gm.
Distilled water	1 litre

The antimony salt and the colouring-matter are dissolved separately; the two solutions are then mixed and filtered. The aniline greens are the only colours suitable, and Poirier's green, 4JE, has given excellent results. This solution is standardised by means of a solution of tannin in ether, perfectly pure and dried previously in a vacuum over sulphuric acid. A solution is made up containing 5 to 6 grms. per litre, and there is added a small quantity of thymol, dissolved in alcohol to prevent mouldiness.

A burette, fitted with a glass cock, is filled with a solution of tannin, and, on the other hand, 20 c.c. of the coloured solution of antimony salt and an equal volume of distilled water are put in a glass tube 35 c.m. in diameter. The coloured solution is raised to a boil, and the tannin liquid is run in, at first by c.c., and afterwards by drops, until the complete decolouration of the liquid, which must be boiled anew after each addition of tannin. There is formed a green flocculent precipitate, which readily collects together, and enables the decolouration of the liquid to be observed. When complete, the volume of the tannin consumed is read off on the burette, and the standard of the antimony solution is thus known.

This method is readily applicable to the analysis of industrial extracts, but as the tannins of these extracts are not identical with the tannins of gall-nuts, which has been selected as a standard, the richness of an extract will be represented in the analysis by an equivalent weight of nut-gall tannin.

This is the case with all volumetric processes, when it is not possible to titrate the liquid with the same kind of tannin which has to be determined. The process of Muntz may be utilised to find the agreement between the gravimetric and the volumetric determination. The process is not vitiated by the presence of gallic acid, but it is not applicable to the determination of tannin in wines.—*Comptes Rendus*, cx., p. 532.

EXAMINATION OF CORPSES FOR ALKALOIDS
AND OTHER NITROGENOUS BASES.

By Dr. ANTON SEYDA.

(Continued from p. 185).

IV. Examination for Metallic Poisons.

For this purpose we use either the matter remaining after extraction with alcohol or the residue from distillation. In the former case the residual alcohol present must be removed by heat; the residue is then stirred up with hot water and potassium chlorate in a porcelain capsule, and chlorinised by the fractional addition of hydrochloric acid until the organic tissue is totally destroyed and all the potassium chlorate is decomposed. The uniform paste thus obtained is heated until all chlorine is driven off, during which any excessive concentration of the hydrochloric solution is obviated by the repeated addition of water as it evaporates. Jeserich's suggestion for the use of chloric acid cannot be acted upon, as the author has never been able to procure it free from arsenic, even 50 c.c. yielding a distinct arsenical mirror.

The thin paste is then placed entirely in a beaker, mixed with tartaric acid to dissolve all the antimony present, strongly diluted with water, and set aside for twenty-four hours.

A. Examination of the Portion Insoluble in
Hydrochloric Acid.

The undissolved residue is filtered off and washed until the washings run through colourless. If the residue is large it should be once more submitted to treatment with potassium chlorate and hydrochloric acid, and dehydrated with alcohol, which is again expelled by ether. For the better extraction of the fat the precipitate is taken from the filter, placed in a beaker, and digested with ether until a fresh portion of the solvent remains colourless. The residue, after the removal of the fat, is then incinerated in a porcelain crucible. The ash is extracted with water containing hydrochloric acid (since it may contain alkaline and earthy-alkaline phosphates and carbonates), and the residue, after being well washed upon a filter free from ash, must be ignited together with the filter in a tared porcelain crucible and weighed when cold.

If the residue does not consist of quartz-sand (fine or coarse) it must be opened up by fusion in a platinum crucible with sodium carbonate (free from alumina and silica). When cold the melt is lixiviated and the lye is let stand in a beaker until clear. Any sediment is filtered off, dissolved in nitric acid, and the solution tested with ammonia, hydrochloric acid (silver), sulphuric acid (lead, barium, strontium), and sulphuretted hydrogen. The filtrate is acidified with hydrochloric acid and evaporated to dryness; the residue dried at 110°, moistened with hydrochloric acid, and taken up in water. Insoluble flocks consist of silica; the solution is tested for sulphuric acid and alumina. In most cases the portion insoluble in chlorine or hydrochloric acid consists of sand, silica, or aluminium silicate. In a notorious case of poisoning with barium chloride, the author found in the residue 0.158 gm. barium sulphate. It occurred only in the contents of one vessel in which had been placed the large abdominal glands, parts of the heart and of the lungs, weighing in all 719 grms. In the lot containing the stomach, the œsophagus, and the duodenum, no barium was present. As it appeared from the evidence, the bulk of the barium chloride had been already expelled by means of Glauber's salts. The barium could neither be extracted from the organs of the corpse by digestion with water nor in hydrochloric acid, consequently it must have been already converted into sulphate in the system.

B. Examination of the Portion Soluble in
Hydrochloric Acid.

The brownish filtrate, freed from chloric acid and chlorine and mixed with the washing-waters, is measured or made up to a known volume (300—500 c.c.). For the process to be followed, the absolute absence of chlorine and chloric acid is essential, a point which must be ascertained by well-known check-reactions with zinc iodide starch paste, or sulphindigotic acid and sodium sulphite. First comes the—

a. Examination for Mercury, Antimony, and Arsenic.

a. Detection and Determination of Mercury. — (The qualitative process is a modification of that of Ludwig and Fürhinger). 50 to 100 c.c. of the liquid are placed in a porcelain dish and neutralised with potassa-lye until the reaction is faintly acid. It is then digested on the water-bath at about 70° for fifteen minutes along with a little bright brass wool. The latter is then taken out, rinsed with water, alcohol, and ether, dried in the exsiccator, and introduced into a tube of sparingly fusible glass charged with granulated copper oxide and drawn out into a narrow end with two prominences. The tube is laid in a combustion furnace, the one end is connected with a Woulff's bottle containing strong sulphuric acid, whilst the capillary end is joined to an aspirator. The copper oxide is first heated, then (whilst a slow current of air is drawn through) that part of the tube where the brass-wool lies is gradually heated and finally raised to redness. After half an hour the heating is stopped, the tube, whilst still hot, is fractured at its point of contraction by means of a drop of water, and the capillary is examined with the naked eye, or with a lens for a mercurial ring. Then, whether mercury globules have been detected or not, a small fragment of iodine is introduced into the capillary at its fractured end, and a current of air or of iodine vapour is drawn through with the application of heat. If the smallest quantity of mercury is present, there appears at the spot a red coating of mercuric iodide, which, on heating, turns yellow and resumes its scarlet colour on cooling.

(To be continued).

NOTE ON A DECA-HYDRATED ACETATE OF
LEAD.

By A. E. FASNACHT and C. R. LINDSEY, B.Sc.

DURING the winter of 1888-9 we found on two occasions crystals that, from their mode of occurrence, were at first thought to be a basic acetate of lead, but which proved on examination to be the normal salt, but crystallised with ten equivalents of water instead of with three. The best crystals were formed on some bristles from a sweeping brush, and were about half an inch long, complete in all their forms; but most of them were implanted by one end. At first they were colourless and transparent, but gradually became opaque, passing ultimately into a milk-white. An analysis shewed—

Pb	40.60	
C ₂ H ₃ O ₂	23.19	by phosphoric acid distillation.
H ₂ O	36.21	by difference.
	100.00	

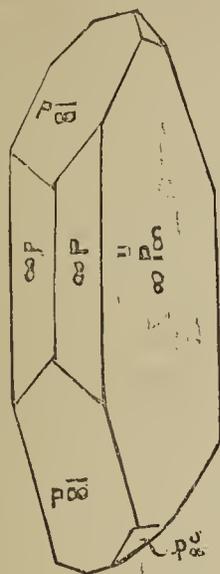
While the calculated percentage of Pb(C₂H₃O₂)₂ + 10H₂O gives—

Pb	40.98
C ₂ H ₃ O ₂	23.37
H ₂ O	35.65
	100.00

The slight difference is no doubt due to the crystals not being perfectly dry; 40.60 of Pb as found requires, ac-

ording to calculation, 23.15 of C₂H₃O₂, which agrees very closely.

The specific gravity as determined in petroleum is 1.689, and the melting-point 72° F. This very low melting-point prevented exact determinations of the crystalline form, as the crystals could not be handled without seriously affecting the reflections from their faces. The comparison of a considerable number of measurements, executed as carefully as possible, appears to leave no doubt that the crystals are rhombic, of the form shown in the figure, in which—



$\infty P = 110^\circ$.

$P_{\infty} = 75$ (over summit).

$\infty P_{\infty}^U : P_{\infty} = 90^\circ$.

These are the most accurately measurable, and are certainly correct within a few minutes.

$P_{\infty}^U = 95^\circ 20'$ (over summit).

$\infty P_{\infty}^U : P_{\infty}^U = 132^\circ 20'$.

$\infty P : P_{\infty} = 130^\circ 20'$ (calculated $130^\circ 28'$).

$\infty P_{\infty}^U : \infty P = 125^\circ$.

These give an axial ratio of—

brachy : macro : prin. = 0.7002 : 1 : 0.9125.

The ordinary crystals with three of water are monoclinic.

Clayton, Manchester,
March 28, 1890.

THE SPONTANEOUS IGNITION OF COAL CARGOES.*

By Professor VIVIAN B. LEWES,

Associate of the Institution of Naval Architects, F.C.S., F.I.C.

(Concluded from p. 188).

(7) RISE in temperature in steam colliers due to the introduction of triple expansion engines and high-pressure boilers.

It has been fully pointed out that anything which tends to increase of initial temperature increases the rapidity of chemical action. Steam at 80 lbs. boiler pressure has a temperature of 324° F. (162° C.), and a common stokehold temperature with boilers worked at this pressure is 100° to 130° F. (or 38° to 54° C.). Steam at a boiler pressure of 155 lbs. has a temperature of 368° F., or 186° C., and gives a corresponding increase of temperature in the

* Read at the Thirty-first Session of the Institution of Naval Architects, March 28, 1890; the Earl of Ravensworth in the Chair.

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Crocodile (original simple low-pressure engines).

Locality.	Date.	Deck.	Coal bunkers.	Engine room.	Stokehold.
1874.					
Channel and Bay	Jan. 15	52	72	98	90
" "	" 18	58	80	99	92
Mediterranean ..	" 23	65	86	98	92
" " "	" 27	66	84	190	92
Red Sea	Feb. 6	68	92	108	106
"	" 10	81	100*	114	110
1875.					
Channel and Bay	Feb. 11	46	66	90	105
" "	" 12	54	70	94	102
Mediterranean ..	" 19	53	74	92	89
" " "	" 26	66	74	98	104
Red Sea	Mar. 4	77	90	104	115
"	" 6	82	94	98	120
Indian Ocean ..	" 12	79	98*	104	114

Malabar (old compound engines).

1885.					
Channel and Bay	Oct. 3	59	85	82	89
" "	" 6	63	86	86	110
Mediterranean ..	" 8	72	90	98	94
" " "	" 9	73	90	96	100
" " "	" 10	70	90	90	110
Red Sea	" 19	81	92	95	107
"	" 20	84	100	96	108
"	" 21	88	104*	104	119
"	" 23	87	102	97	112

Crocodile (compound engines).

1888.					
Channel and Bay	Dec. 4	55	78	78	90
" "	" 6	54	85	80	84
" "	" 8	60	92	82	88
Mediterranean ..	" 12	64	97	80	100
" " "	" 15	60	95	78	90
" " "	" 17	62	112	83	94
Red Sea	" 22	74	113	92	100
"	" 23	80	115	96	103
"	" 24	82	116*	98	110
Indian Ocean ..	" 31	78	99	97	118

Malabar (new triple engines).

1888.					
Channel and Bay	Dec. 13	49	77	78	72
" "	" 14	56	86	86	88
" "	" 16	62	80	84	90
Mediterranean ..	" 18	63	88	90	94
" " "	" 19	62	88	90	94
" " "	" 22	68	87	90	100
" " "	" 23	74	89	90	98
Red Sea	" 28	79	96	102	110
"	" 29	82	100	100	110
"	" 30	84	105*	100	108
"	" 31	83	104	104	110

1889.					
Channel and Bay	Oct. 5	65	84	86	94
" "	" 7	67	84	90	102
Mediterranean ..	" 10	76	100	92	102
" " "	" 11	80	100	93	99
" " "	" 15	79	104	96	100
" " "	" 16	80	106	96	106
Red Sea	" 19	83	106	103	102
"	" 20	86	110	102	110
"	" 21	89	115	108	108
"	" 22	92	120*	112	122

NOTE.—The Registers of the original engines of *Malabar* are destroyed; temperature records of *Crocodile* are given in lieu, for a period when she was fitted with old low-pressure engines.

* Maximum temperature during voyages from Portsmouth to Bombay.

stokehold and other adjacent portions of the vessel, the temperature in the stokehold under these conditions being from 110° F. (43.5° C.) to 140° F. (60°), and increase of about 10° F.

It is, however, difficult in the mercantile marine to get a direct comparison of the increase in temperature due to this cause, but in the service, some of the troopships have been from time to time refitted, and in the case of the *Malabar* and *Crocodile*, the temperatures existing with the old simple low-pressure engines, the old compound engines, and the new triple expansion engines can be contrasted, and will be found in the accompanying Table, for which I am indebted to Mr. White.

From this it will be seen that, taking the voyage throughout, the average increase of temperature in the stokehold from the use of the triple expansion engines is about 5 degrees. This table is of great interest, as the temperatures taken during the outward voyage of the *Crocodile*, December, 1883, point to the coals in the bunkers commencing to heat, and also illustrate where and at what temperature it commenced.

Crossing the Bay, the stokehold and bunker temperatures agree fairly well, but entering the Mediterranean, the stokehold having become heated to 100° F. on the 12th, action commenced in the bunkers, and this rapidly raised their temperature higher than that of the stokehold, the action, however, not being violent, and the bunker temperature rapidly falling below that of the stokehold as the chemical action died away.

Having now discussed the chemical and physical conditions which lead to the phenomenon known as "spontaneous ignition," we can formulate precautions which will tend to prevent such disasters.

1. *The Choice of Coal for Shipment to Distant Ports.*

The coal should be as large as possible, free from dust, and with as little "smalls" as can be helped.

It is better as free from pyrites as possible, in order to prevent disintegration after shipment, and it should contain when air-dried not more than 3 per cent of moisture.

2. *Precautions to be Taken during Shipment.*

No coal should be shipped to distant ports until at least a month has elapsed since it was brought to the surface at the pit's mouth. Every precaution should be taken to prevent breaking up of the coal whilst being taken on board, and on no account must any accumulation of fine coal be allowed under the hatchways.

When possible the coal should be shipped dry, as external wet, by producing oxidation of the pyrites, causes disintegration.

3. *Precautions to be Taken on Board Coal-laden Ships.*

This phase of the question is undoubtedly the most important, and in order to ensure any successful treatment of the coal cargo at sea to prevent undue heating and ignition, the means adopted must be as nearly automatic in their working as possible, as it is useless to expect the master or any officer on board a collier during rough weather, &c., to comply with any instructions, such as daily taking the temperatures in various parts of the cargo, and so on.

The coal compartments should be made gas-tight, as far as the bulkheads separating them from the rest of the ship is concerned; and as no difficulty is found in doing this when provision for forced draught is being made, no difficulty should be found in this case.

When the coal has all been taken in, it should be battened down, and the hatches should not be again opened until the vessel reaches her destination, the only ventilation allowable being a 2-inch pipe just inserted into the crown of each coal compartment, and led 12 feet up the nearest mast, the top being left open. This would be quite sufficient to allow free egress to any gases evolved by the coals, but would not allow undue access of air.

Into the body of the coal cargo itself would be screwed, at regular intervals of about 6 feet, iron pipes, closed at the bottom, and containing alarm thermometers, constructed in the following way:—A long bulb of glass, containing mercury, has an insulated wire inserted into the quick-silver, and making contact with it, whilst the stem attached to the bulb has a second wire in it, so arranged that when a rise of temperature causes expansion of the mercury, in rising in the tube it makes contact, and the wires from these tubes are in connection with an electric bell, index board, and battery in the captain's room, so that the moment the temperature is reached to which the thermometers have been set, the bell rings, and will continue to ring until the temperature again sinks, the spot in which the heating is taking place being indicated by the index board.

In the evidence given before the Commissioners in 1875, Mr. J. Glover strongly advocated the use of carbon dioxide, or carbonic acid gas as it is more usually termed, for extinguishing ignition when it has broken out in a coal cargo, and for stopping heating when it has reached a dangerous pitch. His proposal was to generate the gas by the action of hydrochloric acid upon chalk, and to lead it by gas pipes to the compartment affected, and this gas, being heavier than air and a non-supporter of combustion, was to displace the air and its contained oxygen, and so to prevent further action by surrounding the coal with an atmosphere which could not carry on combustion. The idea was a good one, but there were many difficulties in the way of carrying it out, one being that for every thousand tons of coal carried, 80 cwt. of hydrochloric acid would have had to be shipped, also the gas could not have been driven down into the hold if any serious heating had taken place, as an up current would have been formed and would have carried it away, whilst in this state of gas it fails to give any great cooling effect, and so would have exercised but little influence upon the mass of red hot fuel. These objections weighed so strongly with the Commissioners that in their final Report we find the following sentences:—

"Several methods for generating carbonic acid gas and applying it to the ignited portion of a coal cargo have been proposed for our consideration. We consider, however, that although this gas might be useful by excluding atmospheric air (which is essential to support combustion), yet it will not, as water does, exert any very sensible cooling effect, which is a point of vital importance in the case of a mass of ignited coal. We are of opinion that water and steam are the only agents practically available for the purpose of extinguishing fire in coal cargoes."

Applied in the way which was suggested there is no doubt but that the carbonic acid gas would have been practically useless; but there is another way in which it could be used, which would make it a most powerful cooling agent, an instantaneous quencher of fire, and would prevent any further tendency to heat on the part of the coal treated with it.

If carbonic acid gas is compressed under a pressure of 36 atmospheres at a temperature of 32° F. (0° C.), it is condensed to the liquid state, and can be obtained in steel vessels closed with screw valves. On opening the valve some of the liquid is ejected into the air, and on coming into the ordinary atmospheric pressure, is in a moment converted into a large volume of gas. Conversion from the liquid to the gaseous state means the absorption of a large amount of heat, and so great is this that everything near the stream of new-born gas is cooled down, and some of the escaping liquid is frozen to a solid, having a temperature of -78° C., or -108.4° F.

This liquid carbonic acid gas is now extensively manufactured, and is used abroad to a large extent for aerating waters, driving torpedoes, and for freezing machines; and I should suggest its use in the following way for the checking of ignition in the coal cargo:—

The nozzle attached to the screw-valve on the bottle of condensed gas would have a short metal nose-piece

screwed on to it, the tube in which would be cast in solid, with an alloy of tin, lead, bismuth, and cadmium, which can be so made as to melt at exactly 200° F. (93° C.). The valve would then be opened, and the steel bottle buried in the coal during the process of loading. The temperature at which the fusible metal plug will melt is well above the temperature which could be reached by any legitimate cause, and would mean that active heating was going on in the coal; and under these conditions the pressure in the steel cylinder would have reached something like 1700 lbs., and the moment the plug melted the whole contents of the bottle would be blown out of it into the surrounding coal, producing a large zone of intense cold, and cooling the whole of the surrounding mass to a comparatively low temperature. The action, moreover, would not stop here, as the cold, heavy gas would remain for some time in contact with the coal, diffusion taking place but slowly through the small exit pipe.

When coal has absorbed as much oxygen as it can, it still retains the power of absorbing a considerable volume of carbonic acid gas; and when coal has heated, and then been rapidly quenched, the amount of gas so absorbed is very large indeed, and the inert gas so taken up remains in the pores of the coal, and prevents any further tendency to heating; indeed, a coal which has once heated, if only to a slight degree, and has then cooled down, is perfectly harmless, and will not heat a second time. It is not by any means necessary to replace the whole of the air in the interstices of the coal with the gas, as a long series of experiments show that 60 per cent of carbonic acid gas prevents the ignition of the most pyrophoric substances.

One hundred cubic feet of gas can be condensed in the liquid state in a steel cylinder 1 foot long and three inches diameter, and it has been shown that a ton of coal contains air spaces equal to about 12 cubic feet; therefore, one of these cylinders would have to be put in for every 8 tons of coal, and these would be distributed evenly throughout the cargo, and near the alarm thermometers, which would be set to ring a degree or two below the point at which the fusible plug would melt.

The bell ringing in the captain's room would warn him that heating was taking place, and the bell would continue to ring until the cylinder had discharged its contents, and had cooled down to a safe degree, so that the whole arrangement would be purely automatic, and yet the officers would know if everything was safe.

This liquid is now being made at a comparatively cheap rate, and with any demand for its machinery could be put up at the principal coaling ports to charge empty cylinders at a very low rate, so that the initial cost of the steel cylinders once got over the expenses would not be worth considering, more especially as one, or two at most, would be likely to go off.

If the precautions advocated were taken no danger could arise until the arrival of the ship at her destination, and the commonest precautions would then suffice. On removing the hatches, no naked light must be allowed near them, and no one must be allowed to descend into the hold until all the gases have had time to diffuse out into air. If the cylinders have gone off there will be but little fear of explosion, as a high percentage of the carbonic acid gas lowers the explosive power which the mixture of marsh gas (given off from some coals) and air possess; but the carbonic acid gas would overcome and suffocate a man descending into an atmosphere containing any considerable percentage of it. When a safety lamp, lowered into the hold, continues to burn as brightly as it did in the open air, then it is perfectly safe to descend.

When once coal in a cargo has fired, pumping in water is of practically no use, as the fire is, as a rule, near the bottom of the mass of coal, and the flow of the water is so impeded, that in percolating through the interstices of the heated coal, it is converted into steam before it can reach the seat of combustion. The most effective way to apply

water would be to have four 3-inch pipes laid along the floor of the coal compartments, about 6 feet apart, these tubes having a $\frac{1}{4}$ -inch hole bored in the upper side every foot or so, and each pair of pipes coming through the bulkhead, and connecting on to two 6-inch pipes passing through the side of the vessel, the sea water being prevented from entering by means of screw valves. As soon as the alarm thermometer gave notice that heating had reached a dangerous point, these valves could be opened and the lower portion of the cargo drenched with salt water. This, evaporating rapidly, would give large volumes of water vapour, which, passing up through the heated coal, would lower its temperature, but would not be nearly as effective as the method before advocated. It might, however, be used in conjunction with that method, and would, in many cases, save the carbonic acid gas.

The question of preventing the heating and ignition of stores of coal on land and ready for use in bunkers, cannot be met so well by the use of the liquid gas, and, in these cases, it would be found beneficial to dress the coals with a little tar or tar oil, which would close the pores, and to a great extent prevent oxidation. I believe this was advocated by Lachman about 1870.

Crude petroleum in small quantities for this purpose would also be found valuable, for, as already shown, it has no tendency to oxidise itself, and lowers the tendency in other bodies, besides coating them, and so preventing access of oxygen.

The labour trouble in the coal trade is hampering all branches of industry, and, with increasing difficulty in obtaining coal, all sorts of rubbish will be shipped, and many a cargo of coal will go out during the next few months which, under normal conditions, would never have been allowed on board: and we may expect a heavy increase in the loss of life and property from spontaneous ignition. This will probably result in a rise in the rate of premium, and further check to our export coal trade; and I sincerely trust that, should these gloomy forebodings be fulfilled, the suggestions made in this paper, and based on experimental facts, may be found of value.

In conclusion, I wish to acknowledge my indebtedness to the researches of Dr. Richters, whose papers on the weathering of coal are to be found in Dingler's *Polytechnisches Journal* for 1870; to the Report of the Royal Commissioners on this question in 1876; and, finally, to Mr. Martell for suggesting the subject of this paper.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, April 5th, 1890.

SIR,—We submit herewith the results of our analyses of the 177 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

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

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

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

The whole of the 177 samples examined were found to be clear, bright, and well filtered.

Throughout the month of March the condition of the water furnished to the Metropolis by the Companies taking their supply from the Thames and the Lea has continued to be unexceptionable. The mean proportion of organic carbon present in the Thames-derived samples having been found to be 0.154 part in 100,000 parts of the water, as against a mean of 0.160 part in the previous month's supply.

During the first three months of the year we have examined a total of 534 samples. With the exception of two of the February samples recorded as being "very slightly turbid," the whole were found to be clear, bright, and well filtered. As regards the Thames-derived water, the maximum proportion of organic carbon present in any single sample examined was 0.174 part in 100,000 parts of the water, the mean proportion for the three months being 0.150 part, an exceptionally low result for the first quarter of the year, in which the mean is habitually liable to elevation by reason chiefly of the occurrence of more or less heavy floods, often, indeed, of a succession of floods. It is to be noted, however, that of late years the influence of a flooded state of the rivers upon the character of the water supply is appreciably less than it used to be formerly.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

April 3, 1890.

Dr. HUGO MÜLLER, F.R.S., Vice-President, in the Chair.

Certificates were read for the first time in favour of Messrs. James Robert Appleyard, University College, Dundee; William Henry Blake, 31, Norfolk Street, Sunderland; George Caird, 20, Springfield, Dundee; S. Sydney Monckton Copeman, M.A., M.B., Cantab., 134, York Road, S.E.; Andrew Fairgreve, Sydney, New South Wales; G. H. Findlay, Hawthorn Cottage, Francis Road, Edgbaston, Birmingham; George German, junior, Huntingdon House, Ashby de-la-Zouch; John Archyll Jones, 3, Jedburgh Street, Middlesbrough; Oliver Kirk, Science Schools, South Kensington; Robert Waller Oddy, Waterhouse, Toad Lane, Rochdale.

The following papers were read:—

24. "Note on the Hydrosulphides." By S. E. LINDER and HAROLD PICTON.

The authors find that freshly precipitated metallic sulphides almost always contain hydrogen sulphide; that they are, in fact, hydrosulphides, or the remnants of hydrosulphides; and that if, instead of adopting the usual plan of passing gas through the solution, the metallic salt be allowed to run slowly into a solution of hydrogen sulphide in water in absence of too large an excess of acid, a solution is obtained which can in most cases be freed from dissolved hydrogen sulphide by a current of hydrogen, although this to some extent depends on the character of the acid liberated from the salt. The solu-

tions so obtained are readily precipitated by the addition of metallic salts, a fact long made use of in washing a sulphide such as that of tin, in which case the addition of sodium chloride to the water is always advised.

A large number of experiments on the formation and properties of the metallic hydrosulphides have been made, and, although the work is not yet completed, it is thought to be desirable to indicate generally, and with the aid of two typical examples, the character of the results obtained.

To prepare the higher hydrosulphides, it is found to be necessary to avoid the presence of acid. An unexpected method of accomplishing this has presented itself in certain cases—in that of mercury, for example. If carefully washed mercuric sulphide be treated with hydrogen sulphide and water, it dissolves to a clear brown solution from which uncombined hydrogen sulphide may be removed by a current of hydrogen. Another method which it is hoped will be generally applicable is the treatment of the metallic hydroxides with hydrogen sulphide. Precipitation with sodium hydrosulphide or ammonium hydrosulphide may be resorted to in some cases. By whatever method they are prepared, the hydrosulphides are probably in all cases compounds of high molecular weight. The effect of acids on their formation and constitution is of much interest, as these apparently cause a molecular condensation and increase of complexity, which becomes more marked as the acids become more powerful. Variation in temperature does not appear to exercise any important influence.

The sulphur in the hydrosulphide has been determined as sulphate after oxidation with chlorine, great care having been taken to avoid the precipitation of sulphur during the formation of the sulphide; to make assurance on this matter doubly sure, the authors have in some cases heated the carefully washed sulphate in a current of hydrogen freed from every trace of hydrogen sulphide, the hydrogen sulphide lost on heating being absorbed by potash and oxidised. This method is of special importance as affording confirmation when the combined hydrogen sulphide, as in the case of mercury, is very small in amount.

Copper.—On treating copper hydrate suspended in water with hydrogen sulphide, the hydrosulphide $7\text{CuS}\cdot\text{H}_2\text{S}$ is rapidly formed, and if left for some days in a tightly stoppered vessel, dissolves to a clear brown solution. The effect is the same whether time be given for the solution to form or not. Three results differing from the mean by only about 0.07 in the percentage of sulphur gave as a mean 36.69 per cent of sulphur, the amount calculated for $7\text{CuS}\cdot\text{H}_2\text{S}$ being 36.59 per cent.

In order to prevent the liberation of sulphuric acid during the interaction, sodic acetate was added to the copper sulphate, and the solution formed by adding the mixture to water saturated with hydrogen sulphide was precipitated with ammoniac chloride: two molecular proportions of acetic acid were present for each molecular proportion of CuS . In this case the acetic acid acts in presence of excess of hydrogen sulphide, and has but little effect in breaking down the hydrosulphide. The percentage of sulphur found as 36.00; that calculated for $9\text{CuS}\cdot\text{H}_2\text{S}$ is 35.96 per cent.

In two experiments in which some acetic acid was present at starting, a precipitate was gradually deposited, which was filtered off without adding salt; great difficulty was experienced in effecting filtration owing to the fine state of division of the sulphide. Slightly higher numbers were obtained, probably owing to the deposition of some sulphur, but they serve to indicate that the salt does not alter the composition of the precipitate; the percentages of sulphur found were (1) 36.13, (2) 36.28.

In another case, after adding sodic acetate, the excess of hydrogen sulphide was expelled from the solution of the hydrosulphide by hydrogen. The acetic acid was thus allowed to act upon the solution unsaturated with hydric sulphide. The percentage of sulphur found was

34.67 and 34.56; that calculated for $22\text{CuS}\cdot\text{H}_2\text{S}$ is 34.61.

In this case the excess of sulphur is very small, and it is impossible to assign a formula; it is noticeable that a great molecular condensation has taken place.

In presence of hydrogen chloride, still further loss of sulphuretted hydrogen occurs. All the filtrations were conducted in an atmosphere of hydrogen.

Mercury.—Solutions of two similar quantities of mercuric chloride were taken; after boiling to expel air, one was run into boiled water containing hydrogen sulphide placed in a Drechsel's bottle, access of air being prevented by a current of the gas: the mixture was precipitated by hydrogen chloride. The other, after dilution with boiled water, was made acid and precipitated by hydrogen sulphide. Both precipitates were washed with boiled water, then mixed with boiled water in a Drechsel bottle, and hydrogen sulphide was passed into the liquid till clear solutions were formed. A current of hydrogen was then passed through both (the one being cooled with ice) till they were free from hydrogen sulphide. The amount of barium sulphate obtained from A was 0.8910, from B 0.8916; the amount afforded by the same weight of mercuric sulphide is 0.86375. The mean percentage of sulphur found was 14.166; a compound of the formula $31\text{HgS}\cdot\text{H}_2\text{S}$ would contain 14.171 per cent.

In presence of hydrogen chloride a further molecular condensation takes place, the quantity of attached hydrogen sulphide becoming apparently halved; it is of course impossible to assign an exact formula to a product of so high a molecular weight, but the concordance of the results and its very remarkable stability would make it probable that the compound is a definite one. It withstood extraction with carbon disulphide, and the prolonged washing which this entailed. It did not lose its hydrogen sulphide *in vacuo*, and after drying *in vacuo* it required to be heated for about sixteen hours at 105° in a current of hydrogen before all the hydrogen sulphide was removed. The dryness of the hydrosulphide seems to greatly influence the rapidity with which it loses hydrogen sulphide.

25. "Researches on the Germination of Some of the Gramineæ." Part I. By HORACE T. BROWN, F.R.S., and G. HARRIS MORRIS, Ph.D.

This investigation was undertaken with the view of throwing some light upon the complex metabolic processes which take place during the germination of seeds. The authors, during the progress of the inquiry, have examined and experimented with the seeds of a great number of the grasses, but this, the first part of their paper, is confined almost entirely to a consideration of the changes which take place in *barley* during the early periods of its growth.

The paper is divided into 21 sections, the heads of which are as follows:—

(1). Introduction. (2). Structure of a grain of barley. (3). The visible changes which occur in the embryo and endosperm during germination. (4). The relation of the embryo to the endosperm. (5). Development of excised embryos upon foreign endosperms. (6). The endosperm to be regarded as a storehouse of *dead* reserve material; no residue of vitality recognisable in its cells. (7). Cultivation of excised embryos upon water. (8). Cultivation of excised embryos upon nutrient solutions. (9). Growth of excised embryos upon *starch*, and proof that an amylo-hydrolyst (diastase) is secreted by the growing embryo. (10). The secretion of diastase is localised in the "absorptive epithelium." (11). The secretion of diastase is increased by the presence of a small quantity of acid. (12). The secretion of diastase not stimulated by the presence of *starch*. (13). The secretion of diastase is inhibited by a readily assimilable carbohydrate. (14). The existence of a *cellulose-dissolving* enzyme (cyto-hydrolyst) in the germinating seeds of the grasses. (15). The cyto-hydrolyst, like diastase, is secreted by the "absorptive epithelium." (16). The two varieties of diastase, their genesis and distribution in the resting and germinating seed. (17). Distribution of diastase in the germinating

seed. (18). The "mother-substance" of the "diastase of secretion" is principally derived from the endosperm. (19). Action of "diastase of secretion" upon ungelatinised *starch*. (20). A consideration of the origin of the hydrolytic enzymes of germinated grain. (21). The form in which the reserve *starch* after transformation enters the growing embryo, and the metabolic changes which it there undergoes.

In recording the visible changes which occur in the seed during germination, it is shown that a disintegration and dissolution of the cell-walls of the endosperm always precede any attack upon the cell contents. This breaking down of the cell-wall is shown in a subsequent portion of the paper to depend on the production during germination of a special cellulose-dissolving, or "cyto-hydrolytic enzyme," which, like diastase, is soluble. The action of this enzyme on the cell-walls of some kind of vegetable parenchyma is very energetic. The physiological importance of this cyto-hydrolyst is very great, for, owing to the non-diffusible nature of the amylo-hydrolytic enzyme, diastase, the previous breaking down of the cell-wall is a necessary prelude to the dissolution of the contained *starch-granules*.

The authors show that the appearance of the cyto- and amylo-hydrolysts is due to a specialised secretory function of the layer of columnar epithelium which covers the outer surface of the scutellum. It has hitherto been considered that the function of this epithelium was exclusively that of an absorptive tissue: its absorptive as compared with its secretory functions are, however, of quite secondary importance.

The natural food material, *starch*, does not appear to have any special power of stimulating the cells of the epithelium to increased secretion of a diastase, but the flow both of diastase and of the cyto-hydrolytic enzyme from these cells is affected in a very remarkable manner by the presence of certain carbohydrates. Providing the carbohydrate is one which is readily assimilable by the embryo, such as cane-sugar or maltose, secretion of ferment is checked or even entirely inhibited. No such inhibitory action is, however, produced by such substances as mannitol and milk-sugar, which are entirely without nutritive value. The authors' experiments in this direction point to the secretion of the amylo-hydrolytic and cyto-hydrolytic enzymes as being to some extent *starvation phenomena*. The power of secretion possessed by the epithelium is in some way or other so adapted to the requirements of the young plants as to be only exercised when the supply of tissue-forming carbon compounds begins to fail.

The histological changes which take place in the cells of the epithelium during secretion are very similar to those which have been observed in certain secretory cells of the alimentary tract of animals, and in the secretory cells of some of the insectivorous plants.

The authors confirm the important generalisation of Sachs that the relation of the embryo to the endosperm is that of parasite to host, and they have availed themselves of this relation by cultivating the embryo upon suitable media after separating it from its endosperm, and in this way they have obtained information with regard to the secretory powers of the embryo, and the chemical modifications of its absorbed nutriment, which it would have been impossible to obtain by any other means.

The results of cultivating excised embryos upon various nutrient solutions, more especially of the carbohydrates, are recorded, and it is shown that whilst cane-sugar, invert-sugar, dextrose, lævulose, maltose, raffinose, galactose, and glycerol have all more or less nutritive value, milk-sugar and mannitol do not in any way contribute to the growth of tissue in the young plant. Of all substances tried, cane-sugar has by far the greatest nutritive power. Maltose, although the natural food of the embryo when attached to its endosperm, is decidedly inferior in this respect to cane-sugar. This, at a later point in the paper, is shown to be due to the fact that

maltose, directly it is absorbed by the growing embryo, becomes transformed into cane-sugar by the living cells, and in this form is passed from cell to cell. When cane-sugar is supplied ready formed to the young plantlet, there is manifestly a saving of energy to the living cell, which receives its nutriment in a form in which it is directly available for its requirements.

An examination of the sugars produced during the germination, and of their mode of distribution in the grain, have convinced the authors that the transformed starch of the endosperm is absorbed by the embryo in the form of maltose, and that the seat of production of the cane-sugar which germinated grain contains is the tissues of the embryo itself.

The authors are continuing their work upon the germination of the grasses, and are applying the methods described in this first part of their paper to an elucidation of the chemical changes which the other reserve materials, especially the proteids, undergo in their passage from the endosperm, and of the agencies which are at work in bringing about these transformations.

DISCUSSION.

Mr. THISELTON DYER said that chemists, perhaps, would hardly realise what delicacy of manipulation was required in carrying out experiments such as had been instituted by the authors of the paper; it was a fortunate circumstance that the morphology of the seed in grasses allows of an anatomical separation of the elements. Botanists had already made some progress in localising enzymes: thus Professor Marshall Ward had shown that the enzyme which effects the liberation of the colouring-matter from the glucoside in Persian berries is located in the raphe; and it had long been known that emulsin was not distributed throughout the bitter almond. After referring to the distinction between animals and plants, he said that the plant was similar to the seed, the bud corresponding to the embryo, and the woody shoot to the endosperm. Baranezky had shown that a diastase is omnipresent in plants; and there could be little doubt that it would be found that an enzyme capable of attacking cellulose was equally so.

Professor MARSHALL WARD pointed out that in the seeds of the *Gramineæ*, *Cyperaceæ*, and other families of plants there is a peculiar layer of cells, from one to three or more deep, surrounding the starchy endosperm, and distinguished from the latter by containing no starch but relatively large quantities of proteids: this layer belongs to the endosperm, but as the seed ripens the cells store special proteids instead of the starch-grains which predominate in the other endosperm cells. In the oat there is such a layer, one cell deep, and it has been shown that, during germination, the dissolution of the starch and the cell-walls of the starch-containing cells begins near the surface of this layer, which itself persists, and the cells of which take up food and undergo changes so like those of excreting cells that it was concluded that they excrete the diastatic enzyme. Haberlandt declares that when starch-grains are placed in contact with a piece of this layer kept moist and at proper temperatures, the grains even of the resistant potato-starch are corroded as on germination; whereas control experiments, where all conditions are the same, except the presence of the cells of the proteid layer, showed no such corrosion.

Professor Ward then remarked that the authors' suggestion that more than one enzyme may be excreted according to the nutrition of the cells, and their proof that a cellulose-dissolving enzyme exists in barley, is borne out by various recent researches and by Wortmann's observations on the behaviour of bacteria in a mixture of starch and proteids. Wortmann proved that so long as the bacteria were fed with proteids, they refused to excrete the diastatic enzyme which they produce in abundance when only carbohydrates are at their disposal.

The speaker concluded by drawing attention to several

other cases where such a proteid layer exists—*e.g.*, in the seeds of buckwheat and in the tubers of some potatoes—and remarked on the importance of clearing up this matter, and on the steps towards accomplishing that end attained by the excellent work of the authors of the present paper.

Professor GREEN said that in the case of the date stone his observations led him to believe that the enzyme was independent of the endosperm, and that probably it was located in the epithelial layer, but in castor oil seeds not only the embryo but also the endosperm cells appeared to be possessed of vitality, the fatty matter in the latter undergoing change even when not subject to the action of the embryo; probably the enzyme was present in the form of an enzymogen, as extracts of the seeds were rendered active by acids.

Dr. LAUDER BRUNTON said that it was highly remarkable that in a comparatively highly organised plant the conditions of the embryo was so very similar to that of the embryo in animals: the embryo in both cases appeared to be purely parasitic. In the mammalian embryo proteids are taken up from without, and it is generally assumed that they are assimilated without undergoing much change, but this was by no means certain. Referring to the presence in malt of an enzyme capable of affecting cellulose, he said there was a form of indigestion in which people could not digest cellulose: was it possible to separate the enzymene in question in large quantities?

Dr. ARMSTRONG remarked that many of the results brought forward were highly suggestive from a chemical point of view. The authors came to the conclusion that maltose, which on *a priori* grounds might be regarded as the natural nutriment of a plant, was inferior to cane-sugar, and that in the plant maltose was converted into cane-sugar. Dextrose, according to their observations, did not undergo conversion into cane-sugar, but it gave invert sugar; that is to say, it became partially converted into lævulose, but these constituents of cane-sugar were apparently incapable of interacting. It was known from Emil Fischer's experiments that dextrose could be converted into lævulose, and that maltose was an etheric compound of the acetyl type, formed from two molecules of dextrose, one of which acted as aldehyd, the other as alcohol; it was conceivable that if the "dextrose residue" in maltose underwent a change comparable with that which is involved in the conversion of dextrose into lævulose, a compound would be obtained which, if not identical with cane-sugar, would, perhaps, be easily convertible into cane-sugar by hydration and subsequent dehydration: it is scarcely probable that the keto-group—or its equivalent—of lævulose is preserved in cane-sugar, but if this group were to become $C(OH)_2$ and one of the hydroxyls were to be separated together with an atom of hydrogen of a hydroxyl-group in the other dextrose residue, a more stable etheric compound might result, the properties of which, probably, would be such as are characteristic of cane-sugar. The authors had spoken of the maltose becoming incorporated with the protoplasm, from which the cane-sugar was then elaborated; perhaps the effect was comparable with that exercised by phenylhydrazine in effecting the conversion of dextrose into lævulose through the agency of the osazone.

Dr. Armstrong then took exception to the terms amyolytic, proteolytic, &c., as applied to so-called ferments, pointing out that, whereas the terms electrolysis and hydrolysis implied splitting up *by means of* electricity and water, amyolytic was intended to suggest the splitting up of starch, proteolytic the splitting of proteids. He suggested several expressions less open to objection.

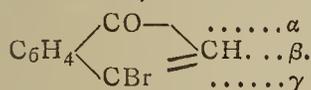
Mr. HERON, referring to the author's conclusion that maltose was not resolved into dextrose during germination, asked how, if this were the case, it was possible to account for the presence of dextrose in malt; he was of opinion that maize diastase did hydrolyse maltose.

Mr. HORACE BROWN said that although, as Mr.

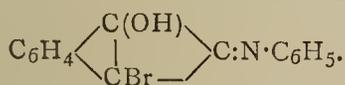
Thiselton Dyer had pointed out, diastase was ubiquitous in plants, that developed during germination appeared to differ in important particulars from ordinary diastase. He had been unsuccessful in isolating an enzyme capable of attacking cellulose from the date stone. Their experiments did not favour the conclusion that the cellulose layer had any marked diastatic power. He might point out that Professor Marshall Ward had been led to a conclusion similar to their own in the case of the cyto-hydrolytic enzyme which he had studied, viz., that its secretion was a starvation phenomenon. All their experiments to determine whether the enzyme existed in the endosperm as an enzymogen had been futile. In preparing the cyto-hydrolytic enzyme from malt, it was necessary to use air-dried malt, as it was destroyed by heating. In his experience there was no marked excess of dextrose in malt.

25. *The Formation of Indene-Derivatives from Dibrom-alphanaphthol.* By R. MELDOLA, F.R.S., and F. HUGHES.

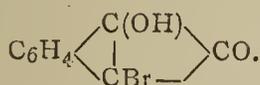
On adding dibrom- α -naphthol to strong nitric acid (1.42 sp. gr.), an oily liquid is first formed, which subsequently solidifies to a mass of crystals, probably consisting of an additive product. If cold fuming nitric acid be used (1.5 sp. gr.), the dibrom- α -naphthol at once dissolves without any evolution of gas, and on pouring the acid solution into water an ochreous precipitate is produced, which, when purified, forms small ochreous scales melting at 127–128°. The substance is regarded by the authors as γ -brom- α -indone,



This compound is converted by the action of aniline into an anilide crystallising in bright red scales melting at 190°. This anilide is acid in character, dissolving in hot aqueous or cold alcoholic soda with a violet colour. The authors consider the formula of the anilide to be—



By boiling with dilute alkali, the anilide is converted into the bromhydroxyindone,—



This latter forms dull orange needles melting at 191°. During the decomposition of the anilide, a strong odour of phenyl-isocyanide is evolved. The barium salt of the bromhydroxyindone forms orange needles of the formula $(\text{C}_9\text{H}_4\text{BrO}_2)_2\text{Ba}\cdot 7\text{H}_2\text{O}$. The aniline salt forms red scales melting at 169° and decomposing at 172°. Other derivatives of the brom-indone, viz., the benzylamide (m.p. 154°) and β -naphthylamide (m.p. about 151°) have been prepared. The authors propose to continue the investigation of these indene-derivatives.

27. *The Action of Chlorhydric Acid on Manganese Dioxide. Manganese Tetrachloride.* By H. M. VERNON.

In 1821, Forchammer showed that when the oxides of manganese, MnO_2 , Mn_2O_3 , and Mn_3O_4 , are dissolved in chlorhydric acid, a dark brown solution is formed, which affords a precipitate consisting of a mixture of oxides of manganese when added to a large quantity of water. W. W. Fisher (*Chem. Soc. Trans.*, 1878, 409) showed that this brown solution contained a higher chloride of manganese, probably the tetrachloride; but S. U. Pickering (*Chem. Soc. Trans.*, 1879, 654) subsequently contended that this higher chloride was Mn_2Cl_6 , his arguments being that when manganese dioxide is dissolved in chlorhydric acid and the solution is poured into water, the amount of dioxide in the precipitate is never more than about 47 per cent of the amount originally used. According to this observer, when the dioxide is dissolved in

chlorhydric acid, manganese sesquichloride is formed, two atomic proportions of chlorine being liberated; when, however, the dissolution of the dioxide is performed in the presence of manganous chloride, the amount of dioxide recovered on precipitation by water is largely increased, this increase being in a greater proportion up to the addition of one molecule of MnCl_2 , and, hence, it would seem to show that this chloride combines with the two atoms of chlorine set free on the dissolution of the dioxide in the acid to form another molecule of Mn_2Cl_6 .

In the present paper the author shows that when manganese dioxide is dissolved in chlorhydric acid, even at ordinary temperatures, of the total amount of chlorine which, on Pickering's supposition, should be evolved almost immediately, less than half is evolved, even in the course of five hours; at -18° chlorine is evolved much more slowly, and at -26° C. only 0.35 per cent of the available chlorine was found to be evolved when air was drawn through the solution during two hours. That this could not be due to the formation in the solution of a solid chlorine hydrate would appear to follow from the observation that no such substance was formed when pure chlorhydric acid was saturated with chlorine at -26° C. It must, therefore, be supposed that the original product of the action of chlorhydric acid on manganese dioxide is the tetrachloride, and that no chlorine is at first formed.

In order to ascertain whether, when the tetrachloride of manganese decomposes an intermediate chloride such as Mn_2Cl_6 is formed, weighed quantities of the dioxide were introduced into the bulb of a Victor Meyer's apparatus surrounded by a bath of water at temperatures varying from 38° C. to 63° C., and known volumes of chlorhydric acid were poured in; the volume of air expelled by the chlorine was measured at half-minute intervals. When the results thus obtained were represented in the form of curves, of which the ordinates represented the volumes of gas evolved and the abscissæ the time, it was found that the curves were perfectly regular; this could not be the case if an intermediate chloride such as Mn_2Cl_6 , more stable than the original tetrachloride, were formed in the solution. The curves expressing the rate of evolution of chlorine from solutions of Mn_2O_3 and Mn_3O_4 in chlorhydric acid were also perfectly regular, which shows that in the one case no chloride such as Mn_3Cl_8 intermediate between Mn_2Cl_6 and Mn_3Cl_8 was formed, and in the other case that no chloride such as $\text{Mn}_4\text{Cl}_{10}$, intermediate between Mn_3Cl_8 and MnCl_2 was formed. These curves, therefore, show that on dissolving any of the oxides of manganese: MnO_2 , Mn_2O_3 , and Mn_3O_4 , the only higher chloride formed is MnCl_4 .

It was also found, contrary to Pickering's statement, that the amount of MnO_2 recovered on precipitating the solution was not always under, but always over 50 per cent at ordinary temperatures, the amount recovered being increased by performing the dissolution of the dioxide in chlorhydric acid saturated with chlorine. The fact that the addition of MnCl_2 to the solution increases the amount of MnO_2 recovered is only what we should expect, just as Wurtz found that PCl_5 dissociated to a less extent when vaporised in PCl_3 vapour.

Special Meeting, May 8th.

Fellows who desire to exhibit objects at the Special Meeting in May are requested to communicate *forthwith* with the Secretaries, in order to give time for the preparation of a descriptive list of the exhibits.

An Arrangement of the Stirrer in taking Melting-Points.—E. C. Holtz (*American Chem. Journal*).—The stirrer is fastened in a cork supported by a horizontal stiff spiral wire 25 to 30 c.m. in length; its other end is fixed in a perforated cork which slides on the rod of an ordinary support, and can be placed at any required height.

PHYSICAL SOCIETY.

April 18th, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

MR. B. CROFT was elected a Member of the Society.

Prof. RÜCKER described the results of "Some Recent Magnetic Work" undertaken by himself and Prof. Thorpe in connection with their Magnetic Survey of the United Kingdom.

In a paper read before the Royal Society last year they have shown that the United Kingdom can be divided into 7 or 8 distinct districts, in each of which a source of disturbance seems to exist. The probable cause of these disturbances the authors believe to be the presence of "magnetic rocks." If this be true, an intimate connection should exist between the magnetic elements of a district and its geological structure. If a magnetic mass be supposed to exist below the surface, then one would expect the vertical force to be greatest above that mass, whilst the horizontal disturbances would tend towards the mass, and would differ in direction on its opposite sides.

With a view to testing more fully than heretofore the magnetic constitution of the districts above referred to, the work (the results of which Prof. Rücker now described) was undertaken.

Two test districts were selected in which numerous observations were taken; one of these is situated on the West Coast of Scotland and the other embraces parts of Lincolnshire and Yorkshire. The first of these districts was chosen for two reasons:—First, because it is very disturbed, and owing to the vast masses of basalt, would be a specially difficult one; and secondly, because it is near the borders of their survey, and is thus particularly open to suspicion that the calculated values of the elements may be inaccurate.

By the aid of Magnetic Maps, Prof. Rücker showed that a centre of disturbance exists to the West of Iona and South of Barra. Both the vertical force and the horizontal disturbances indicate the same position, and hence favour the hypothesis.

In the Lincolnshire and Yorkshire district, extending from the Wash to Appleby, there is a region in which the horizontal disturbances along the East side tend towards the West, whilst along the West side they are, on the whole, directed easterly. This points to a ridge of magnetic material along the middle of the region, and from numerous observations the approximate position of the ridge line has been determined over a length of 150 miles. In Lincolnshire the ridge follows closely the line of Wolds, whilst at the Kettlewell end it is directed towards the Cumberland Lake District. Places of maximum vertical force occur near Market Weighton and Harrogate.

The observers were directed to Market Weighton by Prof. Judd as being situated where the Liassic strata thins out. Harrogate stands on the summit of an anticlinal. The fact that such places of maximum vertical force exist where, according to hypothesis, they would be expected, tends to confirm the supposition, and thus to demonstrate that a very close connection exists between the magnetic elements and the geological structure of a country. This is further confirmed by the observation that in Lincolnshire the line of disturbance follows closely the line of the Wolds, and that from Market Weighton it passes across the plain of York to the Millstone Grit and Limestone, which are the oldest rocks in the neighbourhood.

Mr. WHIPPLE said he had listened with very great pleasure to the interesting details and results given by Prof. Rücker. Never, to his knowledge, had a magnetic survey been conducted with such minuteness and accuracy. The older surveys related chiefly to declination, whilst the determinations of intensity were made in a very primitive way. He looked forward with interest for other important results, which he felt sure would follow from the admirable survey of Profs. Rücker and Thorpe.

A most cordial vote of thanks was accorded to Prof. Rücker for his most interesting and valuable communication.

Mr. T. H. BLAKESLEY, Hon. Secretary, read a paper on "A Theory of Permanent Magnetism." By M. OSMOND.

The author states that iron exists in two distinct physical states, one soft, or " α iron," the other hard, or " β iron." The β variety is non-magnetic, and is formed during heating, hardening, or by electrolysis; whilst the soft or α modification is produced by long annealing.

In a piece of steel the author considers the β molecules to form a rigid framework in which the α molecules become interlocked under the influence of magnetising force, and on the degree of interlocking the permanent magnetism depends. By a graphical method it is shown that the permanent magnetism should be a maximum when the two varieties are present in equal quantities. If the proportions of carbon and manganese in the steel are considerable, nearly all the iron is of the β variety, and the steel is nearly non-magnetisable.

In hardening a piece of ordinary steel the surface layers being cooled most rapidly contain more β molecules than the interior; hence for a certain degree of hardness (when the outer layers have more α molecules than β ones) a laminated magnet will be a better permanent magnet than a solid one, but for a much greater degree of hardness the reverse may be the case.

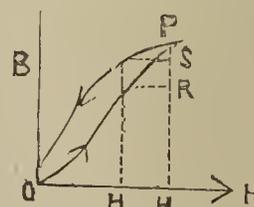
Mr. SWINBURNE asked if the theory would account for the increase of induction which occurs when the circuit of a permanent magnet is closed; most theories founded on the orientation of particles by the magnetising force seemed defective in this respect. Some time ago, he had suggested that the permeability of iron should be tested by first magnetising it one way, and then at right angles to the first direction; recently he had been informed that no increase of permeability was observed when the experiment was performed.

Prof. PERRY said he had subjected iron to magnetsiation in one direction and found the permeability for small forces in a direction at right angles much smaller than he had anticipated; the first magnetising force was kept constant when the small perpendicular one was applied.

Mr. SWINBURNE thought that for such small perpendicular forces the permeability should be nearly infinite. He also said there seemed a sort of angular hysteresis in iron, for if a loose-running armature was turned slowly round by hand, it would come back two or three degrees when left free.

The PRESIDENT remarked that, as far as he could see, M. Osmond's theory does not account for the great influence which a small percentage of tungsten has on the magnetic property of steel, and all theories which failed in this particular must necessarily be imperfect.

Mr. BLAKESLEY pointed out that the ordinary hysteresis curves showed that a small superimposed magnetising force, in a direction different from the primary one, produced only a small change in the induction, and hence would



give a small permeability. For example, the increment $H H'$ (see Fig.) causes an increase, $R P$, in the induction, whilst an equal decrement, $H' H$, produces only a change, $P S$.

Reduction Instrument for Finding the Volume of a Gas under Normal Conditions.—G. Lunge (*Chemiker Zeitung*).—The author recommends for this purpose his nitrometer.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 14, April 8, 1890.

The Normal Presence in the Chyle of a Ferment which Destroys Sugar.—R. Lépine.—The author has discovered a ferment elaborated by the pancreas which destroys sugar. If the pancreas is absent, or if it is experimentally removed, diabetes ensues.

A Fundamental Property Common to the Two Classes of Spectra. Distinctive Characters of Each Class. Periodic Variations of Three Parameters.—H. Deslandres.—This paper will be inserted in full.

The Suppression of Halos in Photographic Proofs.—Paul Henry and Prosper Henry.—The authors succeed in avoiding these halos by covering the back of the plate with a layer of normal collodion holding in solution a small quantity of chrysoïdine. This varnish having an index of refraction little different from that of glass, completely suppresses the halos.

Phosphotrimetatungstic Acid and its Salts.—A. Péchard.—This acid is obtained on evaporating to dryness at temperatures below 100° a mixture of phosphoric and metatungstic acids in any proportions. If the phosphoric acid is in excess the mixture, on being taken up in water and submitted to evaporation, yields only the phosphotrimetatungstic acid. In the contrary case crystals of this acid are deposited. It appears in the form of non-efflorescent crystals, soluble in water and alcohol. A number of the salts of this acid are described.

A Nitroso-chloroplatinate.—M. Vèzes.—This compound, along with potassium chloroplatinate, is obtained on pouring an excess of hydrochloric acid into a saturated solution of potassium platinonitrile. Its composition is given as $PtCl_3(NO)_2KCl$.

On Glycolic Nitrile and the Direct Synthesis of Glycolic Acid.—Louis Henry.—Glycolic nitrile is a liquid similar to water, very mobile, colourless, inodorous, and of a peculiar sweetish taste. Its sp. gr. at 12° is 1.100. It congeals at -72° in a mixture of ether and carbonic snow. It is very soluble in water, alcohol, and ether; insoluble in carbon disulphide, chloroform, and benzene. If mixed with rather more than double its weight of fuming hydrochloric acid there is a violent reaction; ammonium chloride is deposited and there is formation of glycolic acid.

Zeitschrift für Analytische Chemie.
Vol. xxviii., Part 6.

Electrodes in Glass Vessels with Mercurial Contacts.—F. Heerwagen (*Instrumentenkunde*).—The arrangement is shown in an accompanying cut.

Apparatus for working with Hydrofluoric Acid.—E. Cchen (*Chem. Centralblatt*).—The author prefers the old method of opening up refractory minerals in a large lead vessel fitted with a cover. Fluor-spar and sulphuric acid are placed in its bottom and the specimens to be acted upon are placed one above each other, stairlike, in small flat leaden dishes. Another apparatus for working with hydrofluoric acid is proposed by H. C. Andersch (*Chemiker Zeitung*), but it requires the accompanying figure.

Automatic Apparatus for Regulating the Time of Boiling.—Felix Bauer (*Chemiker Zeitung*).—For the details the author is referred to the original.

Tubes for Heating Substances under Pressure.—H. N. Warren.—From the CHEMICAL NEWS.

A Refrigerator for Use in Distillations.—Carl Schlarb (*Chemiker Zeitung*).—The apparatus is shown in an accompanying figure.

A Spirit Blast-Lamp.—R. Rosenlecher (*Chemiker Zeitung*).—An instrument to be used in place of the gas-blast.

The Meldometer.—J. Joly.—From *Industries and Journ. Soc. Chem. Industry*.

Apparatus for Separating and Shaking Out.—R. Schültze (*Chemiker Zeitung*).—A graduated cylindrical receiver for reading off the volume of a distillate.

Pouring out Acids.—L. M. Denies (*American Chem. Journal*).—To the carboy is attached an instrument similar to the mouthpiece of a washing-bottle, air being supplied with a caoutchouc blast instead of with the mouth.

The Purity of Reagents.—M. von Nencki (*Monatshefte für Chemie*).—Copper oxide and lead chromate used in elementary organic analysis are often impure, the former containing lime and the latter lead oxide. The former is detected by extracting the copper oxide with warm dilute acetic acid, throwing down the copper from the solution by means of sulphuretted hydrogen, and then testing the filtrate with ammonium oxalate. The lead oxide in the lead chromate is detected by extraction with dilute acetic acid and precipitation with sulphuric acid. It amounted in one case to 13.27 per cent. L. L. de Koninck (*Angewandte Chemie*) detected manganese peroxide in lead peroxide. He heats a portion of the sample with an excess of concentrated sulphuric acid until it is completely decomposed, and, when cold, treats with water and a fresh portion of the peroxide. On re-heating the red colour of permanganic acid appears if manganese is present.

Ether.—The so-called pure commercial article always contains various impurities which, on spontaneous evaporation, remain behind as an ill-smelling residue. Sulphur is detected by shaking up the sample in question in a test-tube with a drop of pure bright mercury. If the quantity of sulphur is very small the surface of the mercury is merely rendered dull and grey. If there is much sulphur the entire liquid turns grey or black. Pure chloroform does not reduce alkaline permanganate unless a trace of alcohol is present. Bertram Blount (*Analyst*) describes a series of impurities in so-called pure reagents. P. Lohman (*Pharm. Zeitung* and *Chemiker Zeitung*) discusses the purity of commercial reagents required in chemico-legal investigations. Zinc and sulphuric acid can easily be obtained free from arsenic. Hydrochloric acid which fulfils the requirements of the *Pharmacopœia* may contain traces of arsenic. Hydrochloric acid freed from arsenic by means of tin is usually stanniferous. Chloric acid may contain arsenic and usually contains baryta.

Preservation of Sulphuretted Hydrogen in Solution.—D. Lindo.—From the CHEMICAL NEWS.

Purification of Mercury.—H. Nagaoka (*Tok. Sugaku and Annalen der Physik*).—A modification of Bohn's distillatory apparatus.

Iris-Paper is recommended by W. Greenwalt (*Chemiker Zeitung*) as test-paper for alkalimetry and acidimetry. It is obtained by steeping filter-paper in a watery extract of *Iris versicolor* prepared hot. In a neutral state it is blue, and is turned red by acids and green by alkalis.

Separation of Lime, Baryta, and Strontia.—M. Kupferschläger.—*American Journ. Pharmacy and Chemiker Zeitung*.

Separation and Determination of Zirconia.—G. H. Bailey.—From the *Journal of the Chemical Society*.

Detection of Ferric Salts in Strong Acids.—F. P. Venable.—From the *Journal of Analytical Chemistry*.

MISCELLANEOUS.

Improved Bunsen Burner.—We have received from Messrs. J. J. Griffin and Sons, Garrick St., an improved Bunsen burner which appears to possess many advantages over the old form of burner. The burner consists of three pieces only, easily taken apart and put together. The usual central gas jet is dispensed with, and by one single movement the supply of gas and air are simultaneously regulated. The gas passes into the burner through a way cut in the side of the tube, which is open from top to bottom, and cannot, therefore, become choked.

MEETINGS FOR THE WEEK.

- MONDAY 28th.—Medical, 8.30.
— Society of Arts, 8. "Sugar, Tea, Coffee, and Cocoa, their Origin, Preparation, and Uses," by Richard Bannister.
- TUESDAY, 29th.—Royal Institution, 3. "The Place of Oxford University in English History," by The Hon. George C. Brodrick, D.C.L.
— Institute of Civil Engineers, 8.
- WEDNESDAY, 30th.—Society of Arts, 8. "Photographic Lenses," by T. R. Dallmeyer.
— Geological, 8.
- THURSDAY, May 1st.—Royal Institution, 1.30. Annual Meeting.
— Royal Institution, 3. "The Heat of the Moon and Stars" (the Tyndall Lectures), by Prof. C. V. Boys, A.R.S.M., F.R.S.
— Society of Arts, 8. "Design Applied to Wood-carving," By Lewis F. Day.
— Royal, 4.30.
— Royal Society Club, 6.30.
— Chemical, 8. "The Conditions under which Hydrogen Peroxide is Formed from Ether," by Prof. Dunstan and T. S. Dymond.
- FRIDAY, 2nd.—Royal Institution, 9. "Theophile Gautier," by Walter H. Pollock, M.A.
— Physical, 5. "Distribution of Flow in a Strained Elastic Solid," by Chas. A. Caras-Wilson. "Photographs of Rapidly Moving Objects," by C. V. Boys. "The Oscillating Electric Spark," by C. V. Boys.
— Geologists' Association, 8.
- SATURDAY, 3rd.—Royal Institution, 3. "Colour and its Chemical Action," by Captain W. de W. Abney, F.R.S.

THE LONDON HOSPITAL MEDICAL COLLEGE.

The SUMMER SESSION will COMMENCE on THURSDAY, May 1st.

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SCHOLARSHIPS AND PRIZES.—Twenty Scholarships and Prizes are given annually. Students entering in May are eligible to compete for the four Entrance Scholarships in September. Luncheons or dinners, at moderate charges, can be obtained in the Students' Club.

N.B. Special arrangements have been made to meet the requirements of the Examining Board in England so as to enable Students entering in May to pass Part I. (Chemistry and Chemical Physics), and Part II. (Materia Medica and Pharmacy) of the First Examination in July.

The London Hospital is now in direct communication with all parts of the metropolis. The Metropolitan, District, and other railways have stations within a minute's walk of the Hospital and College.

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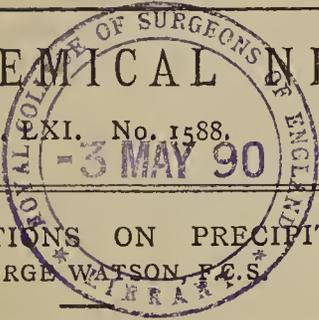
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SOME OBSERVATIONS ON PRECIPITATION.

By GEORGE WATSON, F.C.S.

SEVERAL cases of precipitation are known in which scratches, formed on the sides of the containing vessel, become traced out with a deposit of precipitate while the rest of the glass surface remains otherwise quite uncoated. In some cases—as, for instance, the precipitation of ammonio-magnesian phosphate from weak solution—the scratches appear to exert an attractive force on a liquid in which exists a precipitating tendency or stress, in this way attracting and fixing a precipitate during its formation; in other cases, as I have had occasion to notice, they attract and fix a precipitate after it has been thrown down.

Although this phenomenon has long been known and, indeed, observed by every chemist, I am not aware that anyone has hitherto attempted to explain it, or, in fact, thought that it required any explanation, the remark that the roughened surface of the abrasion acted as nuclei, to which the precipitate attached itself, being considered a sufficient one. This, to my mind, is no explanation, but if, on the contrary, it be viewed as due to the surface-energy of the glass becoming augmented or rendered more potent by abrasion, then, I think, the statement offers a partial explanation of the phenomenon, but not a complete one, for some other factor must be also concerned, otherwise all precipitates, no matter what their nature, would be liable to fixation. This factor I believe to consist in a condensation change in the precipitate from a less to a more dense condition, resulting in the crystalline state, as the two precipitates (basic antimonious chloride and calcic hydric orthophosphate) which I have examined are, when newly thrown down, amorphous and bulky, but pass on standing into heavier crystalline states, and until this change has taken place no precipitate is seen to become fixed on the scratches.

It is not perhaps advisable to take up space with a minute description of the experiments I have made on this subject, a general description, with a summary of the results obtained, being all that is necessary. In the experiments with basic antimonious chloride, a solution of antimonious chloride was made by digesting strong hydric chloride with excess of antimonious oxide in the cold, then filtering and clearing up the somewhat turbid filtrate by the cautious addition of strong hydric chloride. To 100 c.c. of distilled water were then added 5 c.c. of this solution, the whole mixed by agitation, and a number of scratches made on the internal surface of the glass by means of a pointed glass rod. By operating in this way, the following points were noted:—

(a). No fixation occurred until the precipitate had changed into the heavy crystalline condition.

(b). After this change had taken place, new scratches made on the glass were unable to fix any more precipitate on shaking up.

(c). Scratches which had once done work by fixing precipitate, and which had been cleaned from adhering precipitate by washing with hydric chloride and rinsing, were unable to again fix any precipitate when placed in suitable conditions.

(d). Scratches which had already fixed precipitate, but which had only been cleaned by rubbing with a rubber-tipped rod, were apparently sometimes able to again fix a new small quantity of precipitate, this result being probably due to some condensed precipitate from the previous operation still adhering to the glass, as will be shown hereafter.

Similar results are obtained in the case of calcic hydric orthophosphate; my experiments with this substance being made by mixing 50 c.c. of a cold saturated solution of ordinary sodic phosphate with 100 c.c. distilled water and 30 c.c. of a 5 per cent solution of calcic chloride.

But a further study of these experiments leads to other conclusions. Thus, if the adhering precipitate of basic antimonious chloride or of calcic phosphate be rubbed off an abrasion, the latter is found to be a mere hair line in width, while the adhering film of precipitate has a width many times greater. This suggests the idea that the film has grown in width by a process analogous to the growth of a crystal, for, if we imagine the path of the abrasion to be first filled up with a line of condensed precipitate, the widening of this line could only occur by the condensed precipitate itself exerting an attractive force on the contiguous uncondensed precipitate. This, evidently, amounts to saying that the rate of condensation in the case of these precipitates is an accelerating one. Hence, if a quantity of either precipitate be formed in admixture with a preformed quantity of the condensed variety, the periods of time now required for their mutual condensations should be less than those required if no preformed condensed precipitate were present. This I find to be the case; for example, 5 c.c. of the antimonious chloride solution used in the former experiments were precipitated with 100 c.c. of water as usual, allowed to condense, and the clear supernatant poured off. Another 100 c.c. of water were then poured on, another 5 c.c. of antimony solution added, and the whole shaken up. At the same time, a parallel experiment was started, but without having any condensed precipitate previously present, and both glasses were shaken up simultaneously three times at intervals of five minutes. At the end of this time the parallel experiment was unchanged, while in the other the precipitate was completely condensed into the heavy crystalline state. This experiment becomes very striking when performed on a large scale—say, with 50 gallons of water and antimony solution in proportion.

Similar results are obtained in the case of calcic hydric orthophosphate. Thus, 50 c.c. of water, 15 c.c. of a 5 per cent solution of calcic chloride, and 25 c.c. of a cold saturated solution of disodic phosphate were mixed in a test-glass and allowed to condense. The supernatant was poured off the precipitate, and 50 c.c. of water added, then 15 c.c. of the calcic chloride solution, and 25 c.c. of the sodic phosphate solution. A parallel experiment was done at the same time, in every way comparable with the exception of lacking the preformed condensed precipitate. Both glasses were shaken up simultaneously and allowed to stand at rest. Within ten minutes the precipitate, which had been formed in contact with the condensed variety, had settled, leaving a perfectly clear supernatant, while the other had not settled in the least.

These results suggest an analogy to the sudden crystallisation of supersaturated solutions produced by dropping into them a crystal of the dissolved salt. Just as these precipitates rapidly pass from a more to a less tenuous condition on admixture with a quantity of the condensed variety, so in such solutions the dissolved salt rapidly passes from the tenuous state of solution to the condensed state of the crystal on the introduction of a small quantity of the latter. Whence, by analogy, it follows that these cases of crystallisation are condensation changes proceeding at accelerating rates, and it is because they are such that the introduction of a minute crystal of the dissolved salt can bring about the rapid crystallisation of the whole. If they were not such, the crystallisation could not be induced by these means.

As there are some cases—as, for instance, the precipitation of ammonio-magnesian phosphate from weak solution—in which also the precipitate shows this property of fixing itself to abrasions, it may be assumed that similar causes are concerned here, viz., the potent surface-energy of abraded glass combined with the simultaneous occurrence of a condensation change. Whence, going by

analogy, precipitation also, considered generally, comes to be viewed as a condensation change proceeding at an accelerating rate. What appears in most cases as an instantaneous change is, in reality, an accelerating change with an enormously large increment of acceleration. It also follows from analogy that the presence of preformed precipitate in the liquid should not only hasten the starting of precipitation in those cases in which precipitation would start of itself, but should also cause precipitation in those cases in which no precipitate would form of itself. This latter deduction is illustrated in the experiments of Baubigny on the precipitation of nickelous sulphide (CHEM. NEWS, vol. xlv., p. 257, 1882), while the former is exemplified by an observation which I have made during the precipitation of arsenic as sulphide when freeing quantities of phosphoric acid from that impurity. Working with a quantity of 9 or 10 gallons of liquid containing about 50 per cent of H_3PO_4 after the precipitation is fairly under way, but still incomplete, if the current of hydric sulphide be stopped and the precipitate allowed to settle, the supernatant is seen to have a yellowish opalescent appearance. On stirring up vigorously, the precipitate already formed seizes, as it were, the incipient precipitate and pulls it out of solution, leaving, on settling, a clear, or nearly clear, supernatant. The precipitate, at this point, is in the form of large semi-curdy flakes, but after a while these change into smaller and heavier ones, which can again go through the same operation on further gassing with hydric sulphide.

Since writing the above, I have reason to believe, from a further experience of this method of freeing phosphoric acid from arsenic, that the appearances described above only happen when the precipitation is started in the heat, and when a somewhat large proportion of arsenic is present. If the amount of arsenic present be small, and the precipitation wholly conducted in the cold, the sulphide of arsenic is thrown down in a finely-divided state, and only settles after standing for several days.

NOTE ON THE
ADMIXTURE OF ETHYLIC ALCOHOL WITH
WATER.

By THOMAS FARRINGTON, M.A., F.C.S., F.I.C.

It is well known that a slight rise of temperature takes place when alcohol is mixed with water. This phenomenon has seemed to me worthy of quantitative examination, with the view of ascertaining the exact proportions of the liquids which produce the greatest heat effect, and what that heat effect amounts to.

From numerous preliminary experiments I have ascertained that the greatest rise of temperature is about $10^{\circ}C.$, and occurs with mixtures containing from 28 to 50 per cent of alcohol by volume, there being comparatively little variation of final temperature between these limits.

Assuming that the specific heat of mixtures of alcohol and water is directly proportional to the volumes of the components, the greatest heat-effect would occur with a mixture containing 33 per cent of alcohol. As this proportion does not coincide with that which gives rise to the greatest contraction in volume, I intend to further investigate the question with a view to ascertaining if the

two phenomena coincide when the following difficulties in the way of accurate results are overcome:—

1. The specific heat of the resulting compound may not be the same as that calculated in the above manner from those of its components.

2. The evolution of dissolved gases which results on mixing must render the temperature observation incorrect; the liquids must consequently be made and kept apneumatic before mixing.

3. The rise of temperature may interfere with the formation of the probable compound; and in such a case it must be arranged to have the final temperature the same in comparative trials of different mixtures, or the heat must be measured without any final elevation of temperature by the use of the ice calorimeter or such other means.

Through the kindness of Prof. Hartog, of the Queen's College, Cork, I have been able to measure the refractive indices of some mixtures of water and alcohol, and find that the results agree with those calculated from the ordinary formula. As the densities of the solutions are important factors in this formula, it seems certain that the variations in the refractive index follow those in the density. The table below gives (1) the volumes of the components; (2) the specific gravities; (3) the refractive indices, (a) observed, (b) calculated from the formula, (c) calculated from the volumes of the components; (4) the difference of the observed and "mean" refractive indices.

From this it appears that the abnormal variation in the refractive index is greater at the point where the greater contraction in volume occurs.

The most remarkable difference in physical properties between mixtures of alcohol and water and the liquids themselves is that which manifests itself when they run through a comparatively small opening; this phenomenon was observed in the following manner:—The glass stopcock of a burette was so set that the contained liquid might drop slowly out, and the time that equal volumes of the three liquids took to run out was noted. The average of three fairly concordant experiments in each case gave, for the time of running out from the zero point to the end, the following times:—

Water	240 seconds.
Alcohol	270 "
Mixture { Alc. = 1 { H ₂ O = 2 }	.. 346 "

Fearing lest chance filaments might possibly have influenced this result while the liquids ran through so small an aperture, I have confirmed the foregoing experiments by others in which they were allowed to run through the fully opened stopcock. Each result is the average of seven close determinations, the times being taken with the help of a stop-watch.

Water	20.9 seconds.
Alcohol	22.7 "
Mixture	26.9 "

It thus appears that the complex and loosely-combined molecules of ethyl alcohol hydrate find much more difficulty in passing through a small aperture than the smaller molecules of alcohol and water.

4, Waterloo Place, Cork,
April 19, 1890.

	(1) Volume of		(2) Specific Gravity.	(3) Refractive Index.			Difference of (a) and (c).
	Alcohol.	Water.		(a) Observed.	(b) Calculated.	(c) Mean.	
Alcohol	—	—	0.7978	1.3645	—	—	—
Water	—	—	0.9990	1.3320	—	—	—
Mixture	5	10	0.9610	1.352	1.3535	1.343	0.009
Mixture	5	5	0.9348	1.361	1.3622	1.348	0.013

METEORIC ORIGIN OF THE DIAMOND.

HERR A. MEYDENBAUER, writing in the *Bayr. Industr. und Gewerblatt* (thence copied into the *Chemisch-techn. Central Anzeiger*), states that as far back as 1874 he wrote in "Sirius" that "The diamond can only be of cosmic origin, having first arisen simultaneously with the primitive rocks, and having also fallen as a meteorite at later periods of the earth's formation. An appropriate examination of the places where it occurs would elucidate this dark point."

Such an investigation was not undertaken for some time. Dr. Kersten produced, in 1887, an essay on the peculiar features of the occurrence of the diamond. The English geologist, B. H. Carwill, without having the meteoric origin of the diamond in view, remarked that the matrix of diamonds in South Africa had a remarkable similarity to certain meteorites with which he was well acquainted. Finally, two Russian *savants*, on examining a black meteorite which fell on September 4, 1886, at Nowy Uray, in the Government of Pensa (a portion of which is in the Natural History Museum of Vienna), found diamonds in small crystals amounting to one per cent of the total stone.

Whilst all minerals of which the earth is composed, whether primitive, stratified, or metamorphic, possess the same attributes in all latitudes, the diamond occurs in practically available specimens only in a zone of the southern hemisphere extending through Southern Asia, South Africa, and South America. Its alleged occurrence in very small and worthless crystals in the Itacolumite of the Ural does not contradict this derivation, since, according to the author's view, the massive primitive rocks have a similar though more ancient origin.

The above available localities of the diamond contain the residues of not very compact meteoric masses which may, perhaps, have fallen in historical ages, and which have penetrated more or less deeply, according to the more or less resistant character of the surface where they fell. Their remains are crumbling away on exposure to air and sun, and the rain has long ago washed away all prominent masses.

The enclosed diamonds have remained scattered in the river beds, whilst the fine light matrix has been swept away. At the spots where the meteorites fell, and which, from their superficial appearance, did not in the least indicate what was within, there was, above all things, no indication of volcanic action. The information received about the structure of the pits in South Africa agrees completely with the phenomena attending the fall of masses from above, whilst the superficial appearances which attend volcanic action are quite wanting. The matrix contains all the ingredients necessary for a readily fusible slag, and yet there is no trace of fusion, a fact generally overlooked. As to the diamond, which cannot support even a red heat, the hypothesis of a subsequent action has been invented, though there is nothing analogous either in nature or in the artificial circumstances of our laboratories. On the other hand, the traces of heat on the margins and the erect stratification of the adjacent rocks are sure signs of matter striking in from above.

Very decisive is the absence of depth in the adjacent rocks. Never has there been found a cavity or a crevice going down to unknown depths, without which a rise from the earth's interior is unthinkable, and in which, on the supposition that diamonds come from below, they would be found in masses. On the contrary, we hear of exhausted pits, especially in Brazil. The diamond-bearing meteors were there either masses of little density, or they struck upon very hard rocks, burst in all directions, and scattered their rich contents all round. The diamonds found their way into the beds of streams, which became the diggings of the future. That pockets may still remain in clefts and ravines is very probable.

In India the process has undergone modifications

which testify to the accuracy of our supposition. Whilst Cape diamonds are found in the matrix with a surface clear as glass, the Indian diamonds are covered with a blackish crust, as if singed superficially. As constituents of small but numerous meteors of an otherwise pulverulent mass, they were, whilst passing through the atmosphere, exposed for a moment to the action of heat.

The pulverulent mass was retained in the air as the well-known train of the larger meteors, and the diamonds fell to the ground as true meteorites. The diamond is, therefore, a gift of Heaven!

RELATIONS BETWEEN THE COMPOSITION
AND THE ABSORPTION-SPECTRA OF ORGANIC
COMPOUNDS.

By M. ALTHAUSSE and G. KRÜSS.

G. KRÜSS has already found in a great number of organic compounds that the introduction of methyl, oxy-methyl, and carboxyl groups, *i.e.*, those which increase the proportion of carbon in a compound, displace all the absorption bands of a spectrum towards the red. He finds, further, that the bands are displaced towards the blue end of the spectrum if an atom of hydrogen in an organic compound is replaced by a nitro- or amido-group. The authors have verified these conclusions by further experiments, and show that an addition of hydrogen to an organic colouring-matter displaces its absorption towards the blue. If a careful spectroscopic determination is made, what kinds of light are transmitted by the technical solution of a colouring-matter, and which are lost, it can be predicted with moderate accuracy what will be the colour of a substitution derivative of the original colour. If this colour displays in the spectrum a band which absorbs the blue, then on introducing ethyl or methyl a substance is obtained which has in its colour more blue and less green. If the original substance has an absorption band in the red its colour will become redder by ethylation, the band being displaced towards ultra red.—*Deutsche Chem. Gesellschaft Berichte.*

THE SEPARATION AND DETERMINATION
OF TIN AND TITANIUM, WITH ESPECIAL
REFERENCE TO THE ANALYSIS OF
SILICATES

By A. HILGAR and H. HAAS.

THE simultaneous occurrence of stannic and titanous acids in silicates occasions much trouble. The most suitable method for their separation is founded on the fact that mixtures of stannic and titanous acids are reduced in a current of hydrogen at dull redness in such a manner that the stannic acid becomes metal, but titanous acid not. From this mixture, the reduced metal can easily be dissolved out by hydrochloric acid, at 20 per cent, without titanium being dissolved.

The mixture of stannic and titanous acids is placed in a tube of sparingly fusible glass, 15 to 20 c.m. in length, and ignited at dull redness for a quarter of an hour in a current of hydrogen by means of a small Bunsen burner, and then let cool in the current. The reduced mass then rinsed into a beaker with a little water and a few drops of hydrochloric acid, if needed, covered with 30 c.c. of hydrochloric acid at 20 per cent, kept at a gentle boil for half an hour, replacing the liquid as it evaporates, and filtered when cold. From the faintly acid filtrate the tin is precipitated by means of sulphuretted hydrogen, the tin sulphide is washed with water containing ammonium acetate, again reduced in a current of hydrogen, and the

reduced tin is finally converted into stannic acid by means of nitric acid, and weighed as stannic oxide.

The contents of the filter obtained after treatment with hydrochloric acid containing titanium are burnt along with the filter, ignited, and fused in a platinum crucible along with 10 parts of potassium carbonate. The melt is soaked in about 200 c.c. of water, concentrated sulphuric acid is added drop by drop until the acid titanate is dissolved, neutralised with solid sodium carbonate, 2 grms. of concentrated sulphuric acid are further added, the liquid is made up to 400 c.c. and kept at a boil for six hours. All the titanate is separated out, and, after filtration and ignition, it is washed as titanium dioxide.

The analysis of stanniferous and titaniferous silicates is conducted as follows:—5 to 10 grms. of the sifted minerals are stirred up to a thick paste with water in a platinum capsule, mixed with dilute sulphuric acid (1:10) till the mixture becomes thin, fuming hydrofluoric acid is gradually added until the silica is completely removed, high temperatures being especially avoided. When the decomposition of the mineral is complete, and the hydrofluoric acid driven off, the mass is brought to a pasty consistency on the water-bath, rinsed with water into a beaker or a porcelain pan, neutralised with potassium or sodium hydroxide, mixed with two grms. strong sulphuric acid, made up with water to 400 c.c., and kept for six hours at an unbroken boil. The quantities of stannic and titanate acids are thus completely separated in a hydrated state. In the precipitate, which may, at the utmost, contain a little iron, the separation of tin and titanium is effected as already described. The filtrate from this precipitate serves for the determination of the other ingredients of the silicate.—*Berichte d. Deutsch. Chem. Gesellschaft*, vol. xxiii., p. 458.

EXAMINATION OF CORPSES FOR ALKALOIDS AND METALLIC POISONS.

By Dr. ANTON SEYDA.

(Continued from p. 185).

In this qualitative detection of mercury which is always successful, even with very small quantities of mercury, a too prolonged digestion of the brass wool in the liquid must be avoided, since then, in spite of treatment with purifying agents, the organic matter remains deposited upon the brass-wool, when the formation of empyreumatic products interferes with the detection of mercury. In all cases the author therefore places in front a short stratum of copper.

When mercury is present in larger quantities it can be recognised with the naked eye on the amalgamated brass threads. The further chemical detection may be executed in a test-tube in the known manner.

The quantitative determination of mercury is conducted as follows:—Sulphuretted hydrogen is passed into the hot hydrochloric liquid, the precipitate is filtered through a plug of asbestos (previously ignited and well purified with *aqua regia*) in a filter of medium size, and washed with hot strong hydrochloric acid until it runs off colourless. If arsenic sulphide is present the precipitate must undergo a preliminary digestion with yellow ammonium sulphide. The funnel is then inverted, and the asbestos plug, along with the mercury sulphide, is washed with the same acid into a beaker, the funnel is rinsed, and, with the addition of a few drops of nitric acid, cautiously heated until all the mercury sulphide is decomposed, and single flakes of sulphur float about in the liquid. The nitric acid is only to be added in the quantity just necessary, since the mercury sulphide dissolves readily on its addition even in small quantities. The expulsion of the excess of nitric acid is not necessary and not practicable, but any excess may be neutralised. The asbestos is then collected together into a lump by

means of a glass rod, re-introduced into a funnel, and the liquid, which is turbid from asbestos fibres, and from mercury which has escaped oxidation, is again filtered through the plug. If it drops through turbid, it is returned to the funnel until it runs clear. The asbestos is then well washed, the filtrate, which contains hydrochloric acid and a little nitric acid, is diluted with water and mixed with an excess of phosphorous acid. After twenty-four hours, the pure white mercurous chloride is filtered off, washed successively with water, alcohol, and ether, and weighed upon a filter. In the determination of mercury chloride two sources of loss must be remembered: its possible reduction on contact with organic matter, which should hence be avoided, and, secondly, its ready volatility, whence strong heat and great concentration of the liquids should not be applied.

β. Detection and Determination of Antimony.

Fifty c.c. of the liquid are placed in a bright platinum capsule, the excess of acid is partially neutralised with ammonia, and a piece of zinc is introduced. After six hours the liquid is decanted off and the capsule rinsed out with a little water. The smallest quantities of antimony may be recognised by brownish black spots which appear at the bottom and the margin of the platinum dish. A longer action of the zinc should be avoided, as antimony is soluble in concentrated solutions of zinc chloride. It must be remembered that in alloys of antimony and tin the former metal is not indicated by this test if its proportion is 5 per cent, and very doubtfully if it reaches 10 or even 20 per cent. It is therefore necessary in such cases to remove the bulk of the tin by fusion with caustic soda, and applying the above test to the portion insoluble in water.

The author has been compelled to abandon the detection of antimony by means of its volatile hydrogen compounds.

For the determination of antimony, sulphuretted hydrogen is passed into the slightly acid solution, at first at a boiling heat and then, after the removal of the flame, until it is cold. After the precipitate has fully settled, at the expiration of the third day, the excess of sulphuretted hydrogen is expelled by the introduction of a strong current of carbonic acid. If frothing sets in it may be prevented by the addition of ether. The precipitate is filtered off, washed with ammonium acetate, rinsed from the filter into a flask by means of hot dilute solution of sodium sulphide, and into the hot solution sulphuretted hydrogen is passed until it smells strongly of the gas. The contents are filtered, the precipitate washed with dilute sodium sulphide containing sulphuretted hydrogen, the washings are added to the filtrate, which is then, whilst being stirred, mixed very carefully with hydrochloric acid in slight excess. After the first violent reaction is over, the whole is gradually heated and raised to a boil. After twenty-four hours the precipitate is filtered off, washed with ammonium acetate, rinsed into a porcelain capsule, the filter washed with hot solution of sodium sulphide, the contents of the capsule are evaporated upon the water-bath, and cautiously treated at repeated intervals with nitric acid until no further reaction takes place. The residue is moistened with soda-lye, intimately mixed with dry sodium carbonate, the mixture dried and gradually introduced in small portions into melted sodium nitrate in a silver crucible, which consumes the organic matter present. The melt, when cold, is at once lixiviated with water in the silver crucible, the solution is poured into a beaker and allowed to settle.

In twenty-four hours the precipitate, which has a blackish colour from the presence of a little silver or silver oxide, is filtered off and washed with alcohol at 45 per cent containing soda. After a caoutchouc tube has been drawn tightly over the neck of the funnel and tied firmly, it is closed with a clip, and the precipitate is lixiviated for half an hour with a hot solution of tartaric and hydrochloric acids. The clip is then opened, and the liquid is

let off into a beaker. If not clear, it is repeatedly returned to the filter until a clear filtrate is obtained. The residue is washed with a dilute hydrochloric-tartaric solution until the filtrate, even on prolonged standing, no longer gives a reddish precipitate with sulphuretted hydrogen. The washings are then added to the filtrate, concentrated on the water-bath, the excess of acid is neutralised with ammonia, and sulphuretted hydrogen is again introduced into the solution. The antimony sulphide precipitate must have a pure orange colour. Its conversion into antimony antimoniate requires much care and patience, and all the precautions laid down by Bunsen must be closely adhered to. In place of the porcelain cover, convex internally, the author uses a watch-glass during the oxidation with nitric acid, as in this manner the action of the acid can be better observed and regulated.

The purity of the ignited and weighed residue may be thus ascertained:—The crucible, without a lid, is placed in the reductive space of a large burner. On the internal sides of the crucible there soon appears a blackish grey shining layer of metallic antimony, and in a short time the entire contents of the crucible have disappeared if consisting of pure antimony antimoniate. Of course, the antimony cannot then be reserved as an exhibit. In many cases, where the quantity of tin oxide present is not too great, the best result is obtained by determining the antimony from the difference of two weighings.

(To be continued).

ASH DETERMINATION IN RAW SUGARS.*

By F. G. WIECHMANN, Ph.D.

THE method formerly used for determining the ash in sugar consisted in carbonising the sample at a low heat, extracting the soluble salts from the carbonaceous mass by boiling water, igniting the residue, adding this ash to the aqueous extract obtained, and evaporating completely to dryness.

In 1864, Scheibler† published his method of incinerating sugars with sulphuric acid, which proved to possess great advantages over the former method in ease and dispatch of execution. It was only given to the world after the originator had tested it for five years, and carried out by it more than two thousand determinations.

Of course, neither Scheibler's method nor the method of incineration referred to pretend to give the actual amount of salts in the sugar, for by the former the salts are changed into sulphates, while combustion transforms them into carbonates or oxides. Landolt,‡ for instance, holds that the weight of the salts in beet-sugars is about twice the weight of the ash found by analysis.

As the molecular weight of the sulphates is greater than that of the carbonates, Scheibler subtracts 10 per cent from the weight of the sulphate ash, and states that the result is then identical with, or at least corresponds very closely to, the values obtained by the other method. In his paper previously referred to, several analyses are cited in support of this claim.

A cursory search through the literature at hand shows that the method of incinerating with sulphuric acid has been examined into by several chemists, of whom some do not share Scheibler's estimate of its value.

Boivin and Loiseau§ endorsed the method as capable of giving constant results if the combustion were slowly conducted, but claimed that it yielded exceedingly variable values if this condition were not fulfilled. As their experiments, however, were partly carried out under con-

ditions entirely different from those prescribed by Scheibler, their verdict is of little importance.

Dubrunfaut* studied the method chiefly as to the value of the factor 0.9 used in transforming the sulphates into carbonates, and expresses himself as follows:—"In this method sulphuric acid is substituted for the chlorine of the chlorides and for the carbonic acid which is yielded by the organic acid salts and the nitrates. As the relations between the organic acid salts, the nitrates, and the chlorides are very variable in beets, in the molasses, and in the sugars, it stands to reason that the factor 0.9 is nothing but a general average factor which, in many cases, may be considerably far from the truth."

Violette, in an article published in 1873,† states that "this method of incinerating sugars with sulphuric acid, generally adopted at the present time, gives the weight of the ash higher than the true weight of the ash in raw sugars, and this difference is the greater the richer the ash is in salts of soda and alkaline carbonates."

The following year this author wrote a paper entitled‡ "Determination of the Relation between the Real Ash and the Sulphated Ash in the Products of the Sugar Industry," in which he published a table giving a *résumé* of his researches. This table embraces the analysis of raw sugars, beets, and molasses, and shows the difference between the amounts of the real ash and the values obtained by the sulphuric acid method. The differences exhibited are very considerable in many cases.

H. Leplay, in his "Chimie Théorique et Pratique des Industries du Sucre," p. 207, commenting on these figures and on the conclusions which Violette bases on them, says:—"The most striking conclusion to be drawn from the analyses of M. Violette is that this factor is very variable and does not offer sufficient guarantee of correctness for the transformation by calculation of the weight of the sulphates found by analysis into carbonates."

On the other hand, Von Lippmann,§ after giving the analysis of a carbonate ash of a representative sample of beet-sugar, which will be referred to later on, says:—"It seemed of interest to ascertain the relation of this carbonate ash to the sulphate ash which might be obtained from it. Ten grms. of ash were calcined with sulphuric acid in a platinum muffle, and 11.2008 grms. sulphate ash were obtained. If one-tenth be deducted from this figure, as is done in commercial practice, 10.0807 grms. results, instead of 10 grms., thus demonstrating most perfectly the correctness of Scheibler's factor, 0.9, for this case."

Although primarily applied to the determination of ash in beet-sugars and beet-root products, Scheibler's method won its way into general favour, and soon came to be almost the only method employed in practice, and to be applied indiscriminately to the ash determination of all sugars.

In the course of some research work recently carried out by the author, quantitative determinations were made of the ashes of sugars from various countries.

The scheme of analysis adopted was the following:—

Ten grms. of sugar were dissolved in hot water and filtered;|| the residue was thoroughly washed with boiling water, and the filtrate and washings evaporated to dryness. The mass was carefully carbonised, and then extracted with boiling water until nitrate of silver no longer gave the reaction for chlorine. Solution 1 was evaporated to small bulk. Residue 1 was dried, ignited, and weighed. This weight was noted as insoluble ash. The solution and the ash obtained were combined, hydrochloric acid was added, and the solution evaporated to dryness. All the chlorine was then driven off, the residue taken up

* *Journal des Fabricants de Sucre*, 18 Decembre, 1870.

† *Annales de Chimie et de Physique*, 4th Series, vol. xxix., p. 514.

‡ *Journal des Fabricants de Sucre*, Octobre 22, 1874.

§ *Zeitschrift des Vereines für Rubenzucker-Industrie*, vol. xxxi., 1881, p. 399.

|| This was done in every case to have all the analyses made under the same conditions; in most instances it was imperative, for the inorganic suspended impurities (sand, clay, &c.) in a sample often weighed more than the total sugar-ash.

* From the *School of Mines Quarterly*, Vol. xi., No. 1.
† *Zeitschrift des Vereines für Rubenzucker-Industrie*, vol. xiv., p. 188.

‡ *Ibid.*, vol. xviii., p. 68.

§ *Journal des Fabricants de Sucre*, 6 Fevrier, 1868.

with water and a little hydrochloric acid, and filtered. The insoluble residue in the filter was thoroughly washed, and the washings added to the filtrate. Residue 2 is silica. To filtrate 2 added ammonia hydrate, boiled, and filtered. The Residue 3, iron and alumina, was thoroughly washed, and the washings added to filtrate. To filtrate 3 added ammonium oxalate and evaporated to dryness. The ammonia was burned off, and the oxalates changed to carbonates by adding a little ammonium carbonate, and then again driving off the ammonia. The mass was then taken up with water, filtered, washed, and the washings added to the filtrate. This residue, Residue 4, consists of carbonates of calcium and magnesium. The filtrate was evaporated to small bulk, and moistened with ammonium carbonate.

The evaporation was then continued to dryness, the ammonia cautiously driven off, and the residue weighed. This gave the alkalies in the form of carbonates, and this weight, added to the insoluble ash previously determined, represents the total carbonate ash.

This method, while yielding carbonate ash, avoids the possible loss of alkalies by volatilisation, and practically corresponds to the method in vogue before the introduction of Scheibler's process.

As the data thus obtained were carbonate ash determinations of sugars entirely different in their composition from beet-sugars, and of a description that, at least to the writer's knowledge, has not been much studied, it was decided to make on them ash determinations according to Scheibler's method in order to learn whether the results yielded by the two methods would correspond.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 17th, 1890.

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

Messrs. Fred. A. Anderson, Henry H. Bunting, P. A. Cobbold, and D. S. MacNair were formally admitted Fellows of the society.

Certificates were read for the first time in favour of Messrs. James Kear Colwell, 2, Lloyd Street, Lloyd Square, W.C.; William Tait, 115, Rylston Road, Fulham, S.W.

The following were elected Fellows of the Society:— Joseph Barker, Charles Ridgeway Beck David Corrie, William Dixon, Thomas Flower Ellis, Frederick John Hambly, Andrew Cowan Holburn, B.Sc., C.E., William Frederick Laycock, Ph.D., Arthur Sheridan Lea, Herman Lescher, John Stewart MacArthur, Henry D. Mosenthal, George Müller, Ph.B., E. H. Neville, M.A. Camb., Harold Picton, Ernest George Scott, James Sibun, Alexander Smith, Willis Brewin Shuttlewood, Frederick Richard M. Stone, James S. H. Walker.

The following papers were read:—

28. "Phosphorous Oxide." Part I. By T. E. THORPE, F.R.S., and A. E. TUTTON.

The authors describe a method of making phosphorous oxide in quantity by burning phosphorus in air. Pure phosphorous oxide melts at 22.5°, and solidifies at 21°. It boils unchanged in an atmosphere of nitrogen or carbon dioxide at 173°. Vapour density determinations made by Hofmann's method show that its molecular weight corresponds to the formula P₄O₆. In this respect it is analogous to arsenious and antimonious oxides, which are respectively represented by the formulæ As₄O₆ and Sb₄O₆. A determination of the molecular weight by Raoult's method, using benzene, which has no chemical

action on the substance, as a solvent, also indicated the formula P₄O₆.

On heating phosphorous oxide to about 300°, it is decomposed, and at 440° it is wholly changed into phosphorus and phosphorus tetroxide, 2P₄O₆ = 3P₂O₄ + 2P. Phosphorous oxide is readily acted on by light, and in bright sunshine its colour rapidly becomes yellow, and eventually dark red. Observations by Captain Abney show that the violet rays are most active in effecting the change. Curves showing the results of the photometric observations are given in the paper.

As first prepared, phosphorous oxide is obtained in minute crystals, aggregated into a snow-like mass. On allowing the melted oxide to cool, it solidifies in the form of thin prisms capped by pyramids; the crystals frequently attain the length of an inch or more.

The crystals appear to belong to the monoclinic system, and exhibit the pinacoidal faces—

$$a = \{100\} \infty P \infty \text{ and } b = \{010\} \infty P \infty,$$

several prism faces, a pair of orthodomes, and a pair of complementary pyramidal faces. The extinctions upon *a* are parallel to the prism edges, whilst those upon *b* make an angle of about 20° with the prism edges. When the crossed Nicols are parallel to the orthopinacoidal edges, the brush passes across the centre of the field in a line parallel to the vertical axis. The optic axial plane, therefore, appears to be the symmetry plane *b*. The crystallographical relations of P₄O₆, As₄O₆, and Sb₄O₆ are discussed in the paper.

The relative density of liquid phosphorous oxide was found to be 1.9358 at $\frac{24.8}{4}$. Its thermal expansion, as determined by dilatometrical measurements, is expressed by the formula—

$$V = 1 + 0.000913777t - 0.00011175t^2 + 0.00038507t^3.$$

Its relative density at the boiling-point is found to be 1.6859, whence its specific volume is 130.5. The bearing of this observation on the question of the constitution of phosphorous oxide, and on the question of the varying specific volume of combined phosphorus, is then discussed. Previous observations by one of the authors had shown that the specific volume of combined phosphorus is about 25. From the observations of Pisati and De Franchis, and of Ramsay and Masson, the specific volume of free phosphorus is found to be about 20.9. If all the oxygen in phosphorous oxide be considered as single linked, or, in other words, to have the specific volume 7.8, the specific volume of the phosphorus in phosphorous oxide is 20.9, agreeing with the observations of Ramsay and Masson.

The conclusion to which the authors come is that, whilst the variation in the specific volume of phosphorus may be related to the atomic arrangement of the phosphorus atoms in the molecule of the element, and in that of the phosphorous oxide, both of which contain the same number of phosphorus atoms, this variation is not necessarily dependent on or related to the differences in the combining power of the element.

Determinations of the refractive index of phosphorous oxide for the red lithium line, the sodium D line, the green thallium line, and the three brightest hydrogen lines corresponding to C, F, and G have led to the following general expression for the refraction of liquid phosphorous oxide at 27.4°:—

$$\mu = 1.5171 + \frac{817,670}{\lambda^2} - \frac{316,590,000,000}{\lambda^4}.$$

The calculated value of μ for the line A (wave-length 7604) is 1.5311: for a ray of infinite wave-length it is the first term of the above expression, viz., 1.5171. As the rel. den. of liquid phosphorous oxide at 27.4 is 1.9300, the refraction equivalent of phosphorous oxide for *a* is—

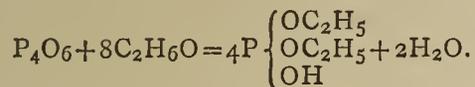
$$\frac{220 \times 0.5311}{1.93} = 60.5$$

for a ray of infinite wave-length it is 58.9.

The bearing of this observation on the refraction equivalent of phosphorus is then discussed.

Contrary to the usual statement of the text-books, cold water has very little action on phosphorous oxide: many days elapse before even a small quantity is dissolved; it then forms phosphorous acid, H_3PO_3 . Hot water acts upon P_4O_6 with explosive violence, forming the red suboxide, phosphoric acid and spontaneously inflammable phosphorated hydrogen.

Caustic alkalies act similarly. On adding ethyl alcohol to the oxide it at once ignites, but with care the two compounds may be caused to interact to form *diethyl phosphite* or *diethyl phosphorous acid* in accordance with the equation—



This substance, which will be described more fully in a subsequent paper by one of the authors and Mr. Parker North, is a liquid of intensely disagreeable smell, of rel.

den. 1.0749 at $\frac{15.5}{4}$, and boiling at $184-185^\circ$. Ether, carbon bisulphide, and benzene dissolve phosphorous oxide unchanged.

Phosphorous oxide spontaneously oxidises to phosphorus pentoxide on exposure to air or to oxygen, and the process of oxidation is attended under diminished pressure by a faint luminous glow. No ozone is formed as the oxidation proceeds. On gently warming the oxide in oxygen, the glow gradually increases in intensity until it passes into flame. In warm oxygen the melted oxide at once ignites and burns with great brilliancy. Care, therefore, is necessary in distilling large quantities of phosphorous oxide to avoid the free access of air; otherwise dangerous explosions may occur.

In contact with ozone, phosphorous oxide glows at the ordinary temperature and pressure.

A small quantity of the oxide thrown into a jar of chlorine at once inflames, but on leading a slow current of the gas over the cooled oxide it is gradually converted into phosphorus oxychloride and the metaphosphoryl chloride of Gustavson: $P_4O_6 + 4Cl_2 = 2POCl_3 + 2PO_2Cl$.

Phosphorous oxide has a well-marked physiological effect, and it is not improbable that the action hitherto attributed to phosphorus, especially as regards its influence on the glycogenic functions of the liver and on tissue change, may be really due to this substance. It is well known that persons employed in the manufacture of lucifer-matches are occasionally attacked by caries of the lower jaw; this is not due to the action of the phosphorus after absorption into the circulation, but to the direct effect of the fumes upon the bone itself: for it has been found that when a bone of an animal fed by phosphorus was exposed no carious change took place; but if one were exposed to the fumes caries was produced, and amongst lucifer-match makers it has been noticed that only those who have carious teeth suffer from necrosis of the jaw (T. Lauder Brunton, "Pharmacology, &c.," 771). The fumes from phosphorus consist largely of phosphorous oxide; by drawing air over phosphorus without allowing it to ignite, and passing the fumes through a narrow strongly cooled tube, a deposit is obtained which melts with the warmth of the hand and gives the reactions for phosphorous oxide. Moreover, the smell of the product is identical with that of pure phosphorous oxide, and it is also identical with the peculiar smell noticed in a lucifer-match manufactory during the making and handling of the "composition" with which the splints are "tipped," and which hangs about the benches where the "boxers" are at work. It is highly probable, as Schönbein long ago surmised, that phosphorus vapour as such is odourless, and that the smell which phosphorus ordinarily possesses is a mixture of that of ozone and of phosphorous oxide.

The authors are continuing the study of this compound, and have already investigated the action upon it of

ammonia, sulphur, sulphuric acid, the chlorides of phosphorus, &c., and they are also engaged in experiments on its behaviour with a number of organic substances, and they promise a further communication on an early date.

29. "The Action of Chlorine on Water in the Light, and the Action of Light on certain Chlorine Acids." By Professor A. PEDLER.

After referring to the somewhat discrepant statements on record regarding the action of chlorine on water in the light, the author describes a long series of experiments made in Calcutta, where the intensity of light is such that a strong solution of chlorine in water, when exposed to the full blaze of the sun during the hot season, is actually seen to effervesce very decidedly. The results show that interaction takes place only under certain conditions, and that more than one change is possible.

In a first series of experiments, known volumes of chlorine and water enclosed in tubes were exposed to light, and at the conclusion of the exposure the tubes were opened under water: the contraction having been measured, the residual chlorine, and subsequently the oxygen which had been produced were estimated. Using 83.5 c.c. chlorine and 4 c.c. water, quantities in the ratio $Cl_2 : 64H_2O$, practically no action was found to have taken place after exposure during a month to strong diffused daylight, and during a second month to the direct action of tropical sunlight; but, the ratio being $Cl_2 : 88H_2O$, about 29 per cent of the chlorine was found to have been active, 6.5 c.c. of oxygen being liberated. Supposing action to have taken place according to the equation $2H_2O + Cl_2 = O_2 + 4HCl$, 7 c.c. of oxygen should have been obtained, an indication that a very small portion of the chlorine had undergone oxidation. The general result of a number of experiments of this kind was that, even in very strong tropical sunlight, water and chlorine interact to but a very slight extent when there are about 100 times as many molecules of water present as of chlorine; when the proportion is about $150H_2O : Cl_2$, action takes place to the extent of perhaps nearly 50 per cent of the possible amount; and, when more than $400H_2O : Cl_2$, interaction takes place much more rapidly, but even then only to about four-fifths of the theoretically possible extent. As the proportion of water is increased, the amount of chlorine which is oxidised becomes somewhat larger.

Chlorine-water saturated at $30-32^\circ$, the average working temperature in a Calcutta laboratory, contains chlorine in about the ratio $708H_2O : Cl_2$. Experiment shows that, when exposed to direct tropical sunlight, such water undergoes decomposition practically entirely in the sense of the equation $2H_2O + 2Cl_2 = O_2 + 4HCl$, an exceedingly small amount of chloric acid being formed. On exposing it to strong diffused daylight inside an open south verandah, either hypochlorous or chloric acid, or both, were formed in somewhat variable amount, the proportion of oxygen being much below that obtained in the previous experiments in bright sunlight. On exposing the chlorine-water to very moderate diffused light opposite the window in a room having a north light, very little, if any, oxygen was liberated, but the chlorine became oxidised to hypochlorous and chloric acids. In no case could chlorous acid or hydrogen peroxide be detected.

On exposing dilute solutions of hypochlorous acid to light, it was found that both oxygen and chloric acid were produced, the proportion of oxygen being larger the greater the intensity of the light. Solutions of chloric acid underwent little or no change.

The author concludes that in its first stages, at all events, the action of chlorine on water is quite similar to that which it exercises on dilute cold solutions of sodium and potassium hydroxides; and that in the subsequent stage it is very similar to that effected in the case of more concentrated and hot solutions of the two hydroxides.

30. "Note on the Explosion of Hydrogen Sulphide and of Carbon Bisulphide with Air and Oxygen. By Professor A. PEDLER.

The author finds that when a mixture of hydrogen sulphide, air, and oxygen is exploded, a normal result is obtained, sulphur dioxide and water being formed. But when carbon bisulphide vapour is similarly treated, a not inconsiderable proportion of the nitrogen of the air becomes oxidised; and after the explosion contraction continues to take place, owing to the formation of sulphuric compounds (chamber crystal, &c.) under the combined influence of the moisture present and the oxide of nitrogen. The results of a large number of experiments are described, showing the effect of various proportions of oxygen and air.

31. "The Action of Light on Phosphorus, and on Some of the Properties of "Amorphous" Phosphorus. By Professor A. PEDLER.

As part of an extensive series of experiments on the action of strong light on substances, the author has studied its effect on phosphorus, and has thereby been led also to examine and compare the several forms of allotropic phosphorus, viz., that produced by the action of light only, that produced at moderate temperatures, the commercial form, and also rhombohedral or metallic phosphorus prepared by dissolving phosphorus in lead at high temperatures.

The conclusion is arrived at that the term "amorphous phosphorus" is a distinct misnomer, and that, so far from commercial "amorphous" phosphorus constituting a separate allotropic modification of the element, it is in reality the same substance as the form called rhombohedral or metallic phosphorus, the very slight differences in character noticed between the substances in question being explained by the difference in the state of division and the slight variations conditioned by their mode of formation. Whether the term amorphous phosphorus can be truly applied to the forms made by the action of light is open to grave doubt; even in this case there appears to be distinct evidence of crystalline form, although, in some instances, a form which appeared to be amorphous was obtained. It is suggested that it would be better to altogether discard the use of the term *amorphous phosphorus*.

The author finds that when phosphorus is exposed to light in contact with liquids containing oxygen, such as alcohol, it tends to enter into action with them. He arrives at the conclusion that neither *in vacuo* nor at ordinary pressures is there any change whatever of red into ordinary phosphorus at 260° as ordinarily stated; and that, practically, no change occurs up to temperatures of nearly 358°, above which, *in vacuo*, change takes place, but exceedingly slowly, even up to 445°. He also describes experiments which tend to show that red phosphorus is not permanent in air, as commonly supposed.

32. "The Action of Phosphoric Anhydride on Fatty Acids." By F. S. KIPPING, Ph.D., D.Sc.

In a previous preliminary note (*Chem. Soc. Proc.*) the author has described the formation of the ketone stearone by the action of phosphoric anhydride on stearic acid; he now gives a detailed account of his experiments with this acid, and also describes the application of the same method to the preparation of dihexyl ketone, $(C_6H_{13})_2CO$, from heptylic acid. Two experiments gave 33 and 25 per cent respectively of the theoretical amount of dihexyl ketone; the yield of stearone being 40—42 per cent of the theoretical.

Dihexyl ketone is found to have the properties already described by Uslar and Seekamp (*Annalen*, cvii., 179). Its hydroxime and hydrazone were both obtained as yellow oils. Dihexyl carbinol was prepared by adding a large excess of sodium to an ethereal solution of the ketone placed in a flask, together with moderately concentrated soda solution; it crystallises from dilute alcohol in plates melting at 41—42°.

NOTICES OF BOOKS.

Pictorial History of Ancient Pharmacy, with Sketches of Early Medical Practice. By HERMANN PETERS. Translated from the German, and revised, with numerous additions, by Dr. WILLIAM NETTER. Chicago: G. P. Engelhard and Co. 1889. 8vo., pp. xiv.—184. Illustrated, cloth.

THOUGH ostensibly a work on pharmacy, these chapters of history contain much information on matters pertaining to chemistry in its early phases. The volume is not merely a translation of Mr. Peters' "Aus Pharmaceutische Vorzeit," as the American editor has added many features of especial interest to English readers, and has re-written some of the chapters in the light of researches not pursued by Mr. Peters. Professional chemists and pharmacutists will find this well illustrated work a mine of information, the materials having been gathered with much diligence from sources not readily accessible. Chapter I., Tutelar Gods and Patron Saints of Pharmacy, treats of the myths of ancient Greece, and of medicine and surgery in symbolism. Chapters II. to V. treat of Pharmacy from the middle ages to the eighteenth century among the Chinese, Egyptians, Germans, and Anglo-Saxons, with sketches of the laws enacted at different periods, and notices of early literature. Chapter VI. deals with Distilling Apparatus in its various forms, and the next chapter with Early Chemico-Pharmaceutical Stoves and Fireplaces. Chapter VIII. discusses Ancient Pharmacopœias. Chapter IX., Medical Superstitions. Chapter X., Pharmacy and the Art of Love. Chapter XI., Alchemy.

As may be judged from the variety of topics here named, the author has not attempted to be exhaustive in each chapter, but in writing on alchemy and medicine he has ever borne their pharmaceutical bearings in remembrance. Chapter IX., on Medical Superstitions, is not so full as the well-known work of Dr. Pettigrew, yet it supplements the latter by contributing data from German sources.

The charm of this volume is, however, in its reproductions of old engravings, interior of chemist's shops ("drug-stores" in American English), portraits, facsimiles of title-pages of rare works, representations of ancient apparatus, and cuts of alchemical metaphors, gleaned from original sources. Not every student of chemistry is the owner of an alchemical library, and few have the time to search the shelves of great libraries for the quaint and curious publications of the sixteenth and seventeenth centuries; therefore this volume places in his hands a choice selection of the most interesting plates, with explanatory text, at a very moderate cost. We note the rude cut of a chemist's shop, dated 1450, another of 1536, and another of 1733, quite elaborate in decorations. We note the facsimile of a journeyman's certificate, 1743, and several reproductions from Maier's "Atalanta Fugiens," 1618, much prized by bibliophiles.

The author states that prominent among the early Virginian colonists was the surgeon and apothecary Dr. Edward Heldon, who had been a friend and pall-bearer of Shakespeare. The first shop distinctively devoted to pharmacy in Boston was opened, in 1646, by William Davies. The first patent medicine was called "Tuscarora Rice," sold as a consumption cure by a Mrs. Masters in 1711. Adulteration began to be practised quite early in New York, coloured sawdust having been sold for rhubarb. In the chapter on alchemy the translator adds some information of Peter Woulfe, of Barnard's Inn, one of the last of English believers in the hermetic art, and states that as recently as 1880 an American named Wise duped a member of the Rohan family (a collateral descendant of the "necklace cardinal") by pretending to make gold. Wise secured a large sum of money and then disappeared.

In the first paragraph of Chapter XI. the author quotes

appropriately Mr. Crookes's address before the B.A.A.S., with reference to the evidence of the decomposition of the elements afforded by the aid of spectrum analysis.

The work seems to have gained rather than lost by the translation; we hope the translator will be encouraged to do as well for Peters's "second series," recently published, as he has for the first.

H. C. B.

A Technological Dictionary of Insurance Chemistry. By W. A. HARRIS, F.R.S.S.A., F.S.S., Phoenix Fire Office Liverpool.

NOT much reflection will be needed to convince our readers that chemistry has much light to throw upon fire insurance. In the absence of chemical knowledge it is impossible to decide what substances are dangerous, *per se*, or in contact with other bodies, or under special conditions of temperature or moisture. To supply such information has been the author's object. He has set himself "the task of endeavouring to find a royal road to an accurate estimation of the various forces at work in the creation of heat, fire, and explosion." This task he has executed very judiciously and successfully. He has rejected chemical formulæ, which, invaluable as they are to the professional student, are simply an encumbrance to persons who are concerned merely with results, without reference to the processes by which they have been reached.

We find here information of a novel and startling character, but, as a rule, unexpected as the author's conclusions often are, we cannot pronounce them out of the question. In some instances, however, we find substances or manufacturing processes set down as dangerous when both theory and experience inform us to the contrary. Thus the manufacture of albumen—egg or blood—is said to be "of a very hazardous character." Now, we must point out that both the raw materials, the finished products, and any refuse are exceedingly incombustible, and, from their non-porous character, incapable of absorbing and condensing gases and vapours. The temperatures used in the operation are, of course, exceedingly low,

On the other hand, that certain manures—dung-hills, stable manure, sewage manures, &c.—being of a fibrous or pulverulent texture, are liable to heating, need not be wondered at. The heat may, perhaps, rarely, if ever, rise to what is commonly known as combustion, but it often reaches a point which deteriorates the manure. Repeated attention is drawn to the danger of organic dusts of various kinds, which, if diffused in common air, may even form very dangerous explosive mixtures. Still less are the public alive to the fact that substances which when dry are perfectly safe may become capable of what is known as spontaneous combustion if slightly damp. It is, we believe, on record that conflagrations are most frequent and most destructive in damp weather.

The author further calls public notice to the neglected fact that wood-work which has for a long time been exposed to temperatures not exceeding that of boiling water undergoes a chemical change and becomes dangerous. Thus beams which have been in contact with steam or hot water pipes have been found charred to some depth. The obvious inference is that such pipes should be made to rest upon incombustible matter only.

The dangers of cotton-waste moistened with oil and allowed to lie in a neglected corner are repeatedly enforced. The number of factories which are burnt down from neglect of this kind is very serious.

Cases are given of accidents from the use of saw-dust to soak up spillage of oils, glycerin, &c. It may also fire if injudiciously mixed with certain acids or salts. Indeed, it should always be looked upon with suspicion, and never let lie in works or warehouses.

Many errors may be found in this work, but as they have no direct bearing on the author's subject they do not

need to be specified. Thus, whether a dye-wood is obtained from India or South America does not affect its dangerous character when finely ground, moistened, and allowed to lie in heaps.

When, however, we remember that water-gas contains from 30 to 40 per cent of carbon monoxide, we cannot help admiring the rashness of the medical men at Boston who have asserted that this mixture is not more dangerous to health than coal-gas.

A little expected, though perfectly conceivable, source of danger is mentioned as existing in leaden roofs and gutters. A deposit is formed which seems capable of igniting in a current of air, and of then setting fire to combustible materials.

The part played by rats in occasioning unaccountable conflagrations is not overlooked. These vermin, it appears, have developed a taste for lucifer matches, which they carry off to their holes and leave in contact with pilferings in the shape of tallow, fragments of paper, &c. It would be wise to allow no matches on ship-board or in warehouses except in iron boxes.

Celluloid is not without its perils. A comb made of this material is said to have become ignited from exposure to a heat of 180° F. As it was at the moment fixed in the hair of a little girl, who was sitting before the fire, the consequences were highly unpleasant.

This work is one of great value not merely to fire insurance companies and their officials, but to manufacturers, warehousemen, shippers, and sea captains, who may derive from it some most important lessons. Even the general public is concerned, as it may be seen from truths brought into prominence in the introduction. Our total national loss from fires is estimated at fourteen millions sterling yearly! Ten millions are annually paid by British insurance companies, and the remaining four millions will not do more than cover the loss on uninsured property. The world's total loss is estimated at sixty-seven millions! This fearful waste, as the author shows, is largely preventible. Hence we think that a debt of gratitude is due to him for the cautions which he gives in so plain and intelligible a manner.

A Treatise on Chemistry. By Sir H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Vol. III. The Chemistry of the Hydrocarbons and their Derivatives; or, Organic Chemistry. Part II. New and thoroughly Revised Edition. London and New York: Macmillan and Co., 1890.

THE present edition of this work has been very thoroughly revised. Much novel matter, as it is pointed out in the Preface, has been introduced, and the derivatives of furfuran, pyrrol, and thiophene will be described in a future volume, along with the derivatives of pyridene and quinoline. The work in its present form displays the thoroughness which won for the former edition such general approbation. Constant and abundant reference is made to the original memoirs used in compilation.

Under Tartaric Acid we find mention of the treatment which Scheele's first scientific paper underwent. Bergman, who had undertaken to lay the memoir before the Stockholm Academy, neglected so to do, and when Scheele rewrote the paper and entrusted it to the Secretary of the Academy, Retzius, the latter edited it in such a manner that much of the credit of the investigation seemed due to him.

We find no mention of any method of distinguishing beet-sugar from cane-sugar. Experienced merchants are said to discriminate between them by taste, and bees are certainly able to do the same, and reject beet-sugar if the product of the cane is accessible. This probably depends on the presence of traces of impurities, which, in practice, are never entirely eliminated.

Speaking of the deplorable explosion of gun-cotton at Stowmarket, in 1871, the authors say that "some of the stock of gun-cotton contained acid, owing either to in-

sufficient washing or to the felonious addition of acid to the properly washed gun-cotton." The facts ascertained during the enquiry, we should submit, entirely eliminate the former alternative. In each of a number of cases which had been sent to Upnor Castle a couple of days before the explosion one disc of discoloured gun-cotton was found, evidently in course of decomposition. The rest of the contents of the cases were sound. Had the cotton been imperfectly washed traces of decomposition would not have been confined to single discs.

The index is very extensive, and, as far as we have been able to test, singularly correct.

CORRESPONDENCE.

VOLUMETRIC ANALYSIS OF COPPER.

To the Editor of the *Chemical News*.

SIR,—I am glad to see a note on the "Volumetric Analysis of Copper" by Mr. R. A. Fessenden in the *CHEM. NEWS*, vol. lxi., p. 183, and that he advocates the use of sodium carbonate instead of ammonia in a solution to be titrated by cyanide of potassium. The writer did the same in the *CHEM. NEWS*, vol. lviii., p. 131, and is pleased to see the confirmation of Mr. Fessenden.—I am, &c.,

J. L. DAVIES.

Hafod Isha Works, Swansea.
April 23, 1890.

MILK ANALYSIS.

To the Editor of the *Chemical News*.

SIR,—I have read Mr. Walls' article on "Milk Analysis" in the *CHEM. NEWS*, vol. lxi., p. 162. Essentially, the same process was described by me on May 27th, 1887, in a paper read before the Royal Society of Canada, of which I enclose a copy. The method "hat sich bewährt," as the Germans say, is always employed here, and has been adopted in some other laboratories. The asbestos fibre used is that produced largely in Canada, and is really asbestiform serpentine or crysotile.—I am, &c.,

THOMAS MACFARLANE
(Chief Analyst I. R. D.).

Laboratory of the
Inland Revenue Department,
Ottawa, April 15, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 15, April 14, 1890.

Artificial Production of Silk.—Emile Blanchard.—The writer suggests the possibility of obtaining silk by an artificial digestion of the leaves of the mulberry, followed by dialysis. He does not come to any definite conclusion.

Action of Nitric Acid upon Aluminium.—A. Ditte.—Both with dilute nitric and sulphuric acid the metal becomes covered with a gaseous stratum which prevents its contact with the acid. If the experiment is prolonged for some days bubbles of gas are slowly formed upon the metal, which dissolves little by little. In a vacuum the action is more rapid. There is no liberation of hydrogen; in very dilute nitric acid there is given off a mixture of nitrogen and nitric oxide, the former predominating,

whilst ammonia remains in the liquid. All these reactions are exothermic, and sometimes one of them is produced almost exclusively. In a vacuum the nitric acid is converted into neutral aluminium nitrate; but the reaction does not then stop, as the nitrate, like the sulphate, is attacked by aluminium, and a sub-salt is formed. If aluminium is heated in a solution of its nitrate bubbles of hydrogen are given off, and if the heating and the concentration of the liquid are kept constant there appears a white granular precipitate of basic nitrate.

Preparation of Hydrobromic Acid.—A. Recoura.—The author causes sulphuretted hydrogen, furnished by a continuous apparatus, to pass through bromine in a tall narrow bottle, surmounted by a stratum of water, or preferably of hydrobromic acid. The gas which issues from this bottle, which is hydrobromic acid, traverses a second bottle containing a solution of potassium bromide, holding a little red phosphorus in suspension. This second bottle entirely arrests all vapours of free bromine escaping from the first bottle. The gas given off does not contain a trace of hydrogen sulphide, and is always pure hydrobromic acid, however rapid the current.

Oxidation of Hypophosphorous Acid by Palladium Hydride in the Absence of Oxygen.—R. Engel.—Palladium hydride determines the oxidation of hypophosphorous acid, yielding phosphorous acid and liberating hydrogen. The hydride seizes an atom of the hydrogen of the hypophosphorous acid and gives it up again immediately in the free state. The residue of the hypophosphorous acid completes its molecule by decomposing water, fixing hydroxyl, and liberating a further atom of hydrogen. The action seems to continue indefinitely. With 0.5 grm. of palladium hydride the author has decomposed the phosphorous acid from 500 grms. barium hyposulphite without any decrease in the activity of the precipitate.

Oxidising and Decolourising Properties of Charcoals.—P. Cazeneuve.—If the decolourising properties of charcoals are chiefly due to a mechanical fixation of the colours upon the carbonaceous matter, we must not overlook the action of the oxygen condensed in the pores in a state comparable to ozone. This oxygen has a destructive action upon certain colours, whilst, on the contrary, it determines the appearance of others which are products of oxidation.

On the Camphoric Acids.—E. Jungfleisch.—A study of the solubilities of ordinary dextro-camphoric acid, of the levo-camphoric acid of *Matricaria*, and of the levo-acid of transformation.

On Potassium Malonate, Quadromalonate, and Quadroxalate.—G. Massol.—A thermo-chemical paper which does not admit of useful abstraction.

Extraction of Raffinose from Molasses. Separation of Raffinose and Saccharose.—L. Lindet.—Four successive operations are necessary for the extraction:—(1) Purification and decolouration of the molasses by means of mercury sulphate, baryta, and methylic alcohol. (2) Dehydration of the methylic solution by means of lime at the boiling-point of methylic alcohol. (3) Precipitation of the methylic solution by ordinary alcohol. (4) Crystallisation of the precipitate in ethyl alcohol at 80–85°.

Zeitschrift für Analytische Chemie.
Vol. xxviii., Part 6

Determination of Traces of Iron in Alums and Aluminium Sulphate.—R. R. Tatlock.—From the *Journal Soc. Chem. Industry*.

Determination of Gallium.—Lecoq de Boisbaudran (*Annales de Chimie*) calls attention to the volatility of gallium chloride, Ga₂Cl₆, which occurs even in the evaporation of hydrochloric solutions. If sulphuric acid is added to the hydrochloric solutions no loss of gallium

occurs, even on heating the residue to dull redness. In evaporating hydrochloric solutions of gallium chloride in quantitative investigations, apparatus must be used which permits of condensation of fumes. The best absorbent is potassa-lye.

Method for Separating Gold, Platinum, Antimony, Arsenic, and Tin.—M. Silva (*Bull. Soc. Chimique de Paris*), MM. Dirvell and Bricout (*ibidem*) and Ad. Carnot (*Comptes Rendus*).—Already noticed.

Determination of Arsenic in Pyrites.—John Clark.—From the *Journ. Soc. Chem. Industry*.

Determination of Arsenic in Metallic Copper.—J. Clark.—From the same source.

Volumetric Determination of Phosphorus in Iron and Steel.—E. D. Campbell.—From the *Journal of Analyt. Chemistry*.

Detection and Determination of Iodine, Bromine, and Chlorine.—M. Dechan.—From the *Journal of the Chem. Society*.

Theophylline.—A. Kossel (*Ber. Deutsch. Chem. Gesellschaft*).—A base obtained from the extract of tea, $C_7H_8N_4O_2 + 2H_2O$, but distinct in properties from its isomers theobromine and paraxanthine. It is soluble in water, alcohol, and ammonia; it melts at 264° . It forms with hydrochloric acid, sulphuric acid, gold, and platinum chlorides, definitely crystalline salts, and with mercuric chloride a crystalline sparingly soluble double salt. If theophylline is evaporated with chlorine-water it gives a scarlet residue, passing into violet on the addition of ammonia. Theophylline is converted into caffeine by the introduction of a methyl-group.

Imperialine.—K. Fragner (*Ber. Deutsch. Chem. Gesells.*).—Already noticed.

Reactions of a Number of Alkaloids, Glycosides, and Kindred Bodies with Sulphovanadic Acid.—F. Kundrat.—Already noticed.

Reaction for Acetanilide.—M. Denigès (*Soc. Pharm. Bord. per Chemiker Zeitung*) points out that acetanilide, like all anilides, if boiled with an alcoholic solution of sodium hypobromide, gives an orange precipitate, and evolves a distinct odour of methyl cyanide.

Corresponding Reactions of Carbazol and Pyrrol.—S. C. Hooker.—Already inserted.

Reactions of Some Phenols and Analogous Bodies with Chloroform and Alkalies.—G. A. Raupenstrauch (*Soc. Pharm. Bordeaux and Chemiker Zeitung*).—The coloured reaction which occurs in the action of chloroform and the alkalies is characteristic for all phenols and pheneloid bodies, and does not, therefore, at once indicate the presence of any given body. The author boiled 2 c.c. of a solution of 1 part of a phenol in 1000 parts of chloroform in a test-tube with a fragment of caustic potassa and diluted to the margin of visibility. Carbohc acid gave a pale red tinge at 1 in 60,000; orthokresol a lilac at 1 : 80,000; meta-kresol more inclining to orange at the same dilution; thymol, a splendid purple red with a violet cast, 1 : 20,000; guajacol, cherry-red with a blue cast passing into violet blue, 1 : 100,000; resorcine, 1 : 500,000; β -naphthol, prussian blue passing into green and brown up to 1 : 80,000; salol gives the same colouration as carbohc acid; betol the same as naphthol; potassium hydroxide gives more intense colours than sodium hydroxide. In many cases alcohol and ether prevent the reaction. For detecting the phenols in other bodies (the contents of the stomach, in medicines, blood, urine) the author acidulates with dilute sulphuric acid and distils in a current of steam. The first drops which pass over generally contain the phenol. It is shaken up in a parting funnel with 5 c.c. chloroform; the latter is separated from the watery liquid and heated with a fragment of potassa. If the liquid contains alcohol it is first rendered alkaline, the alcohol is distilled off, the residue is acidified, and treated as above. The reaction

may be used for recognising chloroform, chloral, or iodoform.

The Distinction of Resorcine from Carbohc and Salicylic Acids.—H. Bodde.—From the *Analyt and Nederl. Tijdschrift Pharmacie*.

Coloured Reactions and Aldehydic Character of Woody Fibre.—E. Nickel.—No particulars are given.

Detection of Saccharine (Benzoic Sulphinide).—B. Haas (*Chemiker Zeitung and Deutsche Chemiker Zeitung*).—The author condemns the method of Bornstein and gives the preference to the method of Schmitt.

Detection of Chlorine, Bromine, Iodine, and Sulphur in Organic Matter.—C. W. Marsh.—From the *American Chemical Journal*.

Determination of Carbon and Hydrogen by Combustion.—W. L. Dudley.—From the *American Chemical Journal*.

Determination of Tannin.—M. Counciler and Von Schröder.—A reply to the objections urged against the author's method by Simand. The necessity of operating in dilute solutions is shown. The method is, in many cases, preferable to that of Löwenthal, e.g., in the case of extracts of pine-bark.

A New Form of the Hide Filter.—L. Schreiner (*Gerber*).—The apparatus is shown in an accompanying cut. J. Meerkatz has found it possible to use the gravimetric process for determining tannin in acid liquors by previously neutralising with barium carbonate.

Detection of the Elements of the Tissues of Wheat and Rye-Meal.—P. Soltsien (*Pharm. Zeitung*).—Already inserted.

Examination of Butter.—This bulky compilation does not admit of useful abstraction.

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.

A Supposed New Gaseous Element.—The *Chemiker Zeitung* gives an account of a discovery made in Damara Land which appears to be of profound interest. A mining engineer of the name of Lauer, prospecting for gold, came upon a group of funnel-shaped depressions in a tract of weathered diabase. Whilst the ground was elsewhere of a reddish colour (from ferric oxide), in the immediate neighbourhood of these depressions it was of a greenish-grey. There was not a trace of even the lowest vegetation; dried insects and the remains of antelopes, jackals, and lizards, all displayed a remarkable change of colour. One of the party had in his hat a branch of a shrub, which in a very short time lost its green colour and assumed a violet blue, whilst the beards and hair of the travellers appeared as if powdered over with white. A peculiar odour was perceived, intermediate between musk and mercaptan, and on bending down over the fumaroles a slight humming sound was perceived. Three empty bottles were filled with the gas and forwarded to Dr. Antsch, a chemist residing at Cape Town. The latter assigns to this gas the provisional name damarium (D). It is capable of decomposing water and taking the place of the hydrogen. Its combination with oxygen, on electrolysis, evolved at the positive pole a volume only *one-fourth* of that given off at the negative pole. The latter has exactly half the specific gravity of H, and its oxide has the composition D_4H . D is therefore semivalent, or, more correctly, it is the true univalent element of the lowest atomic weight, and must in future be placed at the bottom of our atomic scale. H, Cl . . . must in future be regarded as bivalent; O, S, &c., as quadrivalent. The stereo-chemical view of Le Bel and van't Hoff thus receives a severe blow, and the "tetrahedric representation" becomes impossible. Damarium is the most powerful of all reducing agents. Platinum, gold, silver, lead, and copper are at once reduced from their solutions in the metallic state; ferric salts are reduced in a moment to ferrous salts, and mercuric chloride is converted into calomel. Solution of indigotine is instantly decolourised, and nitrobenzol is converted into aniline. Damarium rapidly separates sulphur from the aqueous solution of SO_2 , and if passed through dilute sulphuric acid it causes an escape of sulphuretted hydrogen. Dr. Antsch, who is intending to prosecute the investigation on the receipt of further material, is of opinion that damarium is an element, perhaps widely diffused, but generally occurring in very minute quantities, and hence hitherto overlooked. Its concentrated occurrence in Damara Land is analogous to the occurrence of the cerium metals,

MEETINGS FOR THE WEEK.

- MONDAY 5th.—Medical, 8.30. (Annual Oration).
 — Society of Arts, 8. "Sugar, Tea, Coffee, and Cocoa, their Origin, Preparation, and Uses," by Richard Bannister.
 — Society of Chemical Industry, 8. "The Dunsmire Process," by Watson Smith. "Some Considerations in the Chemistry of Bleaching," by Messrs. Cross and Bevan. "Mixture in Paper Pulp," by M. L. Griffin.
 — Royal Institution, 5. General Monthly Meeting.
 TUESDAY, 6th.—Royal Institution, 3. "The Art of Engraving—1. Line Engraving," by Louis Fagan.
 — Institute of Civil Engineers, 8.
 — Pathological, 8.30.
 WEDNESDAY, 7th.—Society of Arts, 8. "The Aim and Scope of Higher Technical Teaching," by Dr. Percy F. Frankland.
 THURSDAY, 8th.—Royal Institution, 3. "Flame and Explosives," by Prof. Dewar, M.A., F.R.S.
 — Society of Arts, 5. "The Western Frontier of China," by Demetrius Boulger.
 — Society of Arts, 8. "Design Applied to Wood-carving," by Lewis F. Day.
 — Royal, 4.30.
 — Chemical, 8. (Extra Meeting). Exhibition of Apparatus, &c.
 — Institute of Electrical Engineers, 8.
 — Mathematical, 8.
 FRIDAY, 9th.—Royal Institution, 9. "Colour-vision and Colour-blindness," by R. Brudenell Carter, F.R.C.S.
 — Quekett Club, 8.
 — Astronomical, 8.
 SATURDAY, 10th.—Royal Institution, 3. "Recent Excavations in Greece," by Dr. Charles Waldstein.

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THE CHEMICAL NEWS.

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10 MAY 90

THE RAPID ESTIMATION OF ARSENIC.

By F. W. BOAM, F.C.S.

THE author having occasion to estimate the amount of arsenic (equal to As_2O_3) in a large number of samples of its ores, it became of importance to obtain a quick and accurate method for its determination. The usual known "magnesia" and "uranium acetate" methods are lengthy and require the greatest care in order to be accurate. The "iodine" method, though accurate and quickly performed when employed for "refined white arsenic," is very lengthy and bothering when applied to arsenical ores, and affords several opportunities for error during the preparation of the test solution for titration! Such being the case, the author was led to experiment upon the following modification of the "uranium acetate" method:—

About 1 to 1.5 grms. of the ore, previously dried at 100° and powdered, is taken and boiled to dryness with 20 to 25 c.c. pure strong HNO_3 . When cool, about 30 c.c. strong $NaHO$ solution (30 per cent) are added and boiled for a short time, and the liquid filtered off and diluted to 250 c.c. 25 c.c. of this solution are taken, made acid with a ten per cent solution of sodium acetate, in 50 per cent acetic acid, and the mixture boiled. It is then titrated with a quarter normal solution of uranium acetate (made by dissolving 17.1 grms. uranium acetate in 15 c.c. strong acetic acid, and diluting to 2 litres), 1 c.c. equalling 0.00125 gm. As. A solution of K_4FeCy_6 "spotted out" on a white tile is used as the indicator; a drop of the test solution giving a reddish brown colouration with this when the titration is finished.

This method is applicable to all ores containing arsenic, and which are attacked by HNO_3 . The author has fully tested it against other methods and finds that it holds the palm for rapidity and accuracy. A sample of "arsenical iron pyrites" can be analysed by its means in less than two hours. The difficulty at first met with in employing this method is a tendency to form an insoluble unstable arseniate of iron upon adding the $NaHO$ solution, but the author finds that by employing a moderately strong solution of $NaHO$ in excess, and boiling, this compound is decomposed, whereby the hydrate of iron can be filtered off without loss of arsenic.

Coombe Arsenic Works,
Callington, Cornwall.

ODORISING WATER-GAS.

By Dr. J. LEWKOWITSCH, F.I.C., F.C.S.

THE serious dangers attending life through an unobserved escape of water-gas have led many experimenters to impart to this gas a volatile substance the odour of which would readily indicate the presence of water-gas in the air. All attempts in this direction proved hitherto fruitless, even mercaptan not being adapted for this purpose, as last year's sad occurrence in the Leeds Forge proved.

About that time Baumann published in the *Berichte* (1889, p. 2593) his paper on thio-acetone, and quite naturally it occurred to me that this substance, the powerful odouring properties of which Baumann described in such a vivid manner, might perhaps be usefully applied to the odouring of water-gas.

A few experiments satisfied me that it would be comparatively easy to prepare this substance for the said purpose, especially as it would not be required to prepare a

chemically pure substance, any larger amount of the polymers not being objectionable at all.

Communicated afterwards with the British Water-Gas Syndicate in this town, and the necessary experiments were carried out in the chemical laboratory of the Leeds Forge. Owing to the pressure of other important work and a serious illness, the final experiment, *i.e.*, the admixture to the water-gas, has not yet been carried out.

The substance in question possesses, as was to be expected according to Baumann, a most powerful odour, causing at the same time sickness and headache, when the vapours are highly diluted, *e.g.*, with air. While preparing this thio-acetone one does not meet with very great inconvenience, at least, not greater than experienced when working on similar substances. There is a very curious analogy between the odouring properties of this thio-acetone and other substances of great scenting power, for instance, otto of roses—of course, in a very opposite direction as far as the pleasantness is concerned. The pure rose oil has only a faint and, perhaps, not agreeable smell, but in very dilute solutions the lovely scent is brought out. Similarly, the fearful smell of the thioacetone is brought out when it is diluted with large quantities of air. I had for this a very serious—although at the time a very welcome—confirmation. While distilling the product of the reaction of sulphuretted hydrogen on about 20 grms. of acetone, two workmen, working at the opposite end of the steel works, entered the laboratory complaining of the fearful smell, and declaring that they had been vomiting, felt altogether sick and unable to continue their work.

In conclusion, I wish to point out that acroleine would lend itself admirably to this purpose, as I may conclude from the complaints I had some years ago, caused by very minute quantities of acroleine escaping from the glycerin distilling of the undermentioned works. Experiments on the use of acroleine are being carried out at present. The absence of sulphur in it would recommend it all the more

Whitehall Soap Works, Leeds.

A FUNDAMENTAL PROPERTY COMMON TO BOTH CLASSES OF SPECTRA. DISTINCTIVE CHARACTERS OF EACH CLASS. PERIODIC VARIATIONS WITH THREE PARAMETERS.

By H. DESLANDRES.

M. RYDBERG has recently submitted to the Academy a very interesting study on the succession of vibratory periods in line spectra. He set out from the anterior researches of MM. Lecoq de Boisbaudran, Mascart, Liveing and Dewar, and Cornu and Balmer, and condensed the facts established in certain simple laws.

The author has studied the other class, the band-spectra, from the same point of view, and has proposed two simple laws for the distribution of the rays and the bands. It is convenient to bring them forward anew, but under a form analogous to that adopted by M. Rydberg for the line-spectra. The comparison between the two classes of spectra will thus be rendered easy; it will bring into prominence, on the one hand a fundamental property which is common to both, and on the other the characters peculiar to each class.

Line-Spectra.—The laws of M. Rydberg apply to the bodies which constitute the three first families of Mendeleeff, that is almost all the metals. In these substances the long rays (which are the most important and even the only ones of the electric arc) form groups of two or three rays (doublets or triplets) which succeed each other at regularly decreasing intervals, so as to form series having the same aspect for all bodies.

In the scale of number of waves or of vibrations in

each series the corresponding rays of the doublets or triplets are represented by a function of the whole numbers of the form—

$$N = A - \frac{a}{(m + \mu)^2},$$

N being the number of waves, A , a two constants, μ a constant < 1 , m a whole number. This function has, as its limit, the simplest function—

$$N = A = \frac{a}{m^2}$$

which, for the suitable values of A and a , represents exactly, as was first shown by Balmer, the simple series of the simple rays of hydrogen.

Band-Spectra have given rise to less research than the former, as they are less intense, less easy to produce, and they require a very powerful dispersion. The author has studied at least 12 distinct band spectra, some having more than 40 bands (*Comptes Rendus*, 1886 and 1887). They are due to the non-metallic bodies.

They have one point in common with the line spectra. Any band whatever, with a sufficient dispersion, seems formed by similar groups of one, two, or three rays, or even more, which follow each other at regularly variable intervals. All the bands of one and the same spectrum are similar, and are formed by the same groupings. This structure of similar groups is a fundamental property common to all spectra.

But the distribution of the groups is here different. It is represented for one band by the function $N = A + am^2$, m being a whole number and A and a two constants. For increasing values of m the intervals increase (even in arithmetical progression), whilst the line spectra decrease progressively.

Further, as a spectrum usually comprises several bands, the general law of distribution must be more complex. The author has shown that in the scale of wave-numbers the complete series of similar groups may be represented by a function of three variable parameters,—

$$m_2 n_2 \mu - N = f(n^2 \mu^2) \times m^2 + Bn^2 + \phi(\mu^2);$$

$m_2 n_2 \mu$ being the values of whole numbers, B being a constant, f and ϕ simple functions, the study of which is not yet completed. The function N has three parameters, but in some spectra it is reduced to two or even to one.

This distribution to the dependence of three parameters is a characteristic of band spectra in contradistinction to line-spectra which are governed by a single parameter.

As to the nature of the grouping of the similar rays, the repetition of which forms spectra, it has the same importance in both classes. As in the metallic spectra, there are differences between substances of different families. Thus carbon presents a series of doublets with three parameters, oxygen a series of doublets with two parameters, nitrogen a series of triplets with three parameters, and a series of simple rays having three parameters.

But the occurrence in the spectra of series of rays of three parameters is not surprising. We find in general three groups of periods and three parameters in the problems of periodic variations in which the three dimensions of space intervene; the three parameters corresponded exactly to these three dimensions. Thus, in the problem of the most general vibratory movement of a solid body theory distinctly indicates a total of periods assimilable to a table of three entries. We may affirm that the sounds or the shocks heard at any instant are most commonly complex sounds of three parameters. This character has not been recognised as yet because our senses and our means of investigation do not allow us to separate in the same time many sounds emitted simultaneously.

In optics the conditions are more favourable. The powerful dispersive apparatus at our disposal enables us to separate all the components of any vibration whatever, and to distinguish two neighbouring vibrations which

differ respectively by less than 1.100,000th of their number of waves. Thus the spectra of bands formed of very numerous and very approximating rays have been studied completely. These band-spectra form the first experimental verification of periodic variations with three parameters.—*Comptes Rendus*, cx., p. 748.

NEW METHOD FOR THE SEPARATION OF VANADIC AND TUNGSTIC ACIDS.

By CARL FRIEDHEIM.

THE following method gives trustworthy results:—

The concentrated solution of the salt is mixed in a capacious porcelain capsule on a boiling water-bath with a strong solution of mercurous nitrate, as neutral as possible, until the precipitate formed settles well, and then digested for about twenty minutes with an excess of freshly precipitated mercuric oxide, to neutralise the free acid. When cold, the precipitate—a mixture of the mercury salts of both acids with excess of mercuric oxide—is filtered through a smooth filter, washed with water containing a few drops of mercurous nitrate, which is quickly effected, then rinsed back as completely as possible from the filter into the capsule used for precipitation, and the contents of the capsule are evaporated to a paste. When cold, it is treated with an excess of the strongest hydrochloric acid, stirring carefully, and heated for five minutes upon a boiling water-bath, covered with a watch-glass.

All the vanadium dissolves as vanadyl chloride, almost all the tungstic acid and the bulk of the mercury dissolve also. The blue solution is mixed with much water, when the dissolved tungstic acid is thrown down almost quantitatively, whilst vanadium and mercury remain in solution.

The residue of the precipitate left on the filter is dissolved in hot hydrochloric acid, sp. gr. 1.12, and added to the solution. After twenty-four hours, the precipitate is filtered off, washed with water very slightly acidulated with hydrochloric acid, the residue adhering to the capsule is rinsed into a tared porcelain crucible with a little ammonia, the contents of the filter evaporated to dryness on the water-bath, the filter, still moist, is placed in the crucible, dried in the air-bath at 120°, and ignited with excess of air, at first under a draught-hood, on account of the mercuric chloride: there remains pure yellow tungstic acid. From the filtrate, after heating to 80°, the mercury is thrown down as sulphide by a prolonged introduction of hydrogen sulphide until the precipitate has completely deposited. The filtrate, containing vanadyl chloride, is evaporated to dryness on the water-bath, oxidised with strong nitric acid under a watch-glass on the water-bath, again evaporated, repeating the operation at least twice, and the brown hydrated vanadic acid dissolved in water with the addition of a few drops of nitric acid.

The solution is placed in a weighed platinum capsule, evaporated, the rest of the hydrated vanadic acid which has remained in the porcelain capsule is dissolved in a minimum of ammonia, added to the main quantity, again evaporated, dried at 120° in the air-bath, and then heated in the oxidising flame with excess of air (avoiding melting at first), and finally distributing the diffused mass over the sides of the crucible by agitation. The result contains only one-tenth to one-fifth per cent of the total quantity of WO_3 . To determine it, the contents of filter, after weighing, are treated with dilute sulphuric acid and sulphurous acid at a moderate heat, when all the vanadium is dissolved as vanadyl sulphate. The residue of tungstic acid, after filtration, is washed with very dilute sulphuric acid and weighed. The solution of vanadium is evaporated, the sulphuric acid driven off by heat, and

the residue ignited as above described, when perfectly homogeneous vanadic acid is obtained.

From the filtrate of the mercury salts of the acids the mercury is removed by sulphuretted hydrogen, and the alkali is determined as sulphate, the acid salts, as it is indicated by Krüss, being converted into normal salts by heating in a current of air charged with ammonia.

If the method is to be applied to meta-tungstates, they must first be converted into ordinary tungstates, by boiling and repeated evaporation in ammonia. The solution, freed from any excess of ammonia, is precipitated as described. Lead and silver salts are best decomposed by treatment with a very dilute alkaline hypochlorite, and the remaining metallic and earthy alkaline salts by repeated fusion with sodium-potassium carbonate; the united alkaline liquids are neutralised with acetic acid at a gentle heat and precipitated as directed. Extreme purity of all the reagents is indispensable.—*Berichte Deutsch. Chem. Gesell.*, vol. xxiii., p. 352.

EXAMINATION OF CORPSES FOR ALKALOIDS AND METALLIC POISONS.

By Dr. ANTON SEYDA.

(Continued from p. 211).

2. Detection and Determination of Arsenic.

If the absence of mercury and antimony has been decided, 50—100 c.c. of the liquid are tested directly for arsenic in the Marsh apparatus. Prominent attention must be given to the following points:—

1. The zinc to be used before being placed in the generating flask must be washed with hydrochloric acid, *i.e.*, it must be exposed to the action of the acid for about ten minutes; the solution is then poured off, and the zinc is well washed with water. In this manner the traces of arsenic which often adhere to the zinc on the outside only can be removed.

2. In setting the apparatus in action the gas escaping at the aperture for exit must not be ignited until the operator has satisfied himself, by heating the reduction tube before the first contracted part, that all the atmospheric air has been expelled from the apparatus. In this manner the risk of explosion is avoided.

3. The liquid to be tested must be introduced into the flask in very small portions only, especially at first. In this manner the danger of frothing and running over may be avoided. If a deposit of arsenic appears in the reduction tube, the operator must always wait to see whether it visibly increases before adding a fresh quantity of the liquid.

4. The preparation of arsenical spots may be conveniently omitted, because it succeeds only when arsenic is present in considerable quantity and the escape of hydrogen arsenide is violent, which occasions a necessary loss of arsenic. The qualitative reactions of arsenic can be quite as well carried out with the "mirrors," which also serve better as exhibits than arsenical spots, which easily disappear if chlorine is present in the atmosphere.

If the quantity of arsenic present is not too small, and if it is practicable to obtain two mirrors, the reduction-tube is very carefully cut up with a diamond at its contracted portions, so that there result four pieces, each with half a mirror. With these mirrors the following tests are executed:—

1. One mirror is used for the odour test.
2. The second mirror is tested for its solubility in a freshly prepared solution of sodium hypochlorite.
3. The third mirror is dissolved in nitric acid and silver arsenite (or arseniate) is formed by adding silver nitrate.
4. The fourth mirror is oxidised with nitric acid, and converted into arsenic sulphide by treatment with colourless ammonium sulphide.

These four reactions will be in all cases perfectly satisfactory.

For the quantitative determination, sulphuretted hydrogen is passed into the hot solution for twelve hours; the flask is let stand, closely stoppered, for three to five days, until the precipitate has entirely settled, when the excess of sulphuretted hydrogen is expelled by a current of carbonic acid, and the precipitate is filtered off. A subsequent dulness in the filtrate, which was at first clear, cannot be avoided. The precipitate, consisting chiefly of organic matter, demands no further attention, since we have here to do with traces of arsenic which no longer admit of quantitative determination, as the last residues of arsenic can hardly be precipitated by means of sulphuretted hydrogen. Otherwise the procedure is similar to that described for antimony.

The following points must be remembered:—

1. The arsenic sulphide upon the filter must be dissolved only by means of ammonia or ammonium carbonate, as thus the sulphur present is least likely to pass into solution.

2. The fusion of the ammoniacal residue after treatment with nitric acid must be effected in a porcelain crucible with the readily fusible mixture of potassium-sodium carbonate and potassium nitrate.

3. The arsenic must always be weighed as magnesium pyro-arsenate.

4. A direct precipitation of the arsenic acid in the alkaline solution of the melt must be avoided. The arsenic must be again precipitated with sulphuretted hydrogen in the solution acidulated with nitric acid and freed from carbonic acid and nitrous acid; and after the arsenic sulphide has been converted into arsenic acid the latter, in a clear strong watery solution, must be precipitated with the mixture.

5. The precipitate of ammonium-magnesium arsenic must be re-dissolved in hydrochloric acid on the filter, and the solution again precipitated with ammonia. In this manner an excess of magnesia mixture is avoided, as well as the possible precipitation of magnesium hydroxide. The precipitate of ammonium-magnesium arseniate must be finely crystalline.

6. For converting the arseniate into pyroarsenate de Koninck recommends, when the quantity of arsenic is small, to dissolve the precipitate at once in water containing nitric acid, to evaporate down the solution in a small porcelain crucible on the water-bath, and to ignite the residue gradually and cautiously. By means of this improved method the author has lately succeeded in determining such small quantities of arsenic as 0.0093 to 0.0077 in the organs of dead bodies. A check experiment performed on the latter quantity in Marsh's apparatus gave five distinct arsenical mirrors.

7. Large quantities of magnesium pyroarsenate are preserved as exhibits; smaller quantities are converted into metallic arsenic in the Marsh apparatus, and the mirrors are sealed up.

b. Examination for other Metals, excepting Tin.

If the absence of mercury, antimony, and arsenic has been proved, the hydrochloric solution is put in a flask, rendered alkaline with soda-lye (free from alumina), acidulated with acetic acid, and treated with sulphuretted hydrogen, first at a boil and then until cold.

The contents of the flask are mixed with sodium carbonate until the reaction is distinctly alkaline, and left stoppered until quite clear. It is then filtered, the black precipitate, consisting, in ordinary cases, chiefly of iron sulphide, is drained and washed with a dilute solution of sodium sulphide containing hydrogen sulphide until the filtrate runs off colourless. The filtrate is set aside; the precipitate is put in a well-glazed porcelain capsule carefully oxidised with nitric acid, the evaporated residue is moistened with caustic soda (prepared from the metal), mixed with potassium sodium-carbonate, and the dry mixture is gradually introduced into melting saltpetre in

a silver crucible. In this manner, all organic matter accompanying the sulphides is completely got rid of. The melt is directly lixiviated in the silver crucible, the liquid is carefully supersaturated with hydrochloric acid and filtered into a beaker through asbestos (if manganates are present, otherwise through paper), to remove silver chloride, and the hydrochloric solution is further examined, qualitatively and quantitatively, according to ordinary analytical methods.

(To be continued).

ASH DETERMINATION IN RAW SUGARS.*

By F. G. WIECHMANN, Ph.D.

(Concluded from p. 212).

IN order, however, that the determinations should be perfectly parallel, a separate estimation was made in each sugar of the inorganic suspended impurities, and the amount found deducted from the sulphate ash.

The following table exhibits the results obtained:—

Analysis number.	Sugar.	Polarisation	Carbo-nate ash.	Difference.	
				Sul-phate ash, — $\frac{1}{10}$.	The results obtained as sulphates are;—
1.	Dominica Muscovado.. ..	86.0	1.25	1.06	-0.19
2.	Java, 2nd product	86.5	1.32	0.99	-0.33
3.	" "	88.8	1.06	0.86	-0.20
4.	" "	86.3	1.05	0.79	-0.26
5.	" "	86.7	0.81	0.62	-0.19
6.	" "	87.5	1.26	0.92	-0.34
7.	Trinidad Concrete	84.0	2.47	2.08	-0.39
8.	Ilo-Ilo.. ..	86.6	1.91	1.42	-0.49
9.	" "	80.8	2.30	1.98	-0.32
10.	New Orleans Muscovado	91.2	0.76	0.49	-0.27
11.	New Orleans Muscovado	80.2	3.08	2.68	-0.40
12.	New Orleans Melado	79.1	1.69	1.19	-0.50
13.	New Orleans Melado	52.0	1.42	1.09	-0.33
14.	St. Croix Muscovado . . .	88.0	1.27	1.04	-0.23
15.	Ceroons	83.8	1.78	1.25	-0.53
16.	Brazil	84.1	1.95	1.22	-0.73
17.	Java Stroops ..	77.4	4.16	3.72	-0.44
18.	Mauritius Mol. sugar . . .	86.4	2.87	2.96	+0.09
19.	Superior Cebu Mats . . .	83.2	2.00	1.93	-0.07
20.	Cuba Molasses Sugar	84.2	2.16	2.35	+0.19
21.	Taal Mats	78.5	2.57	1.97	-0.60
22.	Beet 2nd product	92.2	3.06	2.55	-0.51
23.	Java Basket ..	96.7	0.77	0.54	-0.23
24.	St. Kitts Muscovado . . .	88.2	1.13	0.87	-0.26
25.	Syrup, Louisiana	40.9	6.80	6.13	-0.67
26.	Syrup, Sandwich Island Sugar ..	49.2	11.03	10.07	-0.96

The results obtained by the two methods differ very considerably. As the figures yielded by the Scheibler method were almost without exception *lower* than those found by the other process, the suspicion arose that possibly the alkali sulphates might have been partly lost by volatilisation, although this was very improbable, for the incinerations had all been carried out in a muffle exactly as prescribed.†

* From the *School of Mines Quarterly*, Vol. xi., No. 1.

† *Zeitschrift des Vereines für Rubenzucker-Industrie*, vo xvii., p. 338.

However, to settle the question, two tests were made. The sulphate ash of a Java sugar was first very carefully determined; then, in test one, there was added to a sample of the sugar equal in weight to the amount taken for the original ash determination a known amount of dried and powdered potassium sulphate; test two was carried out in exactly the same manner, only anhydrous sodium sulphate was used instead of the potassium salt. The ash determinations were then carried out as before.

The ash originally present in the sugar was 0.680. In test one, after subtracting the weight of the potassium sulphate which had been added, the ash was 0.680. In test two, after allowing for the sodium sulphate, the ash was 0.676, thus proving that the alkali sulphates did not lose in weight by the incineration.

The explanation of these differences must therefore be sought by an analysis of the ash, and the composition of the salts originally present in the sugars must be examined into.

The analyses made showed that the ashes of these sugars contain alkalies (reported in the form of potassium and sodium) ranging from 28.8 to 36.4 per cent; silica (SiO₂) was present from 1.64 to 11.08 per cent.* Two samples had less than 2 per cent; three samples had between 2 per cent and 3 per cent; two, between 3 per cent and 4 per cent; seven, between 4 per cent and 5 per cent; three, between 5 per cent and 6 per cent; three, between 6 per cent and 7 per cent; one had 8.93 per cent, and one 11.08 per cent.

The only silicates soluble in water are the silicates of the alkalies; hence one is forced to the conclusion that the alkalies in these sugars are present, at least in part, in the form of silicates. Analysis further showed the ash in most samples to be rich in sulphates, the sulphuric acid (H₂SO₄) calculated in percentage on the carbonate ash ranging from 4.17 to 31.71 per cent.

How the salts originally present in a sugar are affected by the two methods of ash determination here given is the next question to be considered. The salts in a sugar may be assumed to exist in the form of silicates, sulphates, chlorides, carbonates, phosphates, nitrates, and organic acid salts; for instance, as oxalates, tartrates, malates, and possibly as citrates.

	After simple incineration will be found as—	After incineration with sulphuric acid will be found as—
Silicates	silicates	silicates.
Sulphates	sulphates	sulphates.
Chlorides	carbonates†	sulphates.
Nitrates	carbonates	sulphates.
Carbonates	carbonates	sulphates.
Organic acid salts	carbonates	sulphates.

Looking at this table, it is evident that sugars rich in chlorides, carbonates, and organic acid salts, will, on incineration with sulphuric acid, give results that are higher than those obtained by simple carbonisation, because the molecular weight of the sulphates is greater than that of the chlorides or carbonates, into which form (*i.e.*, carbonates) the organic acid salts are transformed by simple incineration.‡ It was this fact, of course, that Scheibler bore in mind when he called for the subtraction of one-tenth from the weight of the sulphate ash; it was this fact, too, that gave rise to the difficulties of the French chemists cited, who found that Scheibler's factor would *not* bring the sulphate ash into agreement with the ash obtained by simple incineration.||

* This represents silica, or rather silicates *in solution*, as all suspended sand, &c., had been removed by filtration.

† Certainly in part, if not wholly.

‡ That the organic acid salts can be greatly in preponderance appears from analyses made by Laugier, *Comptes Rendus*, 1878, p. 27, who found in analysing the fill-mass of a refinery (fourth product), that over 70 per cent of the salts present, which themselves amounted to 10 per cent of the sugar, consisted of organic acids.

|| In France, at one time, the factor 0.8 was used in official analyses, while 0.9 was adopted in commercial work.

If, however, the sugars analysed are similar in composition to those here examined; that is to say, if they be rich in silicates and sulphates, the case is an entirely different one, for although it would be extremely difficult, if not impossible, to assign formulæ for the silicates of the alkalis (as those which occur in nature range between the limits $4M_2O, SiO_2$ and $M_2O, 2SiO_2$),* yet, as the silicates of the alkali metals "dissolve with greater facility in proportion as they contain a larger quantity of base,"† the molecular weight will, in any case, be equal to, or greater than, that of the alkaline sulphates, and, therefore, the subtraction of one-tenth will bring the figures below the true value. To illustrate this, the following table, while bringing once more the carbonate ash values previously recorded, gives the sulphate ash values as found; that is to say, *without subtraction of one-tenth*, but of course, as before, allowing for the inorganic suspended impurities.

Analysis number.	Sugar.	Polarisation.	Carbonate ash.	Sulphate ash.	Difference. The results obtained as sulphates are:—
1.	Dominica Muscovado	86.0	1.25	1.21	-0.04
2.	Java, 2nd product	86.5	1.32	1.25	-0.07
3.	" "	88.8	1.06	0.90	-0.16
4.	" "	86.3	1.05	0.89	-0.16
5.	" "	86.7	0.81	0.68	-0.13
6.	" "	87.5	1.26	1.04	-0.22
7.	Trinidad Concrete	84.0	2.47	2.32	-0.15
8.	Ilo-Ilo	86.6	1.91	1.60	-0.31
9.	"	80.8	2.30	2.20	-0.10
10.	New Orleans Muscovado	91.2	0.76	0.56	-0.20
11.	New Orleans Muscovado	80.2	3.08	2.98	-0.10
12.	New Orleans Melado	79.1	1.69	1.73	+0.04
13.	New Orleans Melado	52.0	1.42	1.23	-0.19
14.	St. Croix Muscovado	88.0	1.27	1.16	-0.11
15.	Ceroons	83.8	1.78	1.44	-0.34
16.	Brazil	84.1	1.95	1.44	-0.51
17.	Java Stroops ..	77.4	4.16	4.15	-0.01
18.	Mauritius Mol. Sugar	86.4	2.87	3.33	+0.46
19.	Superior Cebu Mats,	83.2	2.00	2.24	+0.24
20.	Cuba Molasses Sugar	84.2	2.16	2.67	+0.51
21.	Taal Mats	78.5	2.57	2.44	-0.13
22.	Beet, 2nd product	92.2	3.06	2.85	-0.21
23.	Java Basket ..	96.7	0.77	0.61	-0.16
24.	St. Kitts Muscovado	88.2	1.13	0.98	-0.15
25.	Syrup, Louisiana	40.9	6.80	6.82	+0.02
26.	Syrup, Sandwich Island Sugar ..	49.2	11.03	11.19	+0.16

It will be seen at a glance how much better the results of the two methods agree now; but even so, the sulphate ash is, with few exceptions, *lower* than the other, and, therefore, if anything, one feels tempted to seek for a factor by which to *increase* the sulphate ash. The exceptions noted are the very ones to prove the rule, or rather to bear out the explanation given, for Nos. 26, 18, and 19 are lowest in silica, containing respectively 0.96, 1.64, and 1.69 per cent. No. 20 contains 2.64 per cent silica, but is the lowest in sulphates, and so these sugars in their composition approach more closely the beet sugars examined by the European chemists, the ash

analysis of which, made by Von Lippmann,* may be regarded as typical. In this analysis (of a carbonate ash of beet-sugar) he reports, among other constituents,—

Potassium	50.87
Sodium	9.13
Sulphuric acid	2.04
Silicic acid	0.10

In view of the important part that the ash plays in the cost and in the yield of raw sugars, it is certainly a matter of no small consideration to have an analytical method which may be depended upon.

To devise an analytical process by which the *actual amount of salts* in a sugar could be ascertained in everyday practice, that is to say, by which the salts present could be quickly and accurately determined, seems, in our present state of knowledge, an impossibility, unless, indeed, the electric-conducting power of dilute sugar solutions shall prove to be the means by which this end will be attained.†

Whether any of the numerous methods proposed for determination of the ash—as, for instance, Dubrunfaut's‡ suggestion of burning the sugars off with spongy platinum, ignition in a current of pure oxygen, or the combustion with oxide of zinc, as recently recommended by Lucien§—would prove superior to Scheibler's method, cannot here be inquired into.

The great advantage of incineration with sulphuric acid, especially as it is now practised, with addition of a little ether is not to be questioned. The possible objection as to the expense of platinum muffles, where several must be used on account of the number of daily determinations, has been overcome in our laboratory by the use of muffles made of Russian sheet-iron, which may be had at one-hundredth the cost of the platinum ware, which last, on an average, between three and four months, and which give absolutely no contamination to the sugar ashes burned off in them.

While thus fully appreciating this analytical method, there is no reason why countenance should be lent to the practice of changing an *absolute value* obtained by analysis into a *problematical figure* by means of a factor which may give results concordant, too high or too low, according to the nature of the sugar examined, and which, as far as this item is concerned, leaves to the purchaser really no clue as to how his sugars will turn out. Why not accept, as already suggested by Dubrunfaut,|| as a working factor the sulphate ash actually obtained? This, at least, represents a definite value upon which calculation may be based, and it is difficult to understand how the one-tenth subtraction can have held its sway to the present day, when its misleading influence—at least in one direction—was pointed out already ten years ago.

NOTES FROM THE LABORATORY OF SMITH COLLEGE.¶

By J. T. STODDARD.

A New Test-Tube Holder.—The annoyance experienced in using the common wooden test-tube holder led me some years ago to attempt to devise a holder which should serve its purpose more perfectly. The wooden holder is clumsy, its rubber band rots and is liable to give way at awkward moments, the peg becomes unglued and drops out, and even in its best estate it holds securely

* *Zeitschrift des Vereines fur Rubenzucker-Industrie*, vol. xxxi., 1881, p. 399.
† *Ibid.*, vol. xxxix., p. 432.
‡ *Journal des Fabricants de Sucre*, Dec. 18, 1870.
§ *Bulletin de l'Association des Chimistes*, 1889, p. 356.
|| *Le Sucre*, 1878, vol. ii.
¶ *Journal of Analytical Chemistry*, Vol. iv., Part 1, January, 1890.

* Watts' "Dictionary of Chemistry," vol. v. p. 244.
† *Loc. cit.*

only medium-sized test-tubes. Tubes of more than two centimetres cannot be inserted sideways, larger ones are not taken at all, and a separate holder must be used for small test-tubes and ignition-tubes.

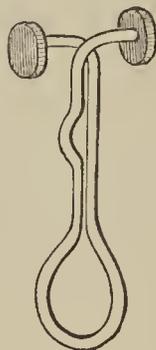
The new holder has been in use in my laboratory for four years now, and has given such good satisfaction that I venture to call attention to it in a form recently somewhat improved. It is made of brass wire, and opens by



pressure on the straight sides of the handle; its jaws open to the width of 5 c.m., and it holds firmly any tube from 5 m.m. up. It thus serves for ignition-tubes as well as for all sizes of test-tubes.

I have recently had a larger size made of stiffer wire for the purpose of holding flasks, &c. It proves very convenient as a holder of wash-bottles when one is washing with boiling-water, and also for holding beakers when decanting hot solutions. Both sizes are furnished by the Victor Manufacturing Co., Northampton, Mass.

A Modified Form of Pinchcock.—As is shown in the cut, the modification consists in making a side-bend in one of the limbs and omitting the double wire which serves as a guide in the ordinary form. The pinchcock can be opened by springing the limbs apart, and thus is



readily put on a tube connected at both ends without breaking connections; and when placed so that the tube lies in the side bend, leaves the tube open while retaining its place. The side bend was suggested by a note in *Ztschr. Anal. Chem.*, xxiv., 399.

Filtration under Pressure.—The introduction of this method of rapid filtration into my qualitative laboratory has resulted in a very considerable gain in the amount of work accomplished by the class in the time at his disposal. A quarter-inch iron pipe connects each place with a Chapman's aspirator, the pressure being regulated for the whole system by connecting at one point a side neck tube containing mercury, and having a tube open to the air thrust through the cork to a proper distance below the surface of the mercury. The use of brass gas-cocks on the exhaust pipe is not to be recommended, as they are affected by the ammonia and other gases which escape from the filtrates, and soon turn hard and often stick fast. A pinchcock on the tubing used to connect the filtering

flask is an efficient substitute, but it is better to use it only during working hours and to relieve the rubber tubing from its pressure at the close of work, plugging the tube with a short piece of glass rod. By treating the filter-papers with nitric acid of sp. gr. 1.42, as proposed by Francis (*Ztschr. Anal. Chem.*, xxvi., 351), the use of platinum cones is rendered unnecessary, and the paper is in much better condition for the removal of precipitates. In this connection I wish to call attention to the remarkable efficiency of the Chapman aspirator. I have used an inch aspirator for three or four years, in place of the ordinary air-pump, for exhausting receivers, &c., in my lectures, and find it not only gives a high vacuum (the residual pressure being that of aqueous vapour at the temperature of the water running through the aspirator), but works with great rapidity. With our water pressure of about 70 pounds, a receiver of 3600 c.c. capacity is exhausted to the above limit (at this season about 10 m.m. of mercury) in a minute and a half.

SUMMARY OF USEFUL TESTS WITH THE BLOWPIPE.*

By A. J. MOSES.

The following selection includes only the tests used in the instruction at the Mineralogical Laboratory of the School of Mines. It is believed that the omitted tests have always been omitted for cause, either as less characteristic or less easily obtained, or from the need of some unusual or not easily handled reagent.

The details of ordinary manipulations, such as obtaining beads, flames, coatings, and sublimate, are omitted, and the results alone stated; unusual manipulations are described. The bead tests are supposed to be obtained with oxides; the other tests are, in general, true of all compounds not expressly excluded. The course to be followed in the case of interfering elements is briefly stated.†

ALUMINIUM, Al.

With Soda.—Swells and forms an infusible compound.
With Borax or S. Ph.—Clear or cloudy, never opaque.
‡ *With Cobalt Solution.*—Fine blue when cold.

AMMONIUM, NH₃.

In Closed Tube.—Evolution of gas with the characteristic odour. Soda or lime assists the reaction. The gas turns red litmus-paper blue and forms white clouds with HCl vapour.

ANTIMONY, Sb.

On Coal, R. F.§—Volatile white coat, bluish in thin layers, continues to form after cessation of blast.

With Bismuth Flux—

On Plaster.—Orange-red coat, made orange by (NH₄)₂S.

On Coal.—Faint yellow or red coat.

In Open Tube.—Dense, white, non-volatile, amorphous sublimate. The sulphide, too rapidly heated, will yield spots of red.

In Closed Tube.—The oxide will yield a white fusible sublimate of needle crystals, the sulphide a black sublimate red when cold.

Flame.—Pale yellow-green.

With S. Ph.—Dissolved by O. F. and treated on coal with tin in R. F. becomes grey to black.

Interfering Elements.

Arsenic.—Remove by gentle O. F. on coal.

* From the *School of Mines Quarterly*, vol. xi., No. 1.

† *School of Mines Quarterly*, vol. viii., p. 259, and vol. x, p. 321.

‡ Certain phosphates, borates, and fusible silicates become blue in absence of alumina.

§ This coat may be further tested by S. Ph. or flame.

Arsenic with Sulphur.—Remove by gently heating in closed tube.

Copper.—The S. Ph. bead with tin in R. F. may be momentarily red, but will blacken.

Lead or Bismuth.—Retard formation of their coats by intermittent blast, or by boracic acid. Confirm coat by flame, not by S. Ph.

ARSENIC, As.

On Smoked Plaster.—White coat of octahedral crystals.

On Coal.—Very volatile white coat and strong garlic odour. The oxide and sulphide should be mixed with soda.

With Bismuth Flux—

On Plaster.—Reddish orange coat, made yellow by $(\text{NH}_4)_2\text{S}$.

On Coal.—Faint yellow coat.

In Open Tube.—White sublimate of octahedral crystals. Too high heat may form brown suboxide or red or yellow sulphide.

In Closed Tube.—May obtain white oxide, yellow or red sulphide, or black mirror of metal.

Flame.—Pale azure blue.

Interfering Elements.

Antimony.—Heat in closed tube with soda and charcoal, treat resulting mirror in O. F. for odour.

Cobalt or Nickel.—Fuse in O. F. with lead and recognise by odour.

Sulphur.—(a). Red to yellow sublimate of sulphide of arsenic in closed tube. (b). Odour when fused with soda on coal.

BARIUM, Ba.

On Coal with Soda.—Fuses and sinks into the coal.

Flame.—Yellowish green improved by moistening with HCl.

With Borax or S. Ph.—Clear and colourless, can be framed opaque-white.

BISMUTH, Bi.

On Coal.—In either, flame is reduced to brittle metal and yields a volatile coat, dark orange-yellow hot, lemon-yellow cold, with yellowish white border.

*With Bismuth Flux**—

On Plaster.—Bright scarlet coat surrounded by chocolate-brown, with sometimes a reddish border. The brown may be made red by ammonia.†

On Coal.—Bright red coat with sometimes an inner fringe of yellow.

With S. Ph.—Dissolved by O. F. and treated on coal with tin in R. F. is colourless hot, but blackish grey and opaque cold.

Interfering Elements.

Antimony.—Treat on coal with boracic acid, and treat the resulting slag on plaster with bismuth flux.

Lead.—Dissolve coat in S. Ph. as above.

BORON, B.

All borates intumesce and fuse to a bead.

Flame.—Yellowish green. May be assisted by—(a) Moistening with H_2SO_4 ; (b) Mixing to paste with water and boracic acid flux ($4\frac{1}{2}$ pts. KHSO_4 , 1 pt. CaF_2); (c) By mixing to paste with H_2SO_4 and NH_4F .

BROMINE, Br.

With S. Ph. Saturated with CuO.—Treated at tip of blue flame, the bead will be surrounded by greenish blue flame.

In Matrass with KHSO_4 .—Brown choking vapour.

Interfering Elements.

Silver.—The bromide melts in KHSO_4 and forms a

* Sulphur two parts, potassic iodide one part, potassic bisulphate one part.

† May be obtained by heating S. Ph. on the assay.

blood-red globule which cools yellow and becomes green in the sunlight.

CADMIUM, Cd.

On Coal R. F.—Dark brown coat, greenish yellow in thin layers. Beyond the coat, at first part of operation, the coal shows a variegated tarnish.

On Smoked Plaster with Bismuth Flux.—White coat made orange by $(\text{NH}_4)_2\text{S}$.

With Borax or S. Ph.—O. F. clear yellow hot, colourless cold, can be flamed milk-white. The hot bead touched to $\text{Na}_2\text{S}_2\text{O}_3$ becomes yellow.

R. F. becomes slowly colourless.

Interfering Elements.

Lead, Bismuth, Zinc.—Collect the coat, mix with charcoal dust, and heat gently in a closed tube. Cadmium will yield either a reddish brown ring or a metallic mirror. Before collecting coat, treat it with O. F. to remove arsenic.

CALCIUM, Ca.

On Coal with Soda.—Insoluble and not absorbed by the coal.

Flame.—Yellowish red improved by moistening with HCl.

With Borax or S. Ph.—Clear and colourless, can be flamed opaque.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.

Annual Meeting, May 1, 1890.

SIR JAMES CRICHTON-BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE Annual Report of the Committee of Visitors for the year 1889, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Real and Funded Property now amounts to above £82,000, entirely derived from the contributions and donations of the Members.

Fifty-one new Members were elected in 1889.

Sixty-three Lectures and Nineteen Evening Discourses were delivered in 1889.

The books and pamphlets presented in 1889 amounted to about 283 volumes, making, with 539 volumes (including periodicals bound) purchased by the Managers, a total of 822 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., F.R.S., M.Inst.C.E.

Managers—Sir Frederick Abel, C.B., D.C.L., F.R.S.; Sir Benjamin Baker, K.C.M.G., M.Inst.C.E.; The Right Hon. Arthur J. Balfour, M.P., LL.D., F.R.S.; George Berkley, M.Inst.C.E.; William Crookes, F.R.S.; Warren W. de la Rue; Edward Frankland, D.C.L., LL.D., F.R.S.; Charles Hawksley, M.Inst.C.E.; William Huggins, D.C.L., LL.D., F.R.S.; David Edward Hughes, F.R.S.; Alfred Bray Kempe, M.A., F.R.S.; The Right Hon. Earl Percy; Edward Pollock; William Chandler Roberts-Austen, F.R.S.; Basil Woodd Smith, F.R.A.S.

Visitors—John Wolfe Barry, M.Inst.C.E.; Shelford

Bidwell, M.A., F.R.S.; Alfred Carpmal; Arthur Herbert Church, M.A., F.R.S.; Ernest H. Goold, F.Z.S.; George Herbert; John Hopkinson, M.A., F.R.S., M.Inst.C.E.; John W. Miers; Sir Thomas Pycroft, M.A., K.C.S.I.; Lachlan Mackintosh Rate, M.A.; Sir Owen Roberts, M.A., F.S.A.; Arthur William Rücker, M.A., F.R.S.; John Bell Sedgwick, J.P., F.R.G.S.; Joseph Wilson Swan; Thomas Edward Thorpe, Ph.D., F.R.S.

General Monthly Meeting, May 5, 1890.

His Grace the DUKE OF NORTHUMBERLAND, K.G.,
D.C.L., LL.D., in the Chair first;
afterwards,

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.

The following Vice-Presidents for the ensuing year were announced:—

Sir Frederick Abel, C.B., D.C.L., F.R.S.; William Crookes, F.R.S.; Edward Frankland, D.C.L., LL.D., F.R.S.; William Huggins, D.C.L., LL.D., F.R.S.; The Right Hon. Earl Percy; Basil Woodd Smith, F.R.A.S., F.S.A.; Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer; Sir Frederick Bramwell, Bart., D.C.L., F.R.S., Hon. Secretary.

Harry Baldwin, M.R.C.S., A. R. Binnie, M.Inst.C.E.; Miss Frances Busk, J. S. Jeans, A. Kirkman Loyd, Ronald A. Scott, F.R.G.S., F.Z.S.; Mrs. John I. Thorneycroft, John Jewell Vezey, F.R.M.S., and Laundry Walters, were elected Members of the Royal Institution.

John Tyndall, D.C.L., LL.D., F.R.S., was elected Honorary Professor of Natural Philosophy.

The Right Hon. Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S., was elected Professor of Natural Philosophy.

NOTICES OF BOOKS.

The Art of Paper-Making. A Practical Handbook of the Manufacture of Paper from Rags, Esparto, Straw, and other Fibrous Materials, including the Manufacture of Pulp from Wood-Fibre, to which are added Details of Processes for recovering Soda from Waste Liquors. By ALEXANDER WATT. London: Crosby Lockwood and Son.

Mr. WATT may almost be pronounced the "Admirable Crichton" of chemical technology. He has already produced works on such very distinct subjects as soap-making, the leather manufacture, electro-metallurgy, and the art of electro-deposition. These treatises are not mere compilations, but practical works, evincing an actual acquaintance with the arts in question. That they have met recognised wants appears at once from the fact that all of them have appeared in several successive editions. We believe that the volume now before us will also prove useful and acceptable.

The author first speaks of cellulose, its behaviour with acids, its physical and microscopic properties, its determination, and the recognition of its chief modifications. He next comes to the multifarious materials used in the paper manufacture, whereby we are happy to find that he does not overlook the importance of the thorough disinfection of rags. These residues of human life and activity are especially dangerous if imported, as it often happens, from countries where a large part of the population live in a chronic state of misery and degradation, and where personal dirtiness extends to all classes. Few more effective vehicles of zymotic disease can be conceived than rags of such kinds. It must not be supposed that the prevalence of cholera or yellow fever is the only occasion for unusual vigilance. Nor is the danger greatest in rags introduced from India, Egypt, or Spain. Consignments from Russia must require even more scrupulous

care. Mr. Watt figures and describes a "disinfecting machine," by which suspected material may be treated in the bale without the expense, delay, and risk of opening out the packages.

In a chapter on the treatment of rags we find the remark that woollen rags are only used to a very moderate extent "in blotting and filtering-papers, and also in coarse papers and wrappers." For filter-papers woollen rags are, we submit, a most unsuitable material. Such papers require to be rapidly and completely combustible—a property with which the presence of wool-fibre would greatly interfere. It may here be remarked that Mr. Watt gives no instructions for the manufacture of filter-paper—a branch of the trade in which England has never taken as high a standing as Sweden, and, of late years, as Germany.

The processes for the treatment of esparto and of wood are very fully described. There is no mention of the prolonged litigation which has arisen in the German courts concerning the Mitscherlich process. Our author, however, seems to object to the acid methods of reducing wood to a pulp. The mechanical processes he recognises produce an inferior article. One of the defects of papers into which mechanical wood-pulp enters largely is that they are very readily discoloured, not only by the sun's rays, but even by the electric light. This fact has actually been utilised by a partisan of gas-lighting as an argument against the electric light.

Among methods for bleaching paper we find mention of certain electrolytic processes, which, whether they are legally valid or not, present a strong family likeness to the device for which the author's brother, Mr. Charles Watt, obtained a patent on September 25, 1851.

We do not find that the author throws out any cautions as to the escape of waste bleach-liquors into streams. Against this nuisance all authorities on the pollution of rivers and on sewage disposal have protested as destructive to fish and as unfitting the water alike for industrial and for domestic uses.

There is a favourable mention of the improved process of Dr. Lunge, who liberates chlorine or hypochlorous acid from the bleaching lime by the addition, not of the sulphuric or hydrochloric acid, but of the acetic—a very happy invention.

The "loading" materials in vogue are duly noticed, kaolin and calcium sulphate. It is certainly interesting to observe under what varying guises these two minerals figure, haunting us as they do in our dining-rooms, our dressing-rooms, and even in our studies. A better ingredient for loading is agalite, a species of asbestos which has a fibrous texture. It must be admitted that in all but the highest classes of paper "loading," if kept in moderation and skilfully applied, has its advantages. It gives the paper a smoother surface, into which the point of pen or pencil is less disposed to sink.

In speaking of colouring paper stock the author forgets that not all the aniline colours are liable to be injuriously affected by the acid of the alum used in sizing.

The "super-calendered" paper, now so much in fashion that we have heard the failure of a journal ascribed to its being printed on paper with a matt surface, is open to a very serious objection. By the strong reflection of light it injures the eyes of persons who have to read much.

Space, or the want of it, does not permit us to prolong our examination of this interesting work. But we can do no other than recommend it to all of our readers who are connected with or interested in the paper trade, as well as to technological students.

The Extension of Public Analysis. By CHARLES E. CASSAL, Public Analyst for St. George's, Hanover Square, Kensington, Battersea, and High Wycombe.

THIS paper was read at the Worcester Congress of the Sanitary Institute, where it may be said to have figured

as a redeeming feature. The author contends for two much-needed reforms, the adequate enforcement of the existing law and an extension of public analysis. Both these tasks are difficult. The former point is prevented by the blindness of a large part of the magistracy, stipendiary as well as unpaid. They cannot see that the adulterator stands morally on the same plane as the pick-pocket or the shop-lifter, and hence they dismiss fully proved cases, or at best inflict fines which are perfectly farcical. As for the extension of the law, the case is still worse. Any bill having this object would be thrust aside by the necessities of faction, and any ministry which should adopt it would have, at the next election, to encounter the "solid vote" of all those classes of traders whose tricks were interfered with. We quite agree with Mr. Cassal that the analysis of gas and of water should be placed in the hands of competent chemists. Medical officers of health are not always fit to conduct analytical work, and their duties should be kept quite distinct from those of the public analyst. The notion of appointing military men as inspectors of public water supply is regarded on the Continent as farcical. John Bull, it is contemptuously said, "puts his army and navy in the hands of civilians and, as compensation, entrusts matters of public health and of higher education to military officers."

The author most justly urges that poisonous quackeries, hair-dyes, soaps, cosmetics, dyes, wall-papers, children's toys, &c., should be liable to seizure and examination. If poisons are discovered where their presence is unsafe or unessential the punishment ought to be signal.

The tabular list of articles examined and found adulterated shows how much work remains to be done. Perhaps the worst figure is made by Nottinghamshire, where, out of 120 samples taken in 1887, 49, or 40.8 per cent, were found adulterated.

Mr. Cassal may rest assured of our sympathies and support in his endeavours to arouse the authorities and the legislature to a sense of their duty.

Proceedings of the American Pharmaceutical Association at the Thirty-seventh Annual Meeting, held at San Francisco, June, 1889; also, the Constitution, By-Laws, and Roll of Members. Philadelphia: The Association.

THE portion of this report in which we feel interested is that comprising the scientific papers laid before the meeting. The burning question of arsenic in wall-papers returns again. Mr. D. H. Galloway, the author of the paper, declares that when he began his inquiry he supposed that it could be decided by the mere appearance of a paper whether it is arseniferous. This, however, he found is not the case; arsenic is not confined to green colours, but is met with in reds and browns, where it is hard to conjecture what the necessity or even the pretext for its use may be. Prof. Wood, in the Report of the Massachusetts Board of Health for 1883, specifies the following articles as occasionally arseniferous:—"Dress goods, muslins, linen, artificial flowers, curtains, gloves, boot-linings, paper collars, linen collars (one collar containing 10.4 grs. (doubtless grains) of As_2O_3), hat-linings, coloured stockings, linings in baby carriages, bed hangings, coloured candles, and confectionery." To this list may be added painted toys, and even so-called French chalk. Some years ago a woman in one of our northern towns bought some prepared chalk as a cure for heart-burn, and was, by mistake, served with French chalk; she died shortly after with the usual symptoms of arsenical poisoning, and the chalk was found on analysis to contain about 25 per cent of As_2O_3 . *Query*, the motive?

In the paper before us it is further stated that "jellies are made out of glucose (?), and are largely coloured with aniline colours. You will find by testing these jellies that arsenic is present, whether in large quantities or not I do not know, but I know they are contaminated by

aniline colours, which contain arsenic." We must here declare, as the result of our own experience, that the aniline colours now sold by the most eminent manufacturers are free from arsenic.

An illustrated paper on photo-micrography is well worthy of notice. The composition of glucose, as met with in trade, is said to be 40—50 per cent of (factitious) grape-sugar and the same quantity of dextrin. We may here ask whether this glucose is not one of the channels through which arsenic is conveyed into articles of food and drink? The sulphuric acid employed in the manufacture of glucose is not always perfectly free from arsenic.

It is satisfactory to learn that a firm who attempted to sophisticate refined cane-sugar with glucose lost half a million dollars by the experiment.

The chapter on patent and trade-mark laws is very valuable. We must, however, protest against a quotation from the "Encyclopædia Britannica" on the subject of copyright. The author says:—"Historically and in legal definition there would appear to be no doubt that copyright, as regulated by Statute, is a monopoly." In reply, we say that, according to Blackstone, a monopoly is a privilege by which the public at large are prevented from doing something which they were previously free to do. But it is obvious that no one is free to publish a book before it is written, so that the public is deprived of nothing. The sophistry of C. Renouard, here quoted, would be fatal not merely to property in literary works and inventions, but to property of all kinds.

The so-called "patent medicine" business, now worked not so much under the patent laws as under the Copyright and Trade Marks Act, is strongly and justly denounced. The method used in America, which differs little from that pursued in England, is thus described:—"A new preparation is devised, or a compound of old and well-known drugs is mixed, and a name invented by which to designate the compound. This name is registered as a trade-mark; the true or working formula of the preparation is kept secret, and the preparation is marketed under the alleged protection of the trade-mark law. By this system knowledge is concealed, progress in science and art hindered, error inculcated, and the public injured instead of being benefitted." An utterance of this kind from the United States is all the more welcome, as that country is now inundating the world with quack nostrums.

New York State Board of Health. Report of WILLIS G. TUCKER, M.D., Ph.D., Analyst of Drugs.

THIS report refers to the official inspection and analysis of drugs. The classification in use is "good quality" when the preparations fulfil the requirements of the United States Pharmacopœia; "fair" if neither intentionally sophisticated nor decidedly below the standard; and "inferior" if evidently falsified, deficient in strength, partially decomposed, &c. It is remarked that the samples bear no direct relation to their quality. Out of 505 samples examined 43.8 per cent were reported as good, 17.4 as fair, 26.0 as inferior, 11.6 "not as called for," and excessively strong 1.2 per cent. Some of the articles reported "not as called for," were safflower, sold in place of saffron! Saffron has possibly certain medicinal uses, but as a dye-ware it is little better than rubbish.

There is a special report on cigarettes which had been said to be adulterated with opium. This did not prove to be the case, and from financial reasons is very improbable. Dr. Tucker, however, complains of the common sale and use of cigarettes by young children, "whose morals are depraved by the suggestive and openly indecent pictures used to advertise certain brands, which pictures are freely exposed in the store windows, and packed in the boxes with the cigarettes."

Another special report relates to vermin killers, which

may be dangerous to human life, and concerning which the Assembly of the State of New York and the State Board of Health seem greatly exercised.

Poisons for rats may be rendered perfectly safe if made up in the form of *candles*, arsenical, phosphorised, or containing strychnine. Neither children nor domestic animals will eat such dainties. The outcry against the free sale of poisons on either side of the Atlantic seems to be inconsistent, even to the verge of hypocrisis, so long as no restrictions are placed on the traffic in fire-arms and ammunition. The legitimate uses of poisons are far more numerous than those of revolvers and cartridges, and the evil which they can occasion even in bad or careless hands is much slighter.

CORRESPONDENCE.

SCIENTIFIC TERMINOLOGY.

To the Editor of the Chemical News.

SIR,—It is truly said that when a word has once been dirtied no human power can cleanse it. At present, a termination of frequent use in organic chemistry, and a set of paronyms which occur in all scientific and philosophical writings, have been so misused by outsiders that they should, I submit, if possible, be abandoned.

The termination in question is *ine*. We find the inventors of so-called "proprietary" medicines, &c., using it as a tail-piece to the names of their nostrums, though these are mere mixtures, not chemical individuals—not to speak of alkaloids. Not long since I saw a disinfectant advertised as "Listerine"!

Would it not be well to dispense with this termination in chemical treatises? The halogens might be simply called fluor, chlore, brome, and iode; whilst the alkaloids might resume the termination *a* or *ia*, which was at one time in very general use.

A still worse case is the abuse of the term "phenomenon." Every scientific man is, of course, agreed as to the legitimate and etymological meaning of the word—which, for once, coincide. But, unfortunately, showmen and strolling actors applied it to something marvellous. Their example has been followed to such a degree that even eminent physicians are not ashamed to speak of "phenomenal agents." It would be easy in chemical and physical writings to use such words as "appearances," "manifestations," "results," or "reactions" in place of "phenomena."—I am, &c.,

J. W. SLATER.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 16, April 21, 1890.

Obituary.—At the session of April 21 the president announced the death of Prof. Peligot, which took place on Tuesday, April 13. We hope to lay before our readers a sketch of his prolonged scientific activity.

Formation-heat and the Reactions of Hydroxylamine.—MM. Berthelot and André.—The authors give the formation-heat of this compound as 23·8 cal.

Preparation of Iridium Dioxide.—G. Geisenheimer.—The author prepares the hydrated dioxide by heating 3 grms. of iridium to redness for two or three hours in a golden crucible with 10 grms. caustic soda and 3 grms.

sodium nitrate. The mass, when cold, is taken up with boiling water.

Action of Hydrogen Peroxide upon the Oxyc compounds of Manganese.—A. Gorgen.—Contrary to the usual opinion the author finds that in contact with pure crystalline anhydrous dioxide the oxygenated water splits up instantly, but requires about an hour; the effect upon the dioxide varies according as the oxygenated water is slightly alkaline or more or less acid. In experiments where hydrated manganese oxide was put in contact with an excess of oxygenated water the degree of oxidation reached exceeds that of Mn_2O_3 .

Preparation and Formation-Heat of Sodium Erythrate.—M. de Forcrand.—From analogy this heat may be estimated as between 215 and 220 cal.

Chlorine Derivatives of the Amylamines.—A. Berg.—An account of monochloramylamine, dichloramylamine, and chlorodiamylamine.

The Alcoholic Fermentation of Invert-Sugar.—U. Gayon and E. Dubourg.—It results from the author's researches that the alcoholic ferments differ not merely by their form, their action upon saccharose, their fermentive power, &c., but also by their mode of action upon the constituent elements of invert-sugar.

Alcoholic Fermentation and the Transformation of Alcohol into Aldehyd by the Fungus of the Lily of the Valley.—Georges Linossier and Gabriel Roux.—The alcoholic fermentation set up by the fungus in question has rather the characters of fermentation occasioned by mucedo than those of fermentation by beer-yeast. Hence we are justified in eliminating the fungus of the lily of the valley from the group of *Saccharomyces*.

Zeitschrift für Analytische Chemie.
Vol. xxviii., Part 6

Examination of Resins.—Kremel.—The author gives the acid—the Köttsdorf—and the iodine numbers of the most important resins. The potassa taken up by boiling the sample for half an hour with semi-normal alcoholic potassa-lye and titrating back the excess with semi-normal hydrochloric acid and phenolphthalein, is given in a table by R. Williams, taken from the CHEMICAL NEWS. The numbers, multiplied by 10, correspond to the Köttsdorf figures.

Approximate Determination of Resin in Ceresine.—H. Symons.—From the *Pharm. Journal*.

Two New Analytical Methods for the Valuation of Manganese Peroxide.—Paul Charpentier.—Already noticed under *Comptes Rendus*.

Two Impurities in Litharge.—Th. Salzer (*Pharm. Central Halle*).—The impurities are nitrous acid and gypsum. The nitrous acid is dissolved on treating the sample with water. It dissolves also in the preparation of basic lead acetate. Gypsum in litharge renders water strongly alkaline, and may be removed by continued washing.

Valuation of Roofing Slates.—H. Brunner.—The absence of calcium carbonate, tesseral crystals of pyrites, and orthorhombic crystals of markasite must be ascertained microscopically. The height to which water will rise in slips of the sample must also be determined.

Quantitative Determination of Some Tar Colours; in particular, Naphthol Yellow S, Picric Acid, and Certain Azo-Colours.—Christopher Rawson and E. Knecht (*Chemiker Zeitung*).—The authors dissolve 10 grms. "night blue" in 50 c.c. glacial acetic acid and dilute to 1 litre. Solutions of the colours in question are then made of 1 gm. per litre. The *modus operandi* is as follows:—10 c.c. of the blue solution is measured with a pipette into a flask and a known quantity of the picric or naphthol-yellow solution is added. After about a minute the liquid is filtered and the colour of the filtrate

examined. The experiment is then repeated with a fresh quantity of the blue solution and more or less of the picric acid or naphthol yellow solution is added. The mixture is again filtered, the colour of the filtrate examined, and the experiment is repeated until the next drop of the yellow solution produces a yellow colouration in the filtrate. The reaction is applicable to the examination of "night blue" and crystal violet.

Quantitative Determination of Wood-Stuff in Paper.—R. Godefroy and M. Coulon (*Gewerbe Museum Wien*).—Cellulose which has been extracted by boiling with water, alcohol, and ether does not reduce dilute solution of gold chloride at a boil, whilst wood-paste has a powerful reductive action. In examining papers the sample, carefully weighed, is treated first with cold and then with boiling water to remove size, and the alumina present is then extracted by treatment with a boiling solution of tartaric acid in alcohol at 80 per cent. It is dried, extracted with alcohol and ether, and then treated with gold chloride.

Microscopic Examination of Cattle-Foods.—Th. Ritter v. Weinzerl.—100 grms. of the sample, which must have been carefully mixed up, are separated into four portions by passing through sieves with meshes of 1.5, 1, 0.5, and 0.25 m.m. in size. The nature of the foreign ingredients is next ascertained by examination, first with a lens of low power and then with the microscope. The weight of the four portions is then ascertained, and in particular millet-flour and fragments of millet husks are separated optically.

Determination of Chlorine in the Ash of Plants.—Ad. Jolles (*Zeitschrift für Nahrungsmittel*) carbonises 10 grms. of the sample at a low temperature, grinds up the carbon, and moistens it with an alcoholic solution of sodium carbonate (the strength of the alcohol and the proportion of the salt are not given). The alcohol is then burnt off, the carbon pulverised again, soaked again as before, and burnt off twice or thrice, and finally incinerated at dull redness. About 0.5 gm. of the ash is perfectly extracted with cold water containing nitric acid, the silica is separated, though in what manner the author does not mention, the filtrate is run into a quarter litre flask and filled up to the mark. 25 c.c. of this liquid are then accurately neutralised and the chlorine is determined by titration.

Valuation of Coca Leaves.—H. J. Pfeifer.

Valuation of Crude Cocaine from Peru.—E. R. Squibb.—Both these papers are taken from the *Chemiker Zeitung*, to which the reader is referred (vol. xi., p. 818; and xiii., p. 342).

Determination of Ethereal Oils and Essences.—Alb. Levallois.—Noticed under *Comptes Rendus* (vol. xcix., p. 917).

Spectroscopic Behaviour of Ethereal Oils.—W. A. Tichomirow (*Pharm. Zeit. für Russland*).—If fresh colourless oil of citron flowers is shaken up with a saturated watery solution of acid sodium sulphite, after separation of the layers the upper stratum appears first orange, then red, and lastly purple. If the oil thus coloured is diluted until the part of the absorption spectrum between 9 and 10 of the scale is no longer darkened a characteristic absorption-spectrum is obtained. The author appears to have used the spectroscope of Schmidt and Haensch.

Examination of Officinal Grey Mercurial Ointment.—E. Dietrich.—For this paper we must refer to the original.

A New Reaction of Phenacetine.—E. Ritsut (*Pharm. Zeitung*).—If phenacetine is dissolved in cold strong sulphuric acid and there are added a few drops of strong nitric acid the solution at once turns yellow. If more nitric acid is added a colouring-matter of a pure citron yellow separates out,

Examination of Potassium Iodide for Nitrate.—O. Schwarz (*Pharm. Zeitung*).—0.5 gm. of the sample, 1 gm. ground copper sulphate, and 0.8 gm. ground sodium sulphite are placed in a test-tube and covered with 10 c.c. water. The mixture is heated over the naked flame until all the iodine has been separated out as white copper iodide, and the supernatant liquid has a bluish colour. In the filtrate, nitric acid, if present, may be detected by the ordinary reagents.

Determination of Urea.—L. Bleibtren (*Pflüger's Archiv*) finds that his method, which depends on the splitting up of urea by means of phosphoric acid at high temperatures, is applicable to the urine of dogs.

The Determination of Urea by Alkaline Hypobromites.—R. Luther (*Zeitsch. Physiol. Chemie*) shows that the cause why this process does not yield the total nitrogen is that about 1½ per cent of the nitrogen, after the evolution of gas has ceased, remains in a form in which it can be obtained by distillation with alkali as ammonia. Another portion (3–4 per cent) is oxidised to nitric acid.

Determination of Uric Acid in Human Urine.—W. Camerer (*Zeit. f. Biologie*).—The uric acid is precipitated with ammoniacal solution of silver, and the uric acid is calculated from the nitrogen in the precipitate.

Rapid Determination of Iron in Blood.—L. Lapique (*Soc. Biologique*).—Two grms. blood are heated with 3 c.c. pure sulphuric acid in a flask placed in a slanting position until the coagulum first formed is redissolved. It is then let cool and heated again after the addition of a few drops of pure nitric acid until a clear, slightly coloured liquid is obtained which no longer turns brown on heating. It is then diluted and boiled for a few minutes. When cold it is diluted to 40 c.c., and 10 c.c. of a 20 per cent solution of ammonium sulphocyanide are added. The iron is then determined colorimetrically.

Detection of Traces of Mercury in Animal Liquids.—E. Brugnati (*Riforme Medica*).—The author utilises the power of mercurial vapours to reduce gold. 50–100 c.c. of the liquid are acidified with a few drops of hydrochloric acid on the water-bath along with copper wire or copper powder which has previously been ignited in a current of hydrogen, heated to 50°–60°, and then shaken for five minutes. The copper is washed with water and placed in a glass capsule along with an ignited fragment of porcelain which has been moistened with a drop of a 1 per cent solution of gold chloride. The capsule is covered with a watch-glass and heated on the water-bath, when red or violet spots with a gold reflection appear on the porcelain.

Quantitative Determination of Mercury in Urine.—R. Winternitz (*Archiv für Pathologie*).—This paper requires the two accompanying illustrations.

Detection and Estimation of Sugar in Urine.—L. Crismes (*Annal. de la Soc. Med. de Liege*).—The author's process turns on the conversion of safranin into colourless products by reduction.

Detection of Albumen in Urine.—A. R. Cohen (*Weekblad Nederl. Tijd. voor Geneesk.*)—The reagents employed are a solution of bismuth iodide in potassium iodide and a Lugol's solution prepared with acetic acid.

Detection of Blood and Pus in Urine.—C. v. Brücke.—The author adds to 5–6 c.c. urine, 1 c.c. oil of turpentine, and 1 c.c. tincture of guaiacum. A blue colour shows the presence of blood.

Detection of Melanine and Melanogen in Urine.—R. v. Jaksch (*Zeit. Phys. Chemie*) adds moderately diluted solution of ferric chloride, which gives a black precipitate.

An Improvement in the Marsh Apparatus.—E. Lehmann.—The pieces of zinc serving for generating the gas are fixed to a glass rod which works air-tight in the stopper and can slide.

New Method for the Microscopic Examination of Paper.—F. v. Höhnel (*Gewerbe Museum Wien per Chemiker Zeitung*).—The author separates paper fibres into three groups:—(1) Old rag fibre (linen, hemp, cotton); (2) the superior substitutes, consisting chiefly of cellulose (wood-cellulose, straw-cellulose, esparto fibre; (3) the inferior substitutes, woody fibre and jute; by means of the colours produced with iodine and sulphuric acid. He omits to give the sp. gr. of the sulphuric acid, which, he says, is quite essential. He takes linen and cotton fibres from white rags, also some wood-cellulose and white straw-stuff, and boils the fibres together for a few minutes in potassa-lye at 1 to 5 per cent. He washes the lye away and places very small quantities of each kind on the object bearer. It is important that the fibres do not form knots or lumps, but must be carefully teased out with the needle. After the water has been removed by twice pressing in filter-paper he adds a drop of solution of iodide in potassium iodide, so strong that a drop 3 c.m. thick, though clear and transparent, must appear ruby red. The drop must entirely cover the fibres. After one minute's or two minutes' contact the moisture is completely removed by pressure with filter-paper and the fibres are moistened with a drop of sulphuric acid and the cover-glass is applied. Cotton, flax, and hemp must appear of a fine violet-red; wood- and ordinary straw-cellulose pure blue or grey-blue. By this procedure, applied to paper, cotton, hemp, flax, jute bleached white, China-grass and paper-mulberry appear violet-red, wood- and common straw-cellulose appear pure blue, wood-stuff and unbleached jute dark yellow. If the papers contain esparto or maize fibres the sulphuric acid must be more concentrated. The process is applicable only to fine papers.

Examination of Essential Oils.—H. Hager (*Pharm. Central-Halle*).—The author utilises their behaviour with a mixture of equal parts by weight of glycerin (sp. gr. 1.259—1.262) and absolute alcohol. In this manner the oils are divided into two groups, the one forming a turbid solution with two volumes of the alcoholic glycerin and the other a clear solution. Of the former class some remain turbid, even with 16 vols. of the reagent, whilst others become clear if mixed with 3, 4, 5, &c. vols.

MEETINGS FOR THE WEEK.

- MONDAY, 12th.—Society of Arts, 8. "Sugar, Tea, Coffee, and Cocoa, their Origin, Preparation, and Uses," by Richard Bannister.
- TUESDAY, 13th.—Royal Institution, 3. "The Art of Engraving—1. Wood Engraving," by Louis Fagan.
 --- Institute of Civil Engineers, 8.
 --- Royal Medical and Chirurgical, 8.30.
 --- Photographic, 8.
 --- Society of Arts, 8. "The Use of Alloys in Art Metal Work," by Prof. W. C. Roberts-Austen, F.R.S.
- WEDNESDAY, 14th.—Society of Arts, 8. "Prof. Elihu Thomson's Electro-Magnetic Induction Experiments," by Dr. J. A. Fleming, M.A.
 --- Geological, 8.
 --- Microscopical, 8.
- THURSDAY, 15th.—Royal Institution, 3. "Flame and Explosives," by Prof. Dewar, M.A., F.R.S.
 --- Society of Arts, 5. "Jamaica and its Forthcoming Exhibition," by C. Washington Eves, C.M.G.
 --- Society of Arts, 8. "Design Applied to Wood-carving," by Lewis F. Day.
 --- Chemical, 8. Ballot for the Election of Fellows. "On Diethylphosphorous Acid," by Professor Thorpe, F.R.S., and Barker North. "The Ten Isomeric Dichloronaphthalenes" and "The Action of Chlorine on Naphthalene and Naphthalene Derivatives," by Prof. Armstrong and W. P. Wynne. "A Third Naphthaquinone," by Prof. Meldola and Frank Hughes.
 --- Institute of Electrical Engineers, 8.
- FRIDAY, 16th.—Royal Institution, 9. "The Photographic Image," by Prof. Raphael Meldola, F.R.S.
 --- Physical, 5. "On Huyghens' Gearing in Illustration of Electric Induction," by Lord Rayleigh. "Dr. R. König's Researches on the Physical Basis of Music," by Prof. S. P. Thompson.
- SATURDAY, 17th.—Royal Institution, 3. "Recent Excavations in Greece," by Dr. Charles Waldstein.

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17 MAY 90

ON THE MAGNETISATION OF METALS.

By THOMAS T. P. BRUCE WARREN.

It is well known that if a bar of iron or steel be magnetised, there is a linear increase in the magnetic "line of direction," but I am not aware of any previously published experimental data showing whether the increment is cubical, or whether the extension in length, or "line of direction," is accompanied with a diminution in the other linear directions of the mass. My experiments, which have been frequently repeated, show that there must be a diminution in the transverse section of a rod, for the same rod, when magnetised, occupies the same bulk as before being magnetised; in fact, there seems to be a slight diminution. I hope to deal more fully with this portion of the subject in a future communication.

I cannot find that any experiments have been made showing the effects of cubical compression if, for instance, a bar of iron or steel be rigidly prevented from altering its dimensions, would it be possible for the same to acquire a high degree of magnetisation relatively, when under no restraint? The solution of this problem might throw much light on the behaviour of the dipping needle when traversing a country where magnetic rocks are supposed to exist.

Bearing upon this, we must not omit to take into account the screening effect due to the magnetic permeability of the various geological deposits overlying a stratum of high magnetic susceptibility.

An arrangement which I designed some time ago, and which I termed a "Torpedo-finder," is based upon these facts. The position of a submerged torpedo, anchor, or any piece of iron may be indicated by means of the magnet, but, unfortunately, the low permeability of water involves the lowering of the magnet to within a short depth of the plane containing the submerged mass.

An electro-magnet, or solenoid, may be made magnetically stronger than an ordinary magnet. The electro-magnet is lowered to within a few feet of the bottom, the depth of which has been previously ascertained by careful sounding. The electro-magnet is excited by a primary or secondary battery. By means of a delicate dynamometer, the strain due to the electro-magnet and its leading wires are noted, the battery power is increased, when any increased pull will indicate the existence of some disturbing cause in the neighbourhood; by keeping the magnet clear of the bottom and gently steering we avoid uncertainty in the dynamometer indication, as is experienced in dragging over a rough or uneven bottom.

ESTIMATION OF AMMONIA BY RUFFLE'S METHOD.

By ALEXANDER BUCHAN, F.I.C.

AN objection to this method, particularly to those who use iron tubes, is the fusing of the contents of the tube and the consequent trouble of cleaning; so much so, that Mr. Ruffle (*Journal of the Chemical Society*, March, 1881) gives very full directions as to how this can best be done.

If, instead of exactly following the modification of the Association of Official Agricultural Chemists (*CHEMICAL NEWS*, vol. lv., p. 6), one uses soda-lime prepared as follows, instead of ordinary soda-lime, the mixture does not fuse and there is no trouble in cleaning out the tubes:—

Grind quicklime and washing-soda through a riddle of sixteen holes to the lineal inch, mix in equal proportions, and heat over an ordinary fire, in an iron pot, stirring all the time, until no more watery vapour is given off; the pot should only be one-third full, as the mixture swells very much.

The author has tried many plans for the conjoint estimation of nitric nitrogen and ammonia, but none were so good as the Ruffle, and except for the trouble of cleaning the tubes he would never have attempted to find another.

Many tests have been published showing the results obtained by this method compared with the theoretical ammonia, but, so far as the author is aware, none have been shown with a synthetical manure containing much chlorides.

The following may be of interest. A mixture was made as under:—

Parts.		Containing p.c. NH ₃ .	
9	dissolved bone manure ..	1'25	9 × 1'25 = 11'2
1	Belgian phosphate ..	—	—
1½	fish guano	10'41	1½ × 10'41 = 15'6
1½	Liebig's guano	8'62	1½ × 8'62 = 12'9
4	sulphate of ammonia ..	24'75	4 × 24'75 = 99'0
3	chloride of potassium ..	—	—
20			20)138'7
			6'93

Two combustions by the ordinary method, using this special soda-lime, gave 6'97 and 7'03, mean 7'00 per cent.

Part.		Containing p.c. NH ₃ .	
0'8	of the above	7'00	0'8 × 7'00 = 5'60
0'2	pure nitrate of potash	16'83	0'2 × 16'83 = 3'36
			8'96

yielded 8'56 per cent by the modified Ruffle.

It will be observed that this contains much more nitrate than the usual run of manures, and one would therefore expect to get closer results in these cases.

Port Dundas Chemical Works,
Glasgow, May 6, 1890.

BORONISED SILVER.

By H. N. WARREN, Research Analyst.

THE element boron, when in its simplest form, presents no special affinity in general towards the non-oxidisable metals; but, by suitable means, the author has succeeded in combining variable amounts of from 5 to 6 per cent with metallic silver. This peculiar compound, of which I intend giving a brief description, first met my attention in endeavouring to reduce to the metallic state some residual argentic borate which had been specially prepared, containing an excess of free alkali, and intended for electrical research. On reducing this so prepared substance in contact with charcoal at a high temperature a button of metallic silver was obtained, which on close examination was observed to possess several abnormal properties; in so much that the colour of the same, when compared with a standard of pure silver, presented a decided yellow colour; at the same time, being less readily attacked either by the aid of acids or the vapour of sulphur. The presence of boron did not, however, strike me until a much later period, when I substituted for the above mixture one of potassium borofluoride, sodium, and scrap silver; on the application of a strong heat to the same, by the aid of an injector furnace, a button of silver possessing a decided yellow colour was obtained, and averaged after cupellation about 3 per cent difference. After several experiments were performed,

differing slightly from each other, I became influenced that pressure played a considerable part in aiding the combination of the boron, and as an improvement the following method was selected:—

Perfectly dried boric anhydride was obtained by the fusion of pure boracic acid, and intimately mixed with finely precipitated silver; to this was added a sufficiency of magnesium powder, and the whole introduced into a deep iron crucible, which was previously lined with charcoal, the same being provided with a heavy screw lid. The crucible and its contents were next raised and maintained at a white heat for half an hour; the silver thus obtained after extraction from its enclosure presented to all appearance an alloy of gold and silver, being with difficulty dissolved in nitric acid, and much less readily acted upon by the vapour of sulphur. A careful analysis of one of these buttons of so prepared silver showed the presence of 6 per cent boron.

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

MANURE DRYERS.

By VINCENT EDWARDS., F.C.S.

THE object of the following experiments was to ascertain what effect, other than increase of weight and reduction of percentage of phosphate, &c., the addition of substances known as dryers has upon manures. They are added to the manure on removal from the "den" where it has been mixed, and are both for absorbing moisture and reducing the manure in value, so that the price may suit a section of the consumers. There is, of course, no objection to this, as a certain strength is usually guaranteed, but it seems a pity to use for this purpose anything that is detrimental to the manure and dangerous to the crop to which it is applied, especially when the remedy is easy. I have, from time to time, in testing super-phosphates noticed a reduction of strength and decrease of solubility greatly in excess of what would be due to the mere addition of inert chemical matter, and suspected this to be caused by soluble iron and alumina in the dryer. When in a soluble condition these elements are highly injurious to superphosphates, a fact which has been long known, and which renders many kinds of phosphate rock, of otherwise good quality, nearly useless. The ferric phosphate formed on addition of sulphuric acid is extremely insoluble in water, more so than tricalcium phosphate, while the same may be said of aluminum phosphate, though aluminum is not present in so large a quantity in phosphate rocks as iron. The artificial manure made is now so extensive and important that any facts tending to prevent mistakes and errors must be beneficial, and will, I hope, be taken as my apology for presenting the following results:—

I procured a quantity of high class superphosphate, made in the usual way from Norwegian phosphate rock of good quality. This superphosphate gave on analysis 12.7 per cent soluble P_2O_5 , equal to 27.72 $Ca_3P_2O_8$, or, to use the common way of expressing quality, 27.72 per cent "soluble phosphate." With this the experiments were made.

NO. 1 EXPERIMENT.—*Cinders.*—I obtained some cinders from steam coal; I believe they are frequently added to manures from the appearance of samples I have seen, which came from various parts of the country, the makers' names being unknown to me; some of them no credit to any manufacturer, and I am inclined to think some parties in the manure trade are not so straightforward as they might be. But the consumer is to blame if he will buy without an analysis of the principal ingredients, which is now so easily and cheaply obtained. The cinders gave on treatment with HCl, which I considered would extract at once all the soluble iron and

alumina, 12.0 per cent Fe_2O_3 , 1.4 per cent Al_2O_3 , though a small quantity of the iron existed as FeS , H_2S gas being given off on the addition of HCl. I may mention, I find that when treating the insoluble portion of manures with HCl this gas is frequently noticed, and is a suspicious indication, as few phosphates contain any sulphide of iron, though iron pyrites may, of course, occur, and is not nearly so harmful, being quite insoluble in sulphuric acid. I made a mixture of nine parts of the superphosphate and one part of cinders, which certainly had the effect of rendering the manure very dry and friable. I allowed the mixture to stand for fourteen days, which is, I consider, about the time a superphosphate takes in getting from the "den" to the consumer, though it is often stored for weeks or even months, during which the conversion to $Fe_2P_2O_8$ and $Al_2P_2O_8$ is still going on. When analysed, the result of the mixture was 21.6 per cent soluble phosphate; this would indicate that the dryer had reduced the percentage of soluble phosphate by 5.12 per cent instead of 2.77 per cent, the reduction being due to the addition of 10 per cent of inert matter, a serious falling of in quality converting a really good superphosphate into a manure of the poorer class.

(To be continued).

SUMMARY OF USEFUL TESTS WITH THE BLOWPIPE.*

By A. J. MOSES.

(Continued from p. 225).

CARBONIC ACID, CO_2 .

With Nitric Acid.—Heat with water and then with dilute acid. CO_2 will be set free with effervescence. The escaping gas will render lime-water turbid.

With Borax or S. Ph.—After the flux has been fused to a clear bead, the addition of a carbonate will cause effervescence during further fusion.

CHLORINE, Cl.

With S. Ph. Saturated with CuO .—Treated at tip of blue flame, the bead will be surrounded by an intense azure-blue flame.

On Coal with CuO .—Grind with a drop of H_2SO_4 , spread the paste on coal, dry gently in O. F., and treat with blue flame, which will be coloured greenish blue and then azure-blue.

CHROMIUM, Cr.

With Borax or S. Ph.—O. F. reddish hot, fine yellow-green cold.

R. F. in borax, green hot and cold. In S. Ph., red hot, green cold.

With Soda.—O. F., dark yellow hot, opaque and light yellow cold.

R. F., opaque and yellowish green cold.

Interfering Elements.

Manganese.—The soda bead in O. F. will be bright yellowish green.

COBALT, Co.

On Coal, R. F.—The oxide becomes magnetic metal. The solution in HCl will be rose-red, but on evaporation will be blue.

With Borax or S. Ph.—Pure blue in either flame.

Interfering Elements.

Arsenic.—Roast and scorify with successive additions of borax. There may be, in order given:—Yellow (iron), green (iron and cobalt), blue (cobalt), reddish brown (nickel), green (nickel and copper), blue (copper).

* From the *School of Mines Quarterly*, vol. xi., No. 1.

Copper and other Elements which Colour Strongly.—Fuse with borax and lead on coal in R. F. The borax on platinum wire in O. F. will show the cobalt, except when obscured by much iron or chromium.

Iron, Nickel, or Chromium.—Fuse in R. F. with a little metallic arsenic, then treat as an arsenide.

Sulphur or Selenium.—Roast and scorify with borax, as before described.

COPPER, Cu.

On Coal R. F.—Formation of red malleable metal.

**Flame.*—Emerald-green or azure-blue, according to compound.

The azure-blue flame may be obtained—

(a) By moistening with HCl or aqua regia, drying gently in O. F., and heating strongly in R. F.

(b) By saturating S. Ph. bead with substance, adding common salt, and treating with blue flame.

With Borax† or S. Ph.—O. F., green hot, blue or greenish blue cold.

R. F., greenish or colourless hot, opaque and brownish red cold. With tin on coal this reaction is more delicate.

Interfering Elements.

‡*General Method.*—Roast thoroughly, treat with borax on coal in strong R. F., and—

If Button Forms, separate the button from the slag, remove any lead from it by O. F., and make either S. Ph. or flame test upon residual button.

If no Visible Button Forms, add test lead to the borax fusion, continue the reduction, separate the button, and treat as in next test (lead alloy).

Lead or Bismuth Alloys.—Treat with frequently changed boracic acid in strong R. F., noting the appearance of slag and residual button.

Trace.—A red spot in the slag.

Over One Per Cent.—The residual button will be bluish green when melted, will dissolve in the slag and colour it red upon application of the O. F., or may be removed from the slag and be submitted to either the S. Ph. or the flame test.

FLUORINE, F.

Etching Test.—If fluorine is released it will corrode glass in cloudy patches, and in presence of silica there will be a deposit on the glass. According to the refractoriness of the compound the fluorine may be released—

(a) In closed tube by heat.

(b) In closed tube by heat and KHSO_4 .

(c) In open tube by heat and glass of S. Ph.

With Conc. H_2SO_4 and SiO_2 .—If heated and the fumes condensed by a drop of water upon a platinum wire, a film of silicic acid will form upon the water.

IODINE, I.

With S. Ph. Saturated with CuO .—Treated at the tip of the blue flame the bead is surrounded by an intense emerald-green flame.

In Matrass with KHSO_4 .—Violet choking vapour and brown sublimate.

In Open Tube with Equal Parts Bismuth Oxide, Sulphur, and Soda.—A brick-red sublimate.

With Starch Paper.—The vapour turns the paper dark purple.

Interfering Elements.

Silver.—The iodide melts in KHSO_4 to a dark red globule, yellow on cooling, and unchanged by sunlight.

IRON, Fe.

On Coal.—R. F., Many compounds become magnetic. Soda assists the reaction.

**With Borax.*—O. F., yellow to red-hot, colourless to yellow cold.

R. F., bottle-green. With tin on coal, vitriol-green.

With S. Ph.—O. F., yellow to red hot, greenish white cooling, colourless to yellow cold.

R. F., red hot and cold, greenish white cooling.

State of the Iron.—A borax bead blue from CuO is made red by FeO and greenish by Fe_2O_3 .

Interfering Elements.

Chromium.—Fuse with nitrate and carbonate of soda on platinum, dissolve in water, and test residue for iron.

Cobalt.—By dilution the blue of cobalt in borax may often be lost before the yellow of iron.

Copper.—May be removed from borax bead by fusion with lead on coal in R. F.

Manganese.—(a) May be faded from borax bead by treatment with tin on coal in R. F. (b) May be faded from S. Ph. bead by R. F.

Nickel.—May be faded from borax bead by R. F.

Tungsten or Titanium.—The S. Ph. bead in R. F. will be reddish brown instead of blue or violet.

Uranium.—As with chromium.

Alloys, Sulphides, Arsenides, &c.—Roast; treat with borax on coal in R. F., then treat borax in R. F. to remove reducible metals.

LEAD, Pb.

On Coal.†—In either flame is reduced to malleable metal, and yields near the assay a dark lemon-yellow coat, sulphur-yellow cold, and bluish white at border.

With Bismuth Flux:—

On Plaster.—Chrome-yellow coat, blackened by $(\text{NH}_4)_2\text{S}$.

On Coal.—Volatile yellow coat, darker hot.

Flame.—Azure-blue.

With Borax or S. Ph.—O. F., yellow hot, colourless cold, flames opaque-yellow.

R. F. Borax bead becomes clear, S. Ph. bead cloudy.

Interfering Elements.

Antimony.—Treat on coal with boracic acid, and treat the resulting slag on plaster with bismuth flux.

Arsenic Sulphide.—Remove by gentle O. F.

Cadmium.—Remove by R. F.

Bismuth.—Usually the bismuth flux tests on plaster are sufficient. In addition, the lead coat should colour the R. F. blue.

LITHIUM, Li.

Flame.—Crimson, best obtained by gently heating near the wick.

Interfering Elements.

Sodium.—(a) Use a gentle flame and heat near the wick. (b) Fuse on platinum wire with baric chloride in O. F. The flame will be first strong yellow, then green, and lastly crimson.

Calcium or Strontium.—As these elements do not colour the flame in the presence of baric chloride, the above test will answer.

Silicon.—Make into a paste with boracic acid flux and water, and fuse in the blue flame. Just after the flux fuses the red flame will appear.

MAGNESIUM, Mg.

On Coal with Soda.—Insoluble, and not absorbed by the coal.

With Borax or S. Ph.—Clear and colourless, can be flamed opaque-white.

With Cobalt Solution.‡—Strongly heated becomes a pale flesh colour.

* A slight yellow colour can only be attributed to iron when there is no decided colour produced by either flame in highly charged beads of borax and S. Ph.

† The phosphate yields no coat without the aid of a flux.

‡ With silicates this reaction is of use only in the absence of colouring oxides. The phosphate, arsenate, and borate become violet-red.

* Sulphur, selenium, and arsenic should be removed by roasting. Lead necessitates a gentle heat.

† By repeated slow oxidation and reduction a borax bead becomes ruby red.

‡ Oxides, sulphides, and sulphates are best reduced by a mixture of soda and borax.

MANGANESE, Mn.

*With Borax or S. Ph.—O. F., amethystine hot; reddens on cooling. With much, is black and opaque. If a hot bead is touched to a crystal of sodic nitrate, an amethystine or rose-coloured froth is formed.

R. F., colourless or with black spots.

With Soda.—O. F., bluish green and opaque when cold. Sodic nitrate assists the reaction.

Interfering Elements.

Chromium.—The soda bead in O. F. will be bright yellowish green instead of bluish green.

Silicon.—Dissolve in borax, then make soda fusion.

MERCURY, Hg.

With Bismuth Flux:—

On Plaster.—Volatile yellow and scarlet coat. If too strongly heated the coat is black and yellow.

On Coal.—Faint yellow coat at a distance.

†In Matrass with dry Soda or with Litharge.—Mirror-like sublimate, which may be collected in globules.

MOLYBDENUM, Mo.

On Coal.—O. F., a coat yellowish hot, white cold, crystalline near assay.

R. F., the coat is turned in part deep blue, in part dark copper-red.

Flame.—Yellowish green.

With Borax.—O. F., yellow hot, colourless cold.

R. F., brown to black and opaque.

With S. Ph.—O. F., yellowish green hot, colourless cold.‡

R. F., emerald-green.

Dilute (¼) HCl Solutions.—If insoluble, the substance may first be fused with S. Ph. in O. F. If then dissolved in the acid and heated with metallic tin, zinc, or copper, the solutions will be successively blue, green, and brown.

If the S. Ph. bead has been treated in R. F. the solution will become brown.

(To be continued).

EXAMINATION OF CORPSES FOR ALKALOIDS AND METALLIC POISONS.

By Dr. ANTON SEYDA.

(Continued from p. 222).

As regards the metals which are not precipitable by sulphuretted hydrogen in an acid solution, we must remark that the question here is generally the separation of iron, aluminium, and zinc in presence of calcium and magnesium phosphates. The author proceeds as follows:—

The hydrochloric filtrate from the sulphuretted hydrogen precipitate is strongly concentrated on the water-bath in a porcelain capsule, in order to expel sulphuretted hydrogen, mixed with chlorine-water, and evaporated to dryness. The residue is taken up with water, acidified with hydrochloric acid, filtered, the filtrate supersaturated with ammonia, the excess of ammonia nearly expelled by heating on the water-bath; the precipitate is filtered off, the ammoniacal filtrate is acidulated with acetic acid, and sulphuretted hydrogen is passed in at first at a boiling heat and afterwards until cold. The whitish precipitate of zinc sulphide is filtered off and weighed upon a filter. The precipitate upon the filter is dissolved in nitric acid, the solution is mixed with tin in a platinum capsule, and by repeated cautious treatment with nitric all the tin is converted into stannic acid, and hereby the phosphoric acid into insoluble stannic phosphate. The residue is

moistened with nitric acid, taken up in water, and left to settle in a beaker. The supernatant liquid is decanted off, and the precipitate is repeatedly treated with fresh portions of water containing nitric acid in order to extract the obstinate residues of alumina.

The filtrate is then concentrated, mixed with ammonia, the precipitate is filtered off and incinerated in a platinum crucible along with the filter. The ignited residue is fused for half an hour with sodium carbonate, prepared from the bicarbonate.

The melt, when cold, is lixiviated with water, let settle in a beaker, filtered, and in the filtrate the alumina is isolated and determined in the known manner.

c. Detection and Determination of Tin.

The alkaline filtrate from the sulphuretted hydrogen precipitate has still to be tested for the possible presence of tin. To this end it is acidulated with hydrochloric acid, boiled up, and H₂S is passed into the hot solution (which is turbid from the separation of sulphur) until it is cold, and it is then let settle in a moderately warm place for twenty-four hours. The precipitate is then filtered off, well washed with a solution of ammonium acetate, and incinerated along with the filter in a porcelain crucible. The residue is moistened with nitric acid, which is cautiously evaporated off, and the crucible ignited. As the residue always contains an admixture of ferric oxide, it is rinsed quantitatively with water into a silver crucible, the water is evaporated off, its last traces being expelled by gentle heating; caustic soda (prepared from metallic sodium, and dehydrated by previous re-melting) is added, and the mixture is kept in flux for half an hour.

The dark red heat prescribed in manuals of quantitative analysis is not necessary for this operation, and it merely occasions unnecessary damage to the crucible. The conversion of stannic oxide into sodium stannate is effected just at the melting-point of caustic soda.

When cold, the melt is lixiviated with water in the silver crucible, the contents are passed into a beaker and let settle. If a precipitate has been formed, it is filtered off, the filtrate is acidulated with hydrochloric acid, and the tin is precipitated in the usual manner with H₂S, and, finally, weighed again as stannic oxide.

Final Considerations on the Detection of Metals and Poisons in Organisms.

Among the metals normally present in the human organism must be included potassium, sodium, calcium, magnesium, iron, and manganese. In examining a human corpse, we, further, almost always find aluminium, copper, and zinc; more rarely, tin and lead; this circumstance should be kept in view. Generally we must remark that the quantities of the latter metals rarely exceed 10 mgrms. A distinction must be made whether the matter is found in the organs of a child or of an adult, though this point is more a question for the medical expert. The sources of these foreign metals occurring in small quantities in the human organism is the use of implements of iron, lead, zinc, and copper, as well as of foods and drinks, especially including beer. If a metal is detected, the question may arise whether it is a result of prolonged medical treatment or of chronic poisoning. This may be the case with lead, mercury, and especially with arsenic. As to aluminium, it may find its way into the organs of a corpse in the most varied manners, even after death. This will be intelligible if we reflect under what circumstances a *post mortem* is often conducted in villages and small towns, where dust and sand may lie on the tables and fall from the roof. Aluminium may occur in two places, both in the portion soluble and in that insoluble in hydrochloric acid, since if sand is treated with chlorine traces of alumina may be dissolved.

It is well known that organic substances which have been rendered soluble by treatment with chlorine are precipitated to a greater or less extent by H₂S, whether in an acid or an alkaline solution. Its removal by fusing the

* The colours are more intense with borax than with S. Ph.

† Gold-leaf is whitened by the slightest trace of vapour of mercury.

‡ Crushed between damp unglazed paper becomes red, brown, purple, or blue, according to amount present.

sulphuretted hydrogen precipitate with saltpetre is confined, according to general practice, to that part of the precipitate from an acid solution which is soluble in alkaline sulphides (arsenic, antimony, and tin). The fusion process is inapplicable to the other portion (insoluble and alkaline sulphides) on account of the possible presence of mercury; but as, according to the author's procedure, mercury is first sought for, and isolated if necessary, there is no objection to the fusion process.

The author conducts the demonstration of arsenic—in opposition to the practice which is probably universal—directly with the hydrochloric solution of the organic matter, and adopts the indirect way only if a preliminary examination has shown the presence of nitric acid in considerable quantities, or that of mercury or aniline colours.

(To be continued).

TWO METHODS FOR THE DIRECT DETERMINATION OF CHLORINE IN MIXTURES OF ALKALINE CHLORIDES AND IODIDES.*

By F. A. GOOCH and F. W. MAR.

THE determination of chlorine associated with iodine in haloid salts is usually accomplished by differential or indirect means; either the two halogens are determined together in a portion of the assay, while the iodine alone is estimated in a second portion by one or other of well known methods, the difference between the sum of the halogens and the iodine being the chlorine sought; or, the silver salts of the halogens are weighed together and then converted into a single salt, or the metal, the ratio of chloride to iodide in the original salt being found by simple algebraic processes. If the amounts of iodine involved are minute, it is possible to separate that element by Fresenius's method of treatment with nitrous acid and a solvent like carbon disulphide, and then to determine chlorine directly in the residue; but the manipulation of the process is difficult, and the results inaccurate, when much iodine must be removed. The only method which has been deemed generally applicable to the direct estimation of chlorine associated with iodine in haloid salts is based upon Lassaigne's reaction, by which the iodine is precipitated as palladious iodide; but the necessity of removing the excess of palladium by hydrogen sulphide before proceeding to precipitate the chlorine is so irksome that, even in this process, it is found to be more convenient to fall back upon the estimation of chlorine as the difference between the iodine found by the palladium process and the sum of the iodine and chlorine obtained by another test in another portion of the material. A straightforward and easy method for determining the chlorine is obviously desirable, and in the work of which we here give an account we have endeavoured to find such an one.

It is a well-known fact† that when an aqueous solution of hydrochloric acid is boiled a point of concentration is reached, by the excessive loss of acid from stronger solutions and of water from weaker ones, at which for definite barometric pressure the liquid boils at a constant temperature and distils unchanged in composition. It follows naturally that a degree of dilution may be reached beyond which the loss of the acid must be inappreciable. Indeed, Fleischer justifies his use of hydrochloric acid as a standard in alkalimetric processes upon his observation that decinormal solutions of this acid, and even solutions of twice the strength (7.3 grms. to the litre), do not yield after ten minutes' boiling enough acid to redden blue

litmus-paper held in the steam. Hydriodic acid behaves similarly to hydrochloric in the matter of volatilising from aqueous solutions; but to the decomposing action of oxidising agents it is far more sensitive. Our endeavour has been to find conditions under which hydriodic acid may be completely broken up, and its iodine removed from the solution by vaporisation, while the hydrochloric is retained without appreciable loss. As a first step toward the solution of this question, we initiated a series of experiments upon the volatility of hydrochloric acid in solutions containing sulphuric acid, having fixed upon the latter as the most available means of liberating hydrochloric and hydriodic acids from their compounds with the alkaline metals. After a few preliminary experiments with litmus-paper exposed in the steam from boiling solutions, we settled down upon two modes of investigating this point. According to the first, the determination of the chlorine remaining after concentration in solutions made up of water, sulphuric acid, and known amounts of the chloride, by precipitating as silver chloride, filtering the precipitate on asbestos, and weighing, was made the test of volatility of the hydrochloric acid; in the second, the same object was accomplished by estimating the chlorine escaping from the solution, by passing the steam through a condenser and precipitating the acid in the distillate by means of silver nitrate, collecting and weighing the silver chloride as in the former method.

The experiments of series A to series F were carried out according to the first method. In them, portions of a dilute solution of potassium chloride of known value were measured from a burette into Erlenmeyer flasks of 500 c.m.³ capacity, sulphuric acid diluted one-half was added, and the solution was boiled until the flasks and contents removed from the flame and placed upon counterpoised scales just tipped the beam. A few trials sufficed to bring the weight to the required point, and the degree of concentration was determined by this means far more accurately than by lowering the level of the liquid to marks placed upon the flasks. The hydrochloric acid remaining after concentration was determined as described, the comparison of the result with the value of the standard solution of chloride indicating, of course, the total loss in the process.

In the experiments of Series A, B, C, D, the effect is traced of increasing proportions of chlorine as compared with the same amount of sulphuric acid taken. In those of Series C, E, F, the influence of changing proportions of sulphuric acid, while the amount of chlorine remains the same, is brought out. In both sets the evidence is plain that the volatility of the hydrochloric acid is dependent upon the proportion of sulphuric acid as well as upon the amount of the chlorine present. It appears likewise that when the amounts of sulphuric acid present are reasonably small the loss of hydrochloric acid is inconsiderable, if the concentration is not pushed to too great an extreme.

The quantities of chloride dealt with in the experiments (Series A to F) are rather smaller than those which would naturally be handled in practical analysis, so that it seemed best to extend the experimentation to solutions of greater dilution and containing larger amounts of chloride. In the experiments of Series G, and subsequently, the second mode of treatment referred to was adopted. The flask was filled as before, but was connected with an ordinary glass condenser so that the distillate might be collected and measured, and the hydrochloric acid condensed with the steam was estimated by precipitation as silver chloride, the last being dried and weighed as such upon asbestos. The details of the experiments are given in the tabular statement (Series G).

It is obvious from these results that a solution containing 10 c.m.³ of the 1 : 1 sulphuric acid, or 5 c.m.³ of the strong acid, may be concentrated 200 c.m.³ without significant loss of hydrochloric acid. At a concentration of 100 c.m.³ the loss is notable. In later experiments, we

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xxxix., April, 1890.

† Roscoe and Dittmar, *Quart. Jour. Chem.*, xii, 128.

Taken H ₂ SO ₄ [1:1]. C.m. ³ .	Taken KCl = HCl.		Found AgCl = HCl.		Initial volume. C.m. ³ .	Final volume. C.m. ³ .	Error. Grm.
	Grm.	Grm.	Grm.	Grm.			
Series A.							
10	0.05	0.0245	0.0963	0.0245	110	5	0.0000
10	0.05	0.0245	0.0957	0.0243	110	45	0.0002 -
10	0.05	0.0245	0.0945	0.0240	110	40	0.0005 -
10	0.05	0.0245	0.0941	0.0239	110	35	0.0006 -
10	0.05	0.0245	0.0871	0.0221	110	30	0.0024 -
10	0.05	0.0245	0.0821	0.0209	110	25	0.0036 -
Series B.							
10	0.1	0.0489	0.1910	0.0485	110	65	0.0004 -
10	0.1	0.0489	0.1922	0.0488	110	55	0.0001 -
10	0.1	0.0489	0.1908	0.0485	110	45	0.0004 -
10	0.1	0.0489	0.1894	0.0482	110	35	0.0007 -
Series C.							
10	0.2	0.0978	0.3887	0.0976	110	75	0.0002 -
10	0.2	0.0978	0.3838	0.0976	110	65	0.0002 -
10	0.2	0.0978	0.3831	0.0974	110	55	0.0004 -
10	0.2	0.0978	0.3816	0.0970	110	45	0.0008 -
10	0.2	0.0987	0.3746	0.0953	110	35	0.0025 -
10	0.2	0.0978	0.3322	0.0845	110	25	0.0133 -
Series D.							
10	0.4	0.1956	0.7690	0.1955	110	60	0.0001 -
10	0.4	0.1956	0.7682	0.1954	110	50	0.0002 -
10	0.4	0.1956	0.7574	0.1926	110	35	0.0030 -
Series E.							
5	0.2	0.0978	0.3845	0.0978	105	55	0.0000
5	0.2	0.0978	0.3838	0.0976	105	45	0.0002 -
5	0.2	0.0978	0.3823	0.0972	105	35	0.0006 -
5	0.2	0.0978	0.3788	0.0963	105	25	0.0015 -
Series F.							
20	0.2	0.0978	0.3782	0.0962	120	75	0.0016 -
20	0.2	0.0978	0.3602	0.0916	120	65	0.0062 -
20	0.2	0.0978	0.3087	0.0785	120	55	0.0193 -
20	0.1	0.0978	0.2931	0.0745	120	45	0.0233 -

Taken H ₂ SO ₄ [1:1]. C.m. ³ .	Taken KCl = HCl		Initial volume. C.m. ³ .	Final volume. C.m. ³ .	Time in minutes.	Found AgCl. Grm.	Loss of HCl. Grm.
	Grm.	Grm.					
10	1	0.4888	400	300	29	0.0005	0.0001
10	1	0.4888	400	300	22	0.0008	0.0002
10	1	0.4888	350	300	10	0.0004	0.0001
10	1	0.4888	350	300	9	0.0005	0.0001
10	1	0.4888	300	200	25	0.0008	0.0002
10	1	0.4888	200	100	27	0.0021	0.0005
10	1	0.4888	100	50	20	0.0037	0.0009

found that a small part of the precipitate which we weighed in these experiments must in reality have resulted from the action of the solution upon the rubber stoppers and connectors of the apparatus; for the distillate from pure water in the same apparatus yielded a precipitate, probably silver sulphide, which, filtered off and weighed, was found to amount to 0.0003 gm. The figures of Series G, therefore, overstate somewhat the volatility of hydrochloric acid under the circumstances, but the misrepresentation is inconsiderable. We fixed upon 300 c.m.³ as a convenient volume of liquid to manipulate in future experiments, and one sufficiently dilute to guarantee security against the volatilisation of hydrochloric acid when the amount of sulphuric acid does not exceed 5 c.m.³ of the strong acid, and when the quantity of potassium chloride present does not exceed 1 gm.

(To be continued).

ON THE ESTIMATION OF WATER IN PHENOL.

By J. A. WILSON.

A SAMPLE of crude carboic acid (*i.e.*, the liquid remaining after crystallisation of true phenol, and consisting of cresol and higher homologues), when tested by three methods—(No. 1) by distillation; (No. 2) by agitating 1 vol. with 3 vols. saturated salt solution; (No. 3) by agitation with equal vols. of 48–50 per cent hydric sulphate—gave the following results:—

	No. 1.	No. 2.	No. 3.
Water ..	8.6 per cent.	8.00 per cent.	8.25 per cent.

The distillation process gives the true percentage of water, if the distillate be not observed too late; next to this the test with vitriol.

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, May 1st, 1890.

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

MESSRS. Joseph Barker and Thomas Flower Ellis were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Wallis Jenkins, 9, Arnold Street, Anlaby Road, Hull; John McKillop, Pulan Brani, Singapore; John Brooks Thornley, Ivanhoe Terrace, Ashby-de-la-Zouch.

The following papers were read:—

33. "An Investigation of the Conditions under which Hydrogen Peroxide is formed from Ether." By Professor WYNDHAM R. DUNSTAN and T. S. DYMOND.

The authors have investigated the conditions under which hydrogen peroxide is formed from ether. The ether used by them was purified by the usual method, and also by repeated agitation with dilute aqueous chromic acid.

Contrary to the usual statement, the authors find that pure ether, either wet or dry, does not form hydrogen peroxide when exposed to light (daylight or electric light).

Ether prepared from methylated spirit yields hydrogen peroxide when kept for some time, but not if it has been previously purified by means of dilute chromic acid.

Neither water nor dilute sulphuric acid forms hydrogen peroxide when exposed to light in contact with air.

Hydrogen peroxide is formed when ozone acts on ether in the presence of water.

Hydrogen peroxide is produced when certain conditions are maintained during the slow combustion of ether in contact with water. At a low red heat the ether and oxygen appear to interact in a manner similar to that in which ozone and ether interact.

DISCUSSION.

Dr. RICHARDSON said that everything depended on the nature of the glass of the bottles in which the liquids were exposed, and the quality of the light. The authors had spoken of Winchester bottles. Of what kind of glass were the bottles which had been used made? With regard to the method which he had adopted in purifying his ether, so-called pure ether was shaken with water, and then repeatedly distilled from sodium until at last this was unaffected. His more recent experiments led him still to believe that peroxide was formed from water and oxygen on exposure to light.

Professor RAMSAY, speaking of the purification of ether, referred to the investigation of the thermal properties of ether by Professor Young and himself. Regnault states that ether, after standing, no longer has a constant boiling-point, and they had found that such ether acts on mercury, but that after agitation with mercury and distilling it does so no longer. Professor Young and he had prepared ether from alcohol and sulphuric acid, and after washing it with potash and with sulphuric acid, had found it necessary to agitate it about fifty times with water before the iodoform test ceased to afford evidence of the presence of alcohol. Proof that such ether was pure was afforded by the agreement of the determinations of its vapour pressure made by the static and dynamic methods; four specimens were found to give identical results. Some of the authors' specimens may have contained alcohol. He then referred to the experiments which he had made showing that hydrogen peroxide is produced on evaporating water (*Proc. Chem. Soc.*, 1886, 225).

Mr. WOOD asked if any observations had been made of the temperature during exposure; the amount of ether vapour would vary greatly with the temperature. In India he had frequently noticed that ether liberated iodine, but its behaviour in this respect was extremely capricious;

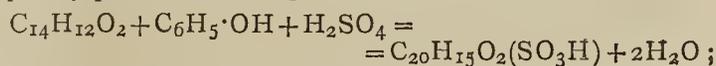
he could scarcely think that the very different behaviour of several bottles of one consignment was due to impurity.

Professor DUNSTAN, in reply to Dr. Richardson, stated that colourless Winchester bottles were employed. The specimen of impure ether which yielded hydrogen peroxide scarcely affected potassium iodide before exposure; another similar specimen had no action on the iodide. He had not been able to confirm Dr. Richardson's statement that hydrogen peroxide is formed when acidified water is exposed to light together with oxygen. In reply to Dr. Ramsay, he stated that the method used to purify the ether must have resulted in the entire removal of alcohol. The experiments now recorded proved that under certain well-defined conditions hydrogen peroxide was not formed from pure ether. It was for those who, like Dr. Richardson and Professor Ramsay, maintained that it is produced under similar circumstances to point out what the necessary condition is. This had not yet been done, and in fact so far apparently no one had suspected that the result might be due to an impurity. He had not been able to detect any hydrogen peroxide in water which had been heated in the manner described by Professor Ramsay in contact with air, although the experiment had been tried many times. With reference to Mr. Wood's remarks, the conditions under which the ether had been exposed were fully described in the paper; the temperature ranged between 15—25°. In London it was not possible to obtain "intense sunlight," but it seemed well established that the electric light is highly active in influencing chemical change. There was evidence that ether prepared from ordinary alcohol sometimes, but not invariably, contains the impurity from which hydrogen peroxide is formed; in any case this impurity would be removed by treatment with chromic acid. As was stated in the paper, the formation of an oxidising substance by the imperfect combustion of ether, to which Mr. Wood had referred, had been observed long ago: in fact Faraday had shown the experiment in his lectures on ozone. It is established by the present results that pure ether yields hydrogen peroxide when it is imperfectly oxidised in contact with cold water.

In reply to the President, he said that, although the period of exposure was the same in the case of the experiments with purified ether, they were made at a later date.

34. "*p*-Desylphenol." By FRANCIS R. JAPP, F.R.S., and G. H. WADSWORTH, Associate of the Normal School of Science.

The authors find that by the action of cold concentrated sulphuric acid on a mixture of benzoïn and phenol *p*-desylphenol-monosulphonic acid is formed:—



and that on heating this with concentrated chlorhydric acid at 150° it is hydrolysed, yielding *p*-desylphenol, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{C}_6\text{H}_4\cdot\text{OH}$. This phenol crystallises from light petroleum in small colourless laminæ melting at 133°; from dilute alcohol in large thin laminæ; and from benzene in warty aggregations with 1 mol. of benzene of crystallisation. It dissolves in caustic alkalies, and is re-precipitated by carbon dioxide.

When heated with acetic anhydride it yields a monacetyl-derivative, $\text{C}_{20}\text{H}_{15}(\text{C}_2\text{H}_3\text{O})\text{O}_2$, which forms aggregations of slender white needles melting at 106—107°.

By acting on the sodium salt with methyl iodide, *p*-desylanisoil, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{C}_6\text{H}_4\cdot\text{OCH}_3$, is obtained. It melts at 90—92°, and is insoluble in caustic alkalies.

On fusion with caustic potash at 200°, *p*-desylphenol is resolved into benzoic acid and *p*-benzylphenol. If the temperature be carried higher the *p*-benzylphenol is oxidised to *p*-hydroxybenzoic acid. On reduction with sodium and boiling amyl alcohol, it is converted into the compound $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, which

crystallises from benzene in tufts of slender needles melting at 161—162°, and yields a diacetyl-derivative melting at 156—157°. Iodhydric acid and amorphous phosphorus at 130°, on the other hand, reduce *p*-desylphenol to dibenzyl and phenol, a carbon linkage being severed in the interaction.

It yielded no hydroxime or phenylhydrazone, although it was subjected to the action of hydroxylamine and of phenylhydrazine under a variety of the most favourable conditions. This negative evidence might be regarded as an indication that the compound does not contain a carbonyl-group: but, apart from the fact that such evidence is not conclusive, the alternative formula in which, for the sake of getting over the difficulty, a union of one oxygen-atom to two directly linked carbon-atoms might be assumed, has so little antecedent probability that the authors hesitate to put it forward, and in the meantime continue to regard the compound as *p*-desylphenol, a constitution with which all its other interactions are in harmony.

Attempts to prepare similar condensation-products of benzoïn with other phenols led to no result.

35: "On Benedikt's Acetyl Values." By J. LEW-KOWITSCH, Ph.D.

In his paper on a new method of examining fats (*Zeitschrift für die Chemische Industrie*, 1887, p. 149), Benedikt proposes a method which is based on the principle that only hydroxylated fatty acids take up the radicle of acetic acid when heated with acetic anhydride, and he asserts that those fatty acids which do not contain the hydroxyl-group remain unaltered; so that the quantities of potash required for neutralising fatty acids before and after treatment with acetic anhydride will be either identical or nearly so, any difference being due to the errors of the method of determination.

While examining a somewhat abnormal sample of tallow, the author was led to doubt the accuracy of this statement, and the following results of experiments which he has made serve to confirm his doubts.

The fatty acids prepared from a sample of fresh town tallow required for neutralisation 19.717 per cent of potash, or, in other words, their "acid value" was equal to 19.717, corresponding to the molecular weight 284.5. 50 grms. of these acids was acetylated with 40 grms. of acetic anhydride in the manner indicated by Benedikt, and both the acid value and the "saponification" value of the acetylated product were then determined. The values found were 160.5 and 217.5 respectively, corresponding to an acetyl value of $217.5 - 160.5 = 57$. A second test gave $216.3 - 159.9 = 56.4$.

In the same way the fatty acids of samples of South American tallow and North American tallow gave the acetyl values 77.8 and 23.93. According to Benedikt the acetyl values ought to have been *nil* or nearly so.

As tallow is considered to consist essentially of a mixture of the glycerides of stearic, palmitic, and oleic acids, it was thought possible that it was the oleic acid which had fixed the acetic acid radicle. A sample of oleic acid obtained from Kahlbaum as pure was therefore examined; it contained, however, some solid acids, which settled out when the acid was kept for some time in a stoppered bottle. To determine the impurities, the acid value and iodine absorption were ascertained: the acid value found was 183, and the iodine absorption 90.14; the theoretical values for oleic acid are 198 and 90.07. Although containing a certain amount of higher homologues, the acid was considered sufficiently pure for the desired purpose: 50 grms. of it when acetylated gave an acid value = 116.50 and a saponification value = 242.05; consequently an acetyl value = 125.55. If the fixing of the "acetyl," however unlikely it might appear, were due to the $\text{CH}=\text{CH}$ -group in the molecule of the oleic acid, the acetylated acids ought to have lost the capacity of taking up iodine. However, the iodine value of the acetylated acids was found to be 87.11, proving clearly that acetyl was not taken up by the $\text{CH}=\text{CH}$ -group. Therefore,

the acetic anhydride must have acted in some other way on the oleic acid, and if so it was not unlikely that palmitic or stearic acid might be acted on in the same way; experiment fully bore out the correctness of this assumption.

50 grms. palmitic acid, the comparative purity of which was proved by an acid value of 213.4 (instead of the theoretical value 219.1), was acetylated and gave an acid value = 143.53 and a saponification value = 226.13; consequently an acetyl value = 82.6.

50 grms. stearic acid—showing an acid value of 203 instead of the theoretical one of 197.5—gave, after being acetylated, an acid value = 138.89 and a saponification value = 221.18; consequently an acetyl value = 82.29.

The author refrains from venturing upon an explanation of these results, merely wishing to point out at present that they contradict Benedikt's assumptions.

Research Fund.

Fellows desiring grants are requested to forward their applications to the Secretaries in order that they may be considered at the next meeting, in June.

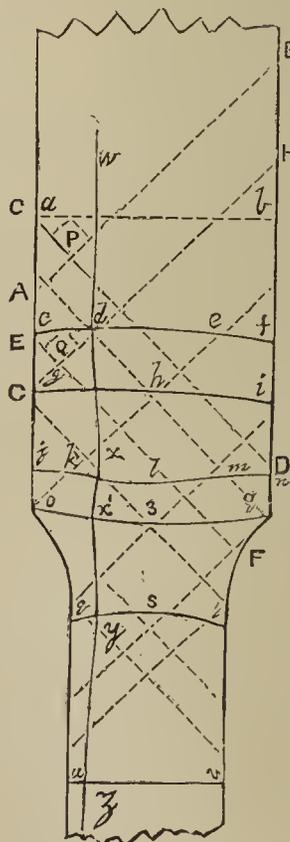
PHYSICAL SOCIETY.

May 2, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

MR. C. A. CARUS WILSON read a paper on "The Distribution of Flow in a Strained Elastic Solid."

The author pointed out that when a bar is subjected to tensile stress the elements of the bar are distorted by the resulting shearing stresses, which attain maxima in planes at 45° to the axis. If the bar be supposed to be divided into elements such as P or Q (see fig.), then, if



the shearing stresses are equal in the two directions parallel to the sides of the elements, the bottom points of the strained elements will be directly below their top corners; whereas, if the stresses be differences in the two directions, there will be a displacement to one side or the other, depending on which side the greatest stress occurs.

Since each inclined section is subject to the same total shearing force, the shearing stress along any section such as EF may be taken as inversely proportional to the length of the line EF , the bar being supposed of uniform thickness. From these considerations it may be seen that an element, P , will be subject to equal stresses, for $AB = OD$; hence the lower point of P will remain vertically below its upper point. In this region, therefore, a horizontal straight line drawn on the unstrained bar will remain horizontal and straight on the strained bar. An element at Q , however, will be subjected to unequal stresses, for EF is $< GH$; hence the lower points of the elements will be displaced towards the axis. This displacement will increase as the distance beyond d and e from the axis increases, and an originally horizontal line will become curved at the ends cd and ef , whilst de will remain straight. In a similar way it was shown that horizontal lines should assume the shapes indicated at ghi , $ijklmn$, opq , rst , and uv in their respective positions, whilst vertical lines should become pinched inwards above and below the shoulder, as shown by the curve $wxyz$. To test whether the reasoning by which the above conclusions were arrived at was satisfactory, a copper bar was carefully prepared, ruled, and subjected to permanent strain. The curvatures of the various lines clearly show the characteristics predicted by theory.

Prof. PERRY enquired whether it was correct to assume the stress uniform over the plane sections inclined at 45° to the axis. He also said that the general character of the flow somewhat resembled that of a viscous fluid passing from a wide to a narrower channel.

Prof. HERSCHEL thought Mr. Carus-Wilson justified in assuming the stress uniform over the diagonal sections; the latter said he only made the assumption as a provisional hypothesis, but the results of his experiment agreed so closely with his theoretical deductions that he thought the hypothesis correct.

Mr. C. V. Boys made two communications:—(1) "On Photographs of Rapidly Moving Objects," and (2) "On the Oscillating Electric Spark."

A collection of apparatus by which he had been able to photograph drops of water in their various stages of formation was exhibited. It consisted of a lantern and lenses by which a trough in which the drops were formed could be strongly illuminated, combined with a camera and revolving disc with one perforation. By this means exposures of about 1/600th of a second could be made about 20 times a second. The slide of the camera was about 3 feet long, and could be moved across the field by hand, so as to take the consecutive impressions on different parts of the plate. The resulting photographs show with remarkable clearness the formation, breaking away, the oscillations of the drops, and their rebounding in the liquid into which they fell. By cutting the photographs into strips, each strip representing a single exposure, and mounting them on a disc, Mr. Boys had arranged a kind of Thaumatrope, which represented the phenomena in a very realistic manner. He also exhibited photographs of small water-fountains broken up into drops by musical sounds, which he had taken by the electric spark without the aid of lenses. The shadows of the drops were sharply defined, even when magnified considerably, and the various stages of transition from the liquid column to the detached particles were well shown. Finding it possible to obtain such good results from a simple spark, it occurred to him that he might get a succession of photographs from the intermittent light of an oscillating spark, and in this he was fairly successful.

An apparatus devised to show the oscillatory character of a discharge was next exhibited in operation. It consisted of a disc carrying six lenses arranged in two sets of three. The members of each set were at different distances from the axis, so that the images of the spark on the screen do not coincide. The disc can be revolved at a high speed, and the successive sparks are seen as bright patches on the screen. By this apparatus a single

discharge can be examined, whereas with Lodge's apparatus it is desirable to have a fairly rapid succession of sparks. Photographs of an oscillatory discharge taken with the apparatus were exhibited, and these show that the duration of the illumination is a considerable fraction of a complete period.

LORD RAYLEIGH said he was greatly interested by Mr. Boys' apparatus. He (Lord Rayleigh) had photographed water-fountains both when broken up and when made to coalesce under electrical influence, but it had never occurred to him that it would be possible to get enough light or sufficient sharpness from a single spark. Mr. Boys' success he believed to be owing to the fact of his using no lenses which would absorb the ultra-violet rays. He also thought the method might be developed so as to give shaded pictures instead of mere representations in black and white.

Mr. GREGORY asked Mr. Boys if he had tried to get greater potentials for his oscillatory discharges by using Dr. Lodge's "impulsive rush" arrangement.

Mr. TROTTER enquired whether the single sparks used to photograph the water fountains were as large as those required to show oscillations.

Mr. Boys said he had not tried Dr. Lodge's "impulsive rush" arrangement because of the enormous capacity of the condensers required. The sparks used to photograph the broken up fountain were very small, being only about 1/4-inch long and from a few jars.

Prof. PERRY asked Lord Rayleigh whether it would be possible to compare the shapes of the water-drops shown in the photographs with the shapes of the liquid surfaces of revolution given by Sir W. Thomson at the Royal Institution some years ago, or whether the changes of shape were too rapid to permit of the surface-tension being all-important.

Mr. Boys thought the motions of the drops would be too rapid, and that inertia would play an important part.

LORD RAYLEIGH pointed out that by forming a drop slow enough the effect of inertia might be made negligible until such time as the unstable state was reached; after that, however, inertia must have considerable influence on the shape.

NOTICES OF BOOKS.

Report of the Commissioner of Internal Revenue for the Fiscal Year ended June 30, 1889. Washington: Government Printing Office.

A GREAT part of the contents of this book have for us no interest, but there are portions relating to the sophistication of articles of food, &c., which are of considerable importance.

Baking-powders are denounced as "the make-shift of the lazy and ignorant bread-maker." They all convey into the system "medicinal doses" of various salts. Of course what is called a medicinal dose must be hurtful if habitually consumed in food. A list is here given of manufacturers of "alum baking-powders." It is satisfactory to find that only one British firm figures in this numerous catalogue, and that it does not bear a name familiar in this country.

"Package coffee," meaning the article sold ready-ground, is heavily tampered with; chicory, peas, beans, rye, maize, wheat, and colouring matters rank as the common adulterants.

Cream of tartar is sophisticated with gypsum, acid calcium phosphate, calcium tartrate (more than 6 per cent), alum, maize, starch, and flour.

Tinned vegetables, all supplied by French firms, are coloured with copper sulphate.

The use of annatto for colouring butter and cheese is open to very grave objections. Dr. B. F. Davenport says, in a report to the State Board of Health of Massachusetts,

1888, "That prepared in French Guiana is considered the superior brand of the dye-stuff. There, in the warehouses, it is reported to be the general commercial custom to improve the colour of the dye-stuff, and prevent its drying by keeping the cake moistened with stale urine (!). The result is that it is a mass of fermentative products, swarming with germs of putrefaction, and smelling rankly of its origin. . . Microscopic examination shows that it is not only alive with bacteria, but that it contains very numerous fungi spores, single or arranged in rows like those found in fermented diabetic urine." Of course the possible presence of pathogenic bacteria in daily produce thus coloured is by no means excluded.

University of Illinois, Agricultural Station, November, 1889,

WE have here a paper on the "Biology of Ensilage," in which the admission is made that ensilage is never truly preserved fodder. The author remarks, truly enough, that the main difference between ensilage and sour-kraut is that the former is made from clover, &c., and the latter from cabbage.

The rest of the pamphlet describes field experiments on oat and maize.

Exercises in Practical Chemistry: An Introduction to Qualitative and Quantitative Analysis. By Dr. W. R. HODGKINSON, F.R.S.E., F.G.S. London: G. Kenning. Third Issue, revised.

THIS little work, we are told, is a reprint from sheets that have been used with considerable success in the instruction of large classes. We find in it no errors, but, on the other hand, we cannot recognise that it possesses any marked advantage over other elementary treatises on chemical analysis.

Terminologia Medica Polyglotta: A Concise International Dictionary of Medical Terms. Compiled by THEODORE MAXWELL, M.D., B.Sc., F.R.C.S. London: Churchills.

THIS work is, we believe, unique in its character and aims. It is, in fact, a polyglot dictionary of the technical language of the medical profession in English, French, Latin, German, Italian, Spanish, and Russian. The terms included are those of anatomy and physiology (human, not general), nosology, pharmacy, chemistry, and, to some extent, physics. Botany is also very fully dealt with. The technical language of zoology is introduced only in the case of venomous and parasitic animals, and of such as furnish medicinal drugs. These various subjects are not taken up separately, the only arrangement adopted being alphabetical.

As far as we can judge the work is characterised by a very high degree of correctness.

The only questionable points are, we believe, to be found in the chemical department. The compiler and his friends have retained for the English names of compounds a terminology which is fast becoming obsolete. Thus, *e.g.*, they write "iodide of iron" where in recent works and memoirs we find almost exclusively "iron iodide," or, if it is desired to be more precise, "ferrous" or "ferric iodide."

Among German chemical terms "potassium" is rarely, if ever, used, its German equivalent being "kalium." In like manner "sodium" and "soda" are rarely used in Germany, save in purely technological works, the scientific equivalents being "natrium" and "natron."

It might have been usefully pointed out that the chemical terms used by physicians and pharmacists in Germany are sometimes widely different from those employed by "pure" chemists and manufacturers, being, in fact, taken from the Latin! Thus a German analyst, researcher, or University professor would call potassium chloride "chlorkalium," whilst in a prescription or in a

pharmaceutical catalogue the same compound would figure as "kaliium chloratum."

It would be unpardonable to omit notice of the wonderful typographical accuracy of this book. In a volume of nearly 500 pp., consisting exclusively of technical matter, and that, moreover, mostly written in foreign languages, we have not been able to meet with any errors of the press. Of course, to the medical profession this work will be of untold value, throwing open to them the literature of most other civilised countries.

Agenda du Chimiste (Chemists' Manual). By G. SALET, Ch. GIRARD, and A. PABST, 1890. Paris: Hachette et Cie.

THIS is a new edition of a useful pocket volume brought down to the present date. It begins with an almanac in which the mediæval "Saints' Days" figure in juxtaposition with the meetings of the Chemical and Physical Societies. Next follows a chapter devoted to physical and mathematical data, and containing, amongst other matters, tables for the reduction of English measures and weights to their metric equivalents. In hydrometry, the scale of Baumé with all its imperfections is still adhered to, though it appears to exist in four modifications. Instruments indicating direct specific gravity do not seem to find much favour in France, and Twaddle's scale is very briefly noticed. The tables of the specific gravities of acids and saline solutions are numerous and valuable.

Thermo-chemistry is treated, as might be expected, at considerable length.

In the second chapter, follow data relative to pure chemistry. The tables of atomic weights are somewhat complex; there are firstly the equivalents and atomic weights of the more common bodies, as they have been adopted in Fremy's "Encyclopedie Chimique," the atomic weights used in the first edition of the "Agenda," and that from the edition of 1886, and lastly the atomic weights arrived at by the most recent researches. Then follow tables for qualitative analysis in the moist way, and tables for blowpipe analysis, with explanatory remarks. No mention is made of the use of the aluminium plate as a support.

A short section is devoted to spectral analysis, attention being principally given to spark-spectra. Absorption-spectra are described and figured in a section of the appendix on p. 462.

Next follows gas-analysis; tables for calculating the results of quantitative analysis; a long table giving the composition and the solubility of the principal inorganic bodies, with brief notes on their other properties; tables of the composition and external characters of minerals, their density, hardness, solubility, fusibility, and crystalline form; the composition and properties of organic bodies; and tables of solubilities.

The third chapter relates to applied and industrial chemistry. It opens with a section on water analysis, in which we find that, as far as the determination of organic nitrogen is concerned, the process of Frankland is ignored, and that of Wanklyn meets with a very momentary notice. The comparison between English, French, and German degrees of hardness is a very useful hint. We cannot agree with the authors when they say that the only waters for consumption are those of underground beds and of streams. The rejection of rain-water is imperative only in districts where the air is polluted or where it is collected on roofs, &c., visited by cats and pigeons, both possible vehicles of diphtheria. We may here add that dogs should be rigorously excluded from the gathering grounds of a municipal water-supply, as they introduce the germs of hydatids.

The bacteriological examination of waters is here spoken of as yielding merely uncertain results. But in the appendix it is discussed at length, and pronounced of great importance.

The instructions for the analysis of a variety of com-

mercial and industrial articles are carefully drawn up, and will often be useful for refreshing the memory of the analyst.

Doubts may be entertained whether the space devoted to a review of the Paris Exhibition might not have been better occupied.

We may notice the suggestions of an International Congress of Chemists on the question of nomenclature. It is satisfactory to find that they propose to reserve the termination "ol" for the alcohols and the phenols, and applying, in its stead, the termination "ene" to the hydrocarbides. It would be better still if the terminations "in" and "ine" could be dispensed with, since they have been seized upon by the inventors of "proprietary" medicines and applied to compounds which, whatever may be their medicinal value, are certainly not chemical individuals. "Listerine" is a name which sets our teeth on edge.

The "Agenda du Chimiste" is a very useful work-table companion.

CORRESPONDENCE.

EXTENSION OF THE DUTIES OF PUBLIC ANALYSTS.

To the Editor of the Chemical News.

SIR,—I have read with much pleasure your review upon Mr. C. E. Cassal's paper upon the extension of the duties of public analysts, in the CHEM. NEWS, vol. lxi., p. 226.

It cannot, I think, be for one moment contended that the extension of their duties would not be desirable—all, I think, are agreed upon that point; but if their duties are to be extended, the present Sale of Food and Drugs Act ought to be entirely replaced by a new Act, the public analyst of to-day abolished, and his place taken by a Government or a State analyst.

The present Act, where it has been properly enforced, has done much to check adulteration, and, if equally enforced throughout the country, would do much good—but such a result, however desirable, will never be attained. The powers conferred upon local authorities to appoint analysts ought to have worked well, but, unfortunately, latterly the most competent and experienced candidates have been rejected for young and inexperienced ones, simply on account of local patronage. Then again, there are analysts in London at the present moment holding appointments under the Act contrary to Section 10 (C) of the Sale of Food and Drugs Act, 1875.

What is now required is a new Act establishing a State laboratory, say, under the control of the Minister of Agriculture, with full powers to analyse the food, drink, and drugs of the country, and a clause also inserted in the Act giving power to the Minister of Agriculture to include or bring under the scope of the Act from time to time any article which is not included under the term food, drink, and drugs, if it should be deemed advisable to do so.—I am, &c.,

WILLIAM JOHNSTONE.

studied are glycollamine, alanine, leucine, asparagine, aspartic acid, tyrosine, and hippuric acid.

Researches on the Condensation of the Vapour of Benzene and of Acetylene under the Influence of the Effluve.—P. Schützenberger.—The ultimate object of these researches is to determine the question of the permeability of the effluve. Whilst the benzene used contained 92.47 per cent of carbon and 7.80 of hydrogen, the condensed products showed from 0.7 to 7.0 per cent of oxygen.

Lead Phosphites and Pyrophosphite.—L. Amat.—An account of neutral lead phosphite, of the nitro-phosphite, the acid phosphite, and pyrophosphite.

Action of Erythrite upon the Alkaline Alcoholates.—M. de Forcrand.—A thermo-chemical paper, not suitable for abstraction.

Action of Lead Oxide upon Toluene; Production of Benzene.—C. Vincent.—The products of the reaction as obtained by the author were about 10 per cent of benzene, a small quantity of stilbene, and a residue of toluene not attacked, as well as water and carbonic acid. At temperatures exceeding 335° there was less benzene and more stilbene and higher carbons. At redness there were obtained, along with the above products, the carbides formed on a simple pyrogenous decomposition of benzene and toluene. The diphenyl formed in small quantity is not derived from benzene originally present in the toluene, but from benzene formed in the reaction.

Thermo-Chemical Researches on the Fibres of Wool and Cotton.—Leo Vignon.—The author gives the quantities of heat in calories evolved respectively by wool and cotton in contact with different reagents.

Zeitschrift für Analytische Chemie.
Vol. xxviii., Part 6.

New Test for Carbon Oxide Hæmoglobine.—K. Katayama (*Virchow's Archiv*).—10 c.c. of the blood diluted to 1.50th are added to 0.2 deep yellow ammonium sulphide and 0.2—0.3 c.c. of a 30 per cent acetic acid, and carefully mixed. The liquid should then react slightly acid. Blood containing carbon monoxide takes a fine rose colour, whilst normal blood is greenish grey or reddish greenish grey. The ammonium sulphide is obtained by adding 2.5 grms. of pure pulverised sulphur to 100 grms. of freshly prepared colourless ammonium sulphide. A spectroscopic examination of the carbon monoxide blood treated as above shows the spectrum of sulphmethæmoglobine (an absorption band between C and D) along with that of the carbon monoxide hæmoglobine. Normal blood under the same conditions shows, along with the sulphmethæmoglobine stripes, the broad absorption-band of reduced hæmoglobine, which, on shaking with air, gives place to the two absorption-bands of air. The presence of such blood can be recognised along with seven parts of normal blood.

Poisoning with Barium Salts.—G. Linossier.—The author detects barium in all the organs; up to 0.56 per cent in the ash of the vertebræ.

Distinction between Nepalín and Aconitine.—K. F. Mandelin.—Nepalín, if evaporated down with a few drops of strong nitric acid, gives a residue smelling of musk. This residue, if treated with a few drops of a solution of potassa in absolute alcohol, gives an intense carmine or purple. Aconitine is quite indifferent in its behaviour.

The Atomic Weight of Platinum and Rubidium, and on Quantitative Determinations with the Help of Platinum Chloride.—W. Dittmar and J. McArthur.—From the *Transactions of the Royal Society of Edinburgh*.

Poisoning with Oxalic Acid.—Russo-Gilberti (*Apotheker Zeitung*).—Crystals of calcium oxalate are found blocking up the ducts of the kidneys.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 17, April 28, 1890.

Formation and Combustion-Heats of Various Nitrogenous Principles derived from Albumenoid Matters.—MM. Berthelot and André.—The substances

MEETINGS FOR THE WEEK.

- MONDAY, 19th.—Society of Arts, 8. "Sugar, Tea, Coffee, and Cocoa, their Origin, Preparation, and Uses," by Richard Bannister.
- TUESDAY, 20th.—Royal Institution, 3. "The Art of Engraving—3. Mezzotint Engraving," by Louis Fagan.
- Institute of Civil Engineers, 8.
- Pathological, 8.30.
- Society of Arts, 5. "The Industrial Arts of Japan," by Lasenby Liberty.
- WEDNESDAY, 21st.—Society of Arts, 8. "The Mannesman Process for Making Seamless Tubes," by J. G. Gordon.
- Meteorological, 7.
- Geological, 8.
- Pharmaceutical, 11. (Anniversary).
- THURSDAY, 22nd.—Royal Institution, 3. "Flame and Explosives," by Prof. Dewar, M.A., F.R.S.
- Royal, 4.30.
- Royal Society Club, 6.30.
- Institute of Electrical Engineers, 8.
- FRIDAY, 23rd.—Royal Institution 9. "The Manners and Customs of the Torres Straits Islanders," by Prof. A. C. Haddon, M.A., M.R.I.A., Dean of Royal College of Science, Dublin.
- Quekett Club, 8.
- SATURDAY, 24th.—Royal Institution, 3. "Recent Excavations in Greece," by Dr. Charles Waldstein.

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(EDITOR: DR. G. KRAUSE, COTHEN, DEUTSCHLAND.)

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THE CHEMICAL NEWS.

VOL. LXI. No. 1591.

CORROSION OF PLATES OF STEAM-BOILERS.

By THOMAS T. P. BRUCE WARREN.

THE *inside* corrosion of the iron plates of a steam-boiler is due at least to two causes; in one case the corrosion, indicated by *pitting*, takes place above the water line, and in the other case by *patches* on the surface covered by incrustation or deposit. In both cases there is a marked absence of uniformity of corrosion, some plates being seriously affected, whilst others in the same boiler and in the same region of the boiler remain intact. This has been explained by the heterogeneous character of the plates, due either to chemical or mechanical differences.

It certainly requires no great amount of chemical skill to determine how far these factors operate in shortening the life of a boiler. A matter which appears to me to have escaped the attention of writers on this subject deserves mention. It is well known that a rolled iron plate has a "skin" or surface which resists oxidation; if we remove this, by scratching or filing, the new surface is rapidly coated with rust on exposure to damp air. If we protect with a varnish those new surfaces corrosion is not perceived. If a freshly rolled plate be cut the surface remains intact, whereas the edges rust in a very short time. If a piece of sheet-iron be immersed in dilute acid the surface, coated with what is known as the natural skin, resists the action more or less, whilst the recently cut surfaces are speedily acted on.

This is no doubt due to a difference in the electrical relation of the surfaces, the one being much more electro-positive than the other. The aggravation of pitting, which is not only local, but, in some parts of the same plate, serious, can be explained in the same way.

In the construction of a boiler there are several operations which destroy the uniformity of surface; the rivets, the holes, whether punched or drilled, all introduce an individual function in the wear and tear of a boiler. The natural skin of an iron plate, if partly removed, exposes a surface which is electro-positive to the other parts, and, when placed in a corrosive liquid, the parts of the plate which are electro-negative actually assist in the destruction of the parts which are less electro-negative; hence it is that pitting is promoted when it once sets in.

The only remedy seems to be the entire removal of the surface after rolling; we might then ensure a uniform surface, when alteration or abrasion would be less likely to lead to local chemical action.

The utility of the magnet for determining inequalities in a boiler plate seems to me very problematical, but the difference of potential when two plates are immersed in the same liquid, as might be observed on an electrometer, would reveal the existence of chemical or mechanical differences of structure which would be favourable to corrosion.

It has been proposed to use zinc as a protection against corrosion; and no doubt, by rendering the boiler surface electro-negative, we might prevent corrosion, but unfortunately the instructions given for its use are misleading. In some cases pieces of zinc are simply thrown into a boiler, so long as they remain *clean* and are in contact with a *clean* boiler plate, the preservative action of the zinc is ensured, but when covered with mud or boiler deposit, they are shielded from further action. If the zinc be suspended or attached *metallically* to the boiler, above the water line, we are more likely to prevent corrosion from volatile acids, the iron being electro-negative to zinc.

The corrosion of the zinc being greatest at the points of suspension, it will in time wear away and fall into the deposit, where it becomes, in an electro-chemical sense, lost, but, so long as it remains suspended, the wear and tear at the points of attachment keep the contacts clean. We must remember that the greatest loss of zinc is where the metallic contacts lie, and that by increasing the area of the zinc plate, so long as the area of contact is constant, we are doing little or no good. The ratio between the areas of contact of the two metals, so as to ensure the maximum advantage, when once determined for any particular water should be most rigidly enforced. When a boiler is cleaned out it is the practice to "put the zinc back again;" clean contacts or drilling fresh holes in the zinc plate if worn much should never be neglected. The surface of the plate should be entirely renewed. It is well known that no metal should be allowed to introduce an electro-positive condition of the boiler-plates. Spelter or sheet-zinc frequently contains a large quantity of lead; in time the zinc dissolves away, leaving a surface richer in lead; we are then in a fair way of doing more harm than good to our boiler plates, in spite of the solubility of chloride of lead.

Soda has been recommended for keeping a boiler clean, and here I think a great deal of carelessness has been introduced by writers on this subject. One-half of a boiler is in contact with a hot solution of caustic soda, the other half not; the condition of the two parts of the boiler electrically, as regards liability to corrosion, must be too evident to need comment.

The unequally heated parts of a boiler will acquire a difference of potential proportional to the energy of the liquid, and here we have probably an explanation for the increased activity of alkaline solutions in removing scale.

From these considerations it will appear that if we can keep a boiler electro-negative, by an independent source of electrification, to any destructive agency which might arise in the boiler, we might reasonably hope to prolong its life.

EXAMINATION OF CORPSES FOR ALKALOIDS AND METALLIC POISONS.

By Dr. ANTON SEYDA.

(Concluded from p. 235).

AS to the objections raised by Otto against this direct determination of arsenic, it is to be remarked that:—(1) A concentration of the strongly hydrochloric diluted liquid may seem altogether superfluous with reference to the sensitiveness of the arsenical reaction. (2) The alleged "brown spots" obtained on the porcelain lid cannot have on the author's process, any disturbing influence, as he on principle refrains from their production.

Independently of the simplicity of execution, this direct determination of arsenic—which was proposed by Marsh himself—cannot be estimated too highly, as we are here secure against the objection of "arseniferous hydrogen sulphide." In the eyes of specialists, this point will, indeed, be of less weight, but the matter is different in actual forensic cases, where an advantageous impression will be produced both on juries and judges by the demonstration of arsenic without the aid of a reagent K_2S sulphuretted hydrogen, which has latterly acquired an evil reputation. The author often effects the detection of arsenic with hydrochloric solutions obtained from parts of organs at once in the direct and indirect manner, and if arsenic is present, the former process has never failed him. In order to be satisfied to what extent the arsenical reaction is interfered with by the presence of nitrates he carried out the following experiment:—

Of a watery hydrochloric solution, containing about 0.75 per cent potassium nitrate and 0.331 per cent arsenious acid, he adds 1 c.c. to parts of organs which

had been stirred up with water and mixed with about 5 grms. potassium chlorate. The chlorination was effected in the manner described above. The filtered hydrochloric solution, free from chlorine, was introduced into the Marsh apparatus, in which hydrogen was evolved from zinc and hydrochloric acid. Fragments of caustic potassa were laid in the calcium chloride tube. After hydrogen had been evolved for eight hours, two arsenical mirrors had been deposited in the reduction tube which corresponded approximately in strength to the quantity of arsenic employed—about 3.0 m.grms. It is to be remarked that a subsequent addition of cane-sugar (free from arsenic) seemed to promote the reaction.

From this experiment it appears that the presence of chlorides, and even of nitrates, does not prevent the formation of gaseous arsenic hydride, at least not to the extent commonly assumed, so long as zinc and hydrochloric acid are present in excess, and the development of hydrogen is allowed to go on for a sufficient time.

In cases of arsenical poisoning such an excess of nitrate as there was used in the above experiment will never occur, since nitrates only occur in the organism in small traces, and, on the other hand, saltpetre, if taken, promptly passes into the urine.

A second supplemental experiment may here be reproduced, which was executed with the following modification:—

In a Marsh apparatus, charged as before with a hydrochloric liquid containing arsenic and saltpetre, hydrogen was generated, and after a time a coating of arsenic appeared in the reduction tube; but as free nitric acid was poured into the flask the escape of hydrogen seemed to cease, as the deposit of arsenic did not become stronger. (The ignition of the gas at the aperture of the reduction tube was not attempted on account of the difficulty of evading the formation of detonating gas within the apparatus). But after some time—about twenty minutes—arsenic again began to deposit in the reduction tube.

From this experiment it would appear that nitrates and free nitric acid in presence of free hydrochloric acid have a different effect upon the formation of gaseous arsenic hydride, so that on the addition of free nitric acid the nascent hydrogen is first consumed in the reduction of the nitric acid, and that afterwards a further reduction of the arsenical compound to gaseous arsenic hydride recommences; but, as free nitric acid can scarcely occur in the examining portions of a corpse, this case has chiefly a theoretical interest. Still, the information to be met with in chemical literature—so far as the author can ascertain—requires an important extension in order to explain all the conditions under which, on the one hand, the formation of gaseous arsenic hydride may be interfered with or hindered, and, on the other, arsenic is reduced from its compounds to a solid hydride or to the free state.

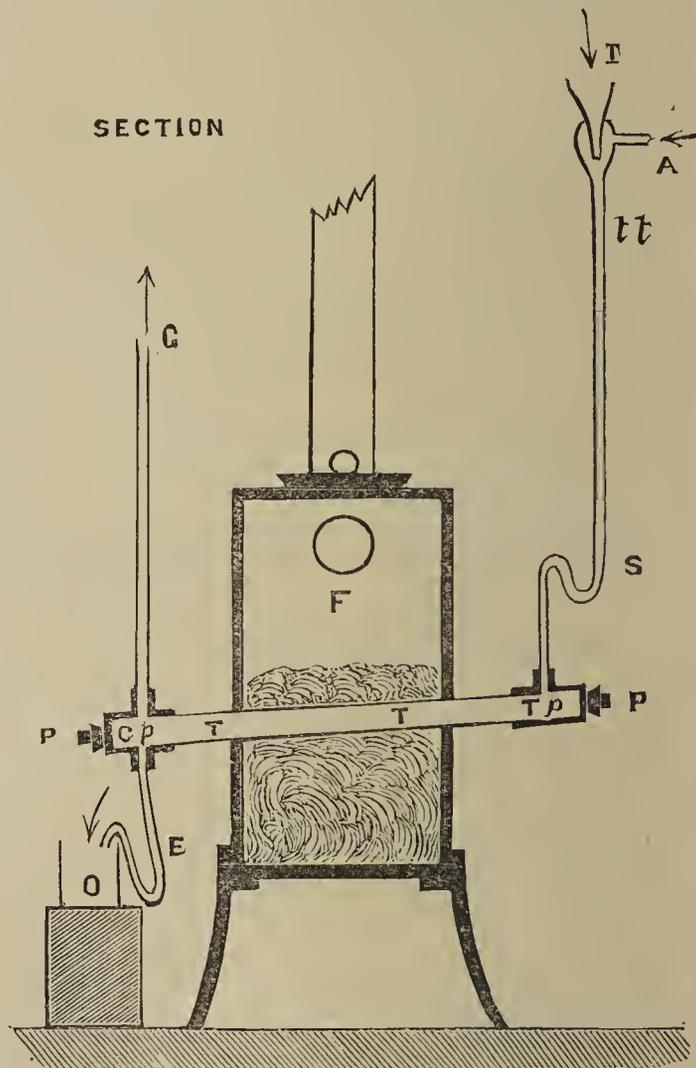
Here the concentration of the solutions and of the acid, its kind, whether sulphuric or hydrochloric, play a great part. It has yet to be decided whether solid arsenic hydride is not converted into the gaseous form in presence of zinc and hydrochloric acid.

Finally, it must be remarked that in examining the organs of a corpse, in poisoning cases in general, only one poison is found, but that we should not overlook how easily in such cases several more or less dangerous substances, inorganic or organic, or both, may have found application (Schweinfurt green, mercuric cyanide, chrome yellow, tinctures, &c.). The more or less unconscious state of drunkenness of a person may have been taken advantage of for the purpose of giving him an effective antidote. Portions of a corpse were once sent to the author to be examined for alcohol, but in addition to alcohol arsenic was found in proportion admitting of a quantitative determination. There was consequently room to suspect that arsenic had been administered to the victim whilst in a state of drunkenness.—*Chemiker Zeitung*.

A SIMPLE GAS GENERATOR.

By F. W. BOAM, F.C.S.

In laboratories where the ordinary coal-gas is not obtainable it is often requisite and sometimes necessary to have a supply of a comparatively pure gas at hand. The usual laboratory appliances for producing gas from benzine, methylated spirit, &c., are oftentimes cumbersome, or require constant attention, or are complete failures. It was in order to meet this difficulty to some extent that the author designed the apparatus herein described and illustrated. It consists of an ordinary circular or square cast-iron stove or furnace, *F*, through the body of which passes a short length of 1½ or 2-inch iron pipe, *T*; preferably such as is used for the conveyance of high-pressure steam. This tube is screwed at each end and a



T-piece, *Tp*, screwed on at the higher end, and at the lower end a "cross-piece" or "four-way socket," *CP*. At the extreme ends are a couple of "plugs," *PP*. These, when unscrewed, admit of a rod being pushed through the tube should a stoppage occur, or for cleaning the tube. Into the branch of the top end is fixed a narrow tube, about ½ inch bore, having an *S*-shape bend towards its lower end, *s*. At the top end it widens out, admitting the nozzle of a funnel, *I*, and the end of a branch tube, *A*. Into the bottom branch of the four-way socket, *CP*, is fixed a tube with a syphon bend, *E*, under the end of which is placed a receptacle to catch any surplus oil, *O*. Into the higher branch is screwed a pipe, *G*, to convey the gases produced to the gas-holder.

To start the apparatus, oil (paraffin oil or any fluid hydrocarbon) is allowed to drop from a vessel placed above the funnel, *I*, into the funnel and thence down the

pipe, *tt*, until it commences to overflow at pipe *E*. When this occurs the fire is lighted in the furnace, *r*, and the oil-supply so regulated that each drop of oil carries down with it a small bubble of air. When the tube, *r*, gets hot a form of paraffin gas will be generated and will pass through the pipe, *g*, into the gas-holder. The best form of gasholder to use is the ordinary sheet-iron dome suspended in a water-tank and counterbalanced by weights attached to cords or chains running over small pulleys. The weight of the holder should be as nearly as possible exactly counterbalanced. If the oil carries along with it too much air, the supply of air may be controlled by means of a piece of rubber tube and a clamp, or a stop-cock. The pressure of the gas is, of course, dependent upon the height of the column of oil in the tubes *tt* and *E*, and therefore, indirectly, upon the length of those tubes. A small apparatus made after this pattern has given very satisfactory results in the author's laboratory, the gas produced being excellent both as an illuminant and for use with Bunsen burners and blast-lamps. It is, of course, also practically free from sulphur compounds, and is suitable for the most delicate work. The cost of the apparatus is next to nothing, and it requires very little attention, while giving a constant and regular supply of gas.

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A SYSTEM OF CHEMICAL REAGENTS
BASED ON THE EQUIVALENTS OF THE
ELEMENTS.

By JOS. REDDROP, F.C.S., F.I.C.

The Concentration of Laboratory Reagents.

IN a recent number of the *Berichte der Deutsch. Chem. Ges.* (1890, p. 31) R. Blockmann calls attention to a matter which is of the greatest importance in the chemical laboratory, viz., the concentration of the reagents employed. I enclose a copy of the *Chemical Trade Journal* containing an abstract of the above, from which it will be seen that the author proposes the adoption of normal or *percentage* solutions for general use in chemical analysis.

In the year 1877, I introduced into the new laboratory at Crewe a number of reagents, the strength of which was based on the chemical equivalents. Since that time, their use has extended until it now includes almost all the reagents in the laboratory, and the advantages derived therefrom have been so decided, especially in chemical analysis, that they are now employed in all our investigations. I have, therefore, great pleasure in forwarding a description of the same for publication in the *CHEMICAL NEWS*, to which journal I have been so largely indebted for chemical information.

Chemical Reagents Based on the Equivalents of the Elements.

An equivalent reagent may be defined as one which contains a milligram equivalent of reacting substance in one c.c. of solution, or a gram equivalent in one litre. A solution of this strength is called an equivalent solution, or an equivalent reagent, and is denoted by the symbol *E*, e.g., *E* sodium carbonate represents a solution containing 53 m.grms., = 0.053 gm. in 1 c.c., or 53 grms. in 1 litre. It will be observed that this is not a *percentage solution*, but one containing parts by *weight* (m.grms.) of substance, in parts by *volume* (c.c.) of solution. The strengths of all the reagents are expressed in terms of *E*,* thus the strength of sulphuric acid, sp. gr. 1.84, is approximately 36 *E*; strong nitric acid, sp. gr. 1.42, is

about 16 *E*; and strong hydrochloric acid, sp. gr. 1.16, is about 10 *E*. Many of the reagents employed are made of *E* strength, but in some cases the substance is not sufficiently soluble to make an *E* solution, and consequently some fractional part thereof has to be adopted instead.

Thus we have $\frac{E}{4}$ hydrogen sulphide, $\frac{E}{20}$ calcium oxide,

$\frac{E}{30}$ calcium sulphate, $\frac{E}{600}$ strontium sulphate (test for barium). The fractional indices may, if preferred, be expressed decimally, thus $\frac{3E}{5}$ or 0.6 *E*. All *E* reagents are

equal in precipitating or *quantitative* reacting power. For example, if we have a quantity of lead salt in solution which requires 36 c.c. of *E* sulphuric acid to exactly precipitate the lead as sulphate (not allowing for free sulphuric acid in excess), it will require the same number of c.c. of *E* ammonium carbonate to precipitate the lead as carbonate, or of *E* potassium chromate to precipitate the lead as chromate. The same quantity of lead in solution could, however, be precipitated by 1 c.c. of 36 *E* sulphuric acid, or by 7.2 c.c. of 5 *E* ammonium carbonate, but it

would require at least 144 c.c. of $\frac{E}{4}$ hydrogen sulphide

(saturated solution) to precipitate the lead as sulphide.

It may here be pointed out that $\frac{E}{N}$ reagents are not made with the same degree of accuracy as the *N* reagents employed in volumetric analysis. Variations in strength to the extent of from $\frac{1}{100}$ th to $\frac{1}{20}$ th part are not considered inadmissible; they may, consequently, be made in almost the same time as those hitherto employed, and the strength, in terms of *E*, is printed on the label of each bottle, thus—

SULPHURIC ACID.
36 *E*.

or

SULPHURIC ACID.
 $36 \frac{H_2SO_4}{2}$.

or

SULPHURIC ACID.
36 *E*. $E = \frac{H_2SO_4}{2}$.

The accompanying Table includes the reagents to which the equivalent system has already been extended.

Column 1 gives the name of the reagent.

Column 2 the molecular formula of the anhydrous substance.

Column 3 the molecular weight of the anhydrous substance.

Column 4 the equivalent weight of the anhydrous substance.

Column 5 gives the strength of reagent as recommended by Fresenius, "Qual. Analysis," 10th English Edition, first in the terms stated by him, and second, as calculated on the equivalent system. This double column is simply given for comparison.

* *E* being used as the symbol of equivalent or equivalents.

Column . Name of Reagent.	2. Symbol;	3. Molecular weight.	4 Equivalent weight.	FRESenius'S SYSTEM.		6. Equivalent System.	
				Strength of Reagent.		Grms. per litre.	Strength.
				As stated.	Calculated in equivalents.		
Sulphuric Acid	H ₂ SO ₄	98	49	Sp. gr. 1·840	36 E	—	36 E
"	"	"	"	1 to 5	6 E	—	5 E
Nitric Acid	HNO ₃	63	63	—	—	49	24 E—
"	"	"	"	—	—	—	16 E
"	"	"	"	Sp. gr. 1·2	6·16 E	—	5 E
Hydrochloric Acid ..	HCl	36·5	36·5	—	—	63	E
"	"	"	"	Sp. gr. 1·12	7·48 E	—	10 E
"	"	"	"	—	—	—	5 E
Sulphurous Acid	H ₂ SO ₃	82	41	—	—	36·5	E
"	"	"	"	—	—	—	4 E—
Carbonic Acid	H ₂ CO ₃	62	31	—	—	—	E
"	"	"	"	—	—	—	10—
Acetic Acid	HC ₂ H ₃ O ₂	60	60	—	—	—	17 E
"	"	"	"	33% of HC ₂ H ₃ O ₂	5·61 E	—	5 E
"	"	"	"	—	—	60	E
Tartaric Acid	H ₂ C ₄ H ₄ O ₆	150	75	—	—	—	5 E
"	"	"	"	—	—	75	E
Citric Acid	H ₃ C ₆ H ₅ O ₇	192	64	—	—	—	5 E
"	"	"	"	—	—	64	E
Oxalic Acid	H ₂ C ₂ O ₄	90	45	—	—	—	3 E
"	"	"	"	—	—	—	2
Hydrofluoric Acid ..	HF	20	20	—	—	—	12 E?
Hydrofluosilicic Acid..	H ₂ SiF ₆	144	72	—	—	—	—
"	"	"	"	—	—	—	E
Hydrogen Sulphide ..	H ₂ S	34	17	Saturated solution	$\frac{E}{4}$	—	$\frac{E}{4}$
Chlorine Water	Cl ₂	71	35·5	Saturated solution	$\frac{E}{5}$	—	$\frac{E}{5}$
Bromine	Br ₂	160	80	—	—	—	37 E
"	"	"	"	—	—	—	E
Bromine Water	"	"	"	—	—	—	$\frac{E}{2}$
Hydrogen Peroxide ..	H ₂ O ₂	34	17	—	—	—	4 E—
"	"	"	"	—	—	—	2 E—
Potassium Hydrate ..	KHO	56	56	—	—	—	5 E
"	"	"	"	—	—	56	E
Sodium Hydrate ..	NaHO	40	40	Sp. gr. 1·13 = 9% Na ₂ O	3·28 E	—	5 E
"	"	"	"	—	—	40	E
Ammonium Hydrate..	AmHo	35	35	—	—	—	20 E—
"	"	"	"	Sp. gr. 0·96 = 10% NH ₃	5·54 E	—	5 E
"	"	"	"	—	—	35	E
Barium Oxide	BaO	153	76·5	BaH ₂ O ₂ .8Aq. 1 to 20	$\frac{E}{3·15}$	—	$\frac{E}{3}$
Calcium Oxide	CaO	56	28	Saturated solution	$\frac{E}{20}$	—	$\frac{E}{20}$
Ammonium Sulphide .	Am ₂ S	68	34	10% NH ₃	5·54 E?	—	5 E
"	"	"	"	—	—	—	E
Sodium Sulphide ..	Na ₂ S	78	39	9% Na ₂ O	3·28 E	34	5 E
"	"	"	"	—	—	39	E
Potassium Cyanide ..	KCy	65	65	—	—	65	E
Potassium Sulphate..	K ₂ SO ₄	174	87	1 to 12	0·96 E	87	E
Potassium Iodide ..	KI	166	166	—	—	166	E
"	"	"	"	—	—	—	E
"	"	"	"	—	—	—	$\frac{E}{5}$
Potassium Chromate .	K ₂ CrO ₄	194·5	97·25	—	—	97·25	E
Potassium Metanti- moniate	KSbO ₃	209	209	Saturated solution	$\frac{E}{68}$	3·07	$\frac{E}{68}$
Potassium Ferrocyanide	K ₄ FeCy ₆	368	92	1 to 12	0·79 E	92	E
Potassium Ferricyanide	K ₆ Fe ₂ Cy ₁₂	658	109·7	—	—	109·7	E
Potassium Sulphocyanate	KCyS	97	97	1 to 10	1·03 E	97	E

Column 7.

8.

Symbol of substance taken.	Method of Preparing Reagent.	Strength of Reagent as found by trial.
—	Sulphuric acid, sp. gr. 1·8427 at 15·5° C. Note (1).	36 E
—	Sulphuric acid diluted to sp. gr. 1·1527 at 15·5°. Note (2).	5 E
—	200 c.c. of 5 E sulphuric acid diluted to 1 litre.	E
—	Nitric acid sp. g. 1·50. Note (3).	22·8 E
—	Nitric acid sp. gr. 1·4268 at 15·5° C. Note (4).	16 E
—	Nitric acid diluted to sp. gr. 1·1656 at 15·5° C. Note (2).	5 E
—	200 c.c. of 5 E nitric acid diluted to 1 litre.	E
—	Hydrochloric acid sp. gr. 1·1611 at 15·5° C. Note (5).	10 E
—	Hydrochloric acid diluted to sp. gr. 1·0843 at 15·5° C. Note (2).	5 E
—	200 c.c. of 5 E hydrochloric acid diluted to 1 litre.	E
—	Water at 15·5° C. saturated with sulphur dioxide (sp. gr. 1·052.	3·7 E
—	Water at 15·5° C. saturated with carbon dioxide. Note (6).	—
—	Acetic acid solid at 10° C. Note (7).	16·9 E
—	294 c.c. of 17 E acetic acid diluted to 1 litre. Note (2).	5 E
—	200 c.c. of 5 E acetic acid diluted to 1 litre.	E
H ₂ C ₄ H ₄ O ₆	375 grm. dissolved and diluted to 1 litre.	5 E
"	75 " " "	E
H ₃ C ₆ H ₅ O ₇ , Aq $\frac{1}{3}$	350 " " "	5 E
"	70 " " "	E
H ₂ C ₂ O ₄ , 2Aq	94·5 " " Note (8).	$\frac{3 E}{2}$
—	Hydrofluoric acid, sp. gr. 1·15.	12·9 E
—	Water at 15·5° C. saturated with hydrogen sulphide.	$\frac{24 E}{100}$
—	Water at 15·5° C. saturated with chlorine.	$\frac{19 E}{100}$
—	Pure liquid bromine. Note (9).	—
—	Water at 15·5° C. saturated with bromine.	$\frac{E}{2}$
—	Hydrogen peroxide, 20 volume solution. Note (10).	—
—	" " 10 " " Note (11).	—
KHO	280 grms. dissolved and diluted to 1 litre. Note (12).	—
"	56 " " " Note (12).	—
NaHO	200 " " " Note (13).	—
"	40 " " " Note (13).	—
—	Ammonium hydrate sp. gr. 0·880. Note (14).	18·9 E
—	Ammonium hydrate diluted to sp. gr. 0·9643 at 15·5° C. Note (2).	5 E
—	200 c.c. of 5 E ammonium hydrate diluted to 1 litre.	E
BaH ₂ O ₂ , 8Aq	52·5 grm. dissolved and diluted to 1 litre. Note (15).	—
—	Water at 15·5° C. saturated with calcium hydrate.	$\frac{97 E}{2000}$
—	Saturate 600 c.c. of 5 E ammonium hydrate with H ₂ S in a corked flask, and then add 400 c.c. of 5 E ammonium hydrate.	5 E
—	200 c.c. of 5 E ammonium sulphide diluted to 1 litre.	E
—	Dissolve 200 grms. of sodium hydrate in 800 c.c. water, saturate one-half with H ₂ S, then add the other half and dilute to 1 litre.	5 E
—	200 c.c. of 5 E sodium sulphide diluted to 1 litre.	E
KCy	65 grms. crystal dissolved and diluted to 1 litre.	—
K ₂ SO ₄	87 grms. dissolved and diluted to 1 litre.	—
KI	166 " " " Note (18).	E
"	33·2 " " " Note (18).	$\frac{E}{5}$
K ₂ CrO ₄	97·25 " " "	E
K ₂ Sb ₂ O ₆ , 7Aq	Saturated solution at 15·5° C.	—
K ₄ FeCy ₆ , 3Aq	105·5 grm. dissolved and diluted to 1 litre.	E
K ₆ Fe ₂ Cy ₁₂	109·7 " " "	E
KCyS	97 " "	E

Column 1. Name of Reagent.	2. Symbol.	3. Molecular weight.	4. Equivalent weight.	5. FRESSENIUS'S SYSTEM.		6. Equivalent System.	
				Strength of Reagent.		Grms. per litre.	Strength.
				As stated.	Calculated in equivalents.		
Sodium Carbonate ..	Na ₂ CO ₃	106	53	2·7 to 5	3·77 E	—	3 E
" " Disodium Phosphate	" "	" "	" "	—	—	53	E
Hydrogen Disodium Phosphate	HNa ₂ PO ₄	142	47·3	1 to 10	0·84 E	47·3	$\frac{2}{3}$ E or E
Sodium Acetate	NaC ₂ H ₃ O ₂	82	82	1 to 10	0·74 E	—	4 E
Sodium Sulphite	Na ₂ SO ₃	126	63	—	—	—	2 E—
Sodium Thiosulphate ..	Na ₂ S ₂ O ₃	158	79	—	—	79	$\frac{E}{2}$ or E
Sodium Hypochlorite ..	NaClO	74·5	74·5	—	—	—	—
Ammonium Acetate ..	AmC ₂ H ₃ O ₂	77	77	—	—	—	5 E
" " " "	" "	" "	" "	—	—	77	E
Ammonium Oxalate ..	Am ₂ C ₂ O ₄	124	62	1 to 24	0·59 E	37·2	$\frac{3}{5}$ E
Hydrogen Di-ammonium Phosphate	HAm ₂ PO ₄	132	44	—	—	44	$\frac{2}{3}$ E or E
Ammonium Carbonate .	Am ₂ CO ₃	96	48	1 sesqui to 5 + NH ₃	5·08 E	—	5 E
" " " "	" "	" "	" "	—	—	48	E
Hydrogen " Ammonium Carbonate	HAmCO ₃	79	—	—	—	—	$\frac{3E}{2}$ or 3 E
Ammonium Chloride ..	AmCl	53·5	53·5	1 to 8	2·34 E	—	5 E
" " " "	" "	" "	" "	—	—	53·5	E
Ammonium Sulphate ..	Am ₂ SO ₄	132	66	—	—	66	E
Barium Chloride	BaCl ₂	208	104	1 to 10	0·82 E	104	E
Barium Nitrate	BaN ₂ O ₆	261	130·5	1 to 15	0·51 E	65·25	$\frac{E}{2}$
Barium Carbonate ..	BaCO ₃	197	98·5	—	—	—	2 E
Strontium Sulphate ..	SrSO ₄	183·5	91·75	—	—	0·153	$\frac{E}{600}$ —
Calcium Chloride	CaCl ₂	111	55·5	1 cryst. to 5	1·83 E	55·5	E
Calcium Sulphate	CaSO ₄	136	68	Saturated solution	$\frac{E}{30}$	2·27	$\frac{E}{30}$
Magnesium Chloride ..	MgCl ₂	95	47·5	—	—	47·5	E
Magnesium Sulphate ..	MgSO ₄	120	60	1 to 10	0·81 E	60	E
Ferrous Sulphate	FeSO ₄	152	76	—	—	76	E
Ferric Chloride	Fe ₂ Cl ₆	325	54·17	—	—	54·17	E
Plumbic Acetate	PbC ₄ H ₆ O ₄	325	162·5	1 to 10	0·53 E	162·5	E
Plumbic Nitrate	PbN ₂ O ₆	331	165·5	—	—	165·5	E
Argentive Nitrate	AgNO ₃	170	170	1 to 20	0·30 E	170	E
" " " "	" "	" "	" "	—	—	—	$\frac{E}{5}$
Argentive Sulphate ..	Ag ₂ SO ₄	312	156	—	—	7·8	$\frac{E}{20}$
Mercurous Nitrate ..	Hg ₂ N ₂ O ₆	524	262	—	—	52·4+	$\frac{E}{5}$ +
Mercuric Chloride ..	HgCl ₂	271	135·5	1 to 16	0·46 E	54·2	$\frac{2}{5}$ E
Cupric Sulphate	CuSO ₄	159·5	79·75	1 to 10	0·80 E	79·75	E
Cupric Chloride	CuCl ₂	134·5	67·25	—	—	67·25	E
Stannous Chloride	SnCl ₂	189	94·5	—	—	94·5+	E+
Auric Chloride	AuCl ₃	303·1	101	1 to 30	0·33 E	20·2	$\frac{E}{5}$
Platinic Chloride	PtCl ₄	339·1	84·8	—	0·77 E	84·8	E
Magnesia Mixture (for Phosphoric Acid) ..	—	—	—	—	—	—	E

Column 7.

8.

Symbol of substance taken.	Method of Preparing Reagent.	Strength of Reagent as found by trial.
Na ₂ CO ₃ , 10Aq	429 grms. dissolved and diluted to 1 litre.	2.94 E
"	143 " " "	0.98 E
HNa ₂ PO ₄ , 12Aq	119.3 " " "	E
NaC ₂ H ₃ O ₂ , 3Aq	544 " " "	3.96 E
Na ₂ SO ₃ , 7Aq	252 " " "	—
Na ₂ S ₂ O ₃ , 5Aq	124 " " "	—
—	294 c.c. of 17 E acetic acid, neutralised with strong ammonium hydrate and diluted to 1 litre.	5 E
—	200 c.c. of 5 E ammonium acetate diluted to 1 litre.	E
Am ₂ C ₂ O ₄ , Aq	42.6 grms. dissolved and diluted to one litre. Note (16).	$\frac{3 E}{5}$
HAm ₂ PO ₄	44 grms. dissolved and diluted to 1 litre.	E
—	196.7 grms. of ammonium sesquicarbonate dissolved in 333.3 c.c. of 5 E ammonium hydrate and diluted to 1 litre.	—
—	200 c.c. of 5 E ammonium carbonate solution diluted to 1 litre.	—
—	A saturated solution made by passing excess of carbon dioxide into 3 E ammonium hydrate.	—
AmCl	267.5 grms. dissolved and diluted to 1 litre.	5 E
"	53.5 " " "	E
Am ₂ SO ₄	66 " " "	E
BaCl ₂ , 2Aq	122 " " "	E
BaN ₂ O ₆	65.25 " " " Note (17).	$\frac{E}{2}$
BaCO ₃	197 grms., freshly precipitated, suspended in water and diluted to 1 litre.	—
SrSO ₄	Water at 15.5° C. saturated with precipitated strontium sulphate.	—
CaCl ₂ , 6Aq	109.5 grms. dissolved and diluted to one litre.	0.97 E
CaSO ₄ , 2Aq	Water at 15.5° C. saturated with precipitated calcium sulphate.	—
MgCl ₂ , 6Aq	101.5 grms. dissolved and diluted to 1 litre.	0.98 E
MgSO ₄ , 7Aq	123 grms. dissolved and diluted to 1 litre.	E
FeSO ₄ , 7Aq	139 " " "	0.97 E.
—	18.67 grms. of iron, as Fe ₂ H ₆ O ₆ , dissolved in 200 c.c. of 5 E hydrochloric acid and diluted to 1 litre.	—
PbC ₄ H ₆ O ₄ , 3Aq	189.5 grms. dissolved and diluted to 1 litre.	E
PbN ₂ O ₆	165.5 " " "	0.98 E
AgNO ₃	170 " " " Note (18).	E
"	34 " " " Note (18).	$\frac{E}{5}$
Ag ₂ SO ₄	Water at 15.5° C. saturated with freshly precipitated argentic sulphate.	$\frac{E}{21}$
Hg ₂ N ₂ O ₆ , 2Aq	56 grms. dissolved in 40 c.c. 5 E nitric acid and diluted to 1 litre, a little mercury being placed in bottle.	$\frac{E}{5}$
HgCl ₂	54.2 grms. dissolved and diluted to 1 litre.	$\frac{2 E}{5}$
CuSO ₄ , 5Aq	124.75 " " "	E
CuCl ₂ , 2Aq	85.25 " " "	0.95 E
SnCl ₂ , 2Aq	112.5 grms. dissolved in 200 c.c. of 5 E hydrochloric acid and diluted to one litre, a little tin being placed in bottle.	0.96 E
—	13.1 grms. of metallic gold, converted into auric chloride, dissolved and diluted to 1 litre. Note (18).	—
—	49.3 grms. of metallic platinum, converted into platinic chloride, dissolved and diluted to 1 litre. Note (18).	—
—	Dissolve 68 grms. MgCl ₂ , 6 Aq in about 500 c.c. of water, add 165 grms. AmCl, then 300 c.c. of 5 E ammonium hydrate, and dilute to 1 litre.	—

Column 6 gives the strength of reagent recommended on the equivalent system, first in grms. per litre, and second in terms of E.

Column 7 gives the chemical formula of the substances used, and the methods by which the reagents are prepared of *sufficient accuracy for general use*.

Column 8 gives the strength of reagent as determined by trial after being prepared by the method given.

Several notes are also appended, to which the reader should refer for further information.

NOTES TO TABLE I.

- (1) Sulphuric acid, sp. gr. 1.842, containing 98.6 per cent, by calculation gives 37.07 E.
Sulphuric acid, sp. gr. 1.84, as supplied, two samples titrated gave 36.6 E and 36.8 E.
- (2) I usually make 5 litres of 5 E acid at a time and adjust the strength by titrating 2 c.c. with standard N sodium hydrate. This can be done more quickly than by using the hydrometer, owing to changes of temperature on dilution. 5 E ammonium hydrate may be made in a similar manner. These 5 E reagents may also be made by simply diluting the concentrated ones to the right degree.
- (3) Nitric acid, sp. gr. 1.50, containing nitrous acid, titrated, gave 22.8 E.
- (4) Nitric acid, sp. gr. 1.424, containing 70.2 per cent, by calculation gives 15.87 E.
Nitric acid, sp. gr. 1.42, as supplied, two samples titrated gave 16.05 E and 16.6 E.
- (5) Hydrochloric acid, sp. gr. 1.160, containing 31.73 per cent by calculation, gives 10.08 E.
Hydrochloric acid, sp. gr. 1.16, as supplied, two samples titrated gave 10.36 E and 10.32 E.
- (6) Carbonic acid. Water at 15° C. dissolves 1.0020 vols. of CO₂; this, by calculation, gives $\frac{100 E}{1114}$.
- (7) Acetic acid, anhydrous, sp. gr. 1.0635, containing 100 per cent, by calculation gives 17.7 E.
Acetic acid, sp. gr. 1.0598, solid at 50° F., as supplied, titrated, gave 16.9 E.
- (8) Oxalic acid. A $\frac{3 E}{2}$ solution does not crystallise out at 15° C., but does so at 10° C.
- (9) Bromine, sp. gr. 2.966, by calculation gives 37.08 E.
- (10) Hydrogen peroxide, 20 volumes, by calculation gives 3.6 E.
- (11) Hydrogen peroxide, 10 volumes, by calculation gives 1.8 E.
- (12) Potassium hydrate, about one-tenth more than the quantity given in the table is required, owing to most samples containing water.
- (13) Sodium hydrate prepared from sodium is employed.
- (14) Ammonium hydrate, sp. gr. 0.88, containing 38 per cent, by calculation gives 19.7 E.
Ammonium hydrate, sp. gr. 0.88, as supplied, three samples titrated gave 18.0 E, 16.2 E, and 18.9 E.
- (15) Barium hydrate. The strength of a saturated solution varies considerably with the temperature.
- (16) Ammonium oxalate. A stronger solution than $\frac{3 E}{5}$ crystallises out at the ordinary temperature.
- (17) Barium nitrate is not sufficiently soluble to make an E solution.
- (18) Where reagents are expensive an $\frac{E}{5}$ or $\frac{E}{10}$ solution may be made for qualitative tests.

It will be seen from the Table that a large number of the reagents are made of E strength. Experience, however, has shown that there are cases in which it is necessary to employ certain reagents, and especially the acids, stronger than this; consequently, a number of 5 E

reagents have been introduced, 5 being a convenient figure for calculations on the decimal system. These are more accurately made, and keep more constant in strength than the concentrated reagents, which are liable to a variation of about one equivalent.

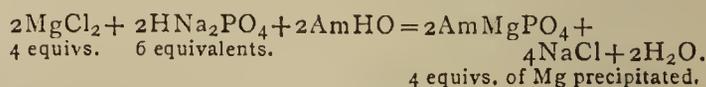
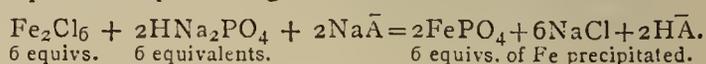
About three-fourths of the reagents given in the Table may be kept in well-stoppered bottles for a considerable time without appreciable change. In the few remaining cases where the variation in strength is considerable, the unwelcome fact is expressed in column 6 of the preceding Table and on the reagent bottles in the following manner:—

Where it is known that the reagent has been made the standard strength, but becomes weaker on keeping, it may be expressed by the sign — placed after the symbol E, thus:— 4 E— Sulphurous Acid. If, on the other hand, there is an increase, of strength, as in the case of the acid solution of stannous chloride kept in contact with metallic tin, it may be expressed thus:— E+ Stannous Chloride. The analyst is thus forewarned as to any irregularity which may occur in the strength of such reagents.

The practical application of these multiple and fractional equivalents is well illustrated by the chlorine and bromine reagents given in the table. Pure liquid bromine is shown as 37 E; a saturated solution of bromine in water as $\frac{E}{2}$; and a saturated solution of chlorine in water $\frac{E}{5}$. Now if we know that 1 c.c. of liquid bromine (37 E) is required to effect a definite amount of oxidation in a solution, we see at a glance by means of these equivalents that it would require 74 c.c. of $\frac{E}{2}$ -bromine-water or 185 c.c. of $\frac{E}{5}$ -chlorine-water to effect the same *quantitative* result.

It may here be pointed out that a few reagents require a double index of their strength, e.g., E or $\frac{2 E}{3}$ hydrogen disodium phosphate.* This reagent behaves as an E solution if employed to precipitate iron as phosphate, but only as $\frac{2 E}{3}$ when employed to precipitate magnesium

as ammonium magnesium phosphate owing to ammonium taking part in the reaction. A reference to the chemical equations representing the reactions will illustrate this:—



(To be continued).

TWO METHODS FOR THE DIRECT DETERMINATION OF CHLORINE IN MIXTURES OF ALKALINE CHLORIDES AND IODIDES. †

By F. A. GOOCH and F. W. MAR.

(Continued from p. 225).

THE next point to be considered was the proper mode of breaking up hydriodic acid and volatilising the iodine thus set free, while leaving the hydrochloric acid fixed.

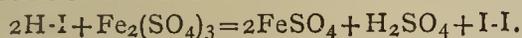
* On this account the second or third label previously given is preferred.

† Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xxxix, April, 1890.

Series H.

Taken H ₂ SO ₄ [1 : 1]. Grms.	Taken iron alum. Grms.	Taken HNO ₃ sp. gr. 1.40. C.m. ³ .	Taken KCl=HCl.		Initial volume. C.m. ³ .	Final volume. C.m. ³ .	Time in minutes.	Found AgCl. Grm.	Loss of HCl. Grm.
			Grm.	Grm.					
—	—	1	1	0.4888	200	100	30	0.0006	0.0002
—	—	1	1	0.4888	100	50	14	0.0010	0.0003
—	—	1	1	0.4888	50	15	10	0.0049	0.0012
10	—	1	1	0.4888	200	100	27	0.0031	0.0008
10	—	1	1	0.4888	100	50	16	0.0116	0.0029
10	5	0.1	1	0.4888	400	300	24	0.0004	0.0001
10	5	0.3	1	0.4888	400	300	30	0.0004	0.0001
10	5	0.5	1	0.4888	400	300	30	0.0004	0.0001
10	5	1	1	0.4888	400	300	27	0.0010	0.0003
10	5	1	1	0.4888	300	200	33	0.0007	0.0002
10	5	1	1	0.4888	200	100	30	0.0025	0.0006
10	5	1	1	0.4888	100	50	15	0.0090	0.0023
10	5	2	1	0.4888	400	300	25	0.0010	0.0003
10	5	3	1	0.4888	400	300	25	0.0010	0.0003
10	5	4	1	0.4888	400	300	30	0.0009	0.0002
10	5	5	1	0.4888	400	300	30	0.0007	0.0002
10	5	10	1	0.4888	400	300	30	0.0018	0.0005

The use of dihydrogen potassium arseniate, which has been utilised to liberate iodine according to a method recently developed in this laboratory,* is precluded by the necessarily high degree of dilution of the solution employed. The first trials were made, therefore, with ferric alum to act as the oxidising agent according to the well-known reaction of Duflos:—



We found by experiment that from a volume of 300 c.m.³ containing 10 c.m.³ of sulphuric acid [1 : 1], 5 grms. of ferric alum, and 0.005 gm. of potassium iodide, every trace of iodine had disappeared so completely after five minutes boiling that nitrous acid and chloroform collected no colour in the cooled liquid. It transpired, however, that when the amount of potassium iodide was increased to 1 gm., iodine was found in considerable amount after boiling for an hour with occasional replacing of the water evaporated, so that the volume should not decrease much below 300 c.m.³. The failure of the iron alum to expel the iodine is not attributable to a deficiency in amount; for the 5 grms. present were capable of decomposing more than a gm. and a half of potassium iodide were the full effect theoretically possible attained. Furthermore, special tests, in which the amount of ferric alum was increased, developed the fact that the increase was but little helpful. The apparent explanation of the phenomenon is that here, as in the liberation of iodine by means of dihydrogen potassium arseniate, there occurs a time in the course of action when for a given degree of dilution an equilibrium is established between the tendency of the oxidiser to oxidise and that of the reduced residue to reverse the action. The obvious modes of securing completed action are the concentrating of the liquid and the reinforcing of the oxidiser. Application of the former is precluded by the danger of volatilising hydrochloric acid; the simplest mode of realising the latter—and, as the result proved, a feasible one—is the re-oxidation of the reduced ferrous sulphate by means of nitric acid.

When a sufficient amount of nitric acid is added to restore the iron to the ferric state, the boiling of the solution resulted in the complete liberation of the iodine. In dilute solutions the amount of nitric acid necessary to oxidise a fixed quantity of ferrous salt is greater than in concentrated solutions. Thus, while 0.1 c.m.³ of strong nitric acid should be more than enough to re-oxidise the iron reduced by 1 gm. of potassium iodide when the full oxidising action is brought out, we found it necessary to add to the dilute solutions with which we worked about 2 c.m.³ of the acid to complete the action satisfactorily. Incidentally, we found that nitric acid by itself—that is,

without the presence of the iron salt—is not effective in liberating the iodine; for, the successive addition of portions of 1 c.m.³ of nitric acid to a solution containing 10 c.m.³ of sulphuric acid [1 : 1], and 1 gm. of potassium iodide in a total volume of 400 c.m.³ until the amount of nitric acid reached 5 c.m.³, the liquid boiling all the time, liberating but little iodine, while the addition at this point of 2.5 grms. of ferric alum determined the evolution of iodine in dense fumes.

The addition of 2 c.m.³, or at the most 3 c.m.³, of strong nitric acid to solutions constituted as has been described, proved to be sufficient to liberate the entire amount of iodine present. The question as to whether the hydrochloric acid is affected by the addition of so much nitric acid was settled in the experiments of the following series. In these determinations a little sulphurous acid was added to each distillate to insure the complete precipitation of the chlorine by silver nitrate, and sufficient nitric acid was added to re-dissolve the silver sulphite thrown down also at first.

It appears in these results that the ferric salt has no perceptible influence upon the hydrochloric acid, and that the presence of nitric acid within reasonable limits does not sensibly increase the loss of hydrochloric acid which takes place under conditions otherwise similar, strong nitric acid to the amount of 5 c.m.³ in a total volume of 300 c.m.³ producing no apparent increment of loss from half a gm. of hydrochloric acid. The nitric acid itself passes easily into the distillate. That the influence of the sulphuric acid is important is again demonstrated in the experiments in which 1 c.m.³ of nitric acid and 1 gm. of potassium chloride were distilled in the one case with, and in the other without, the addition of sulphuric acid.

In the indication of these and previous experiments we found warrant for the prosecution of the quantitative tests of the following series:—

Weighed portions of a standard solution of potassium chloride (whose value was determined by precipitating with silver nitrate with the usual precautions, collecting in a perforated crucible upon asbestos felt the silver chloride found, and drying and weighing it) were transferred to Erlenmeyer flasks of 500 c.m.³ capacity, water was added with 10 c.m.³ of sulphuric acid [1 : 1], 2 grms. of ferric sulphate (either in the form of iron alum or an equivalent amount of ferrous sulphate oxidised in concentrated solution with a sufficiency (0.3 c.m.³) of nitric acid) and 1 gm. of potassium iodide were introduced, the whole volume was brought to 400 c.m.³, and the liquid was boiled with the addition of nitric acid as indicated in the Table, 1 c.m.³ being added after it appeared that all iodine had been expelled.

(To be continued).

* Gooch and Browning, *American Journal of Science*, vol. xxxix., p. 288.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London
Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act, 1871.*

London, May 6th, 1890.

SIR,—We submit herewith the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 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, 164 were found to be clear, bright, and well filtered, four being recorded as "very slightly turbid."

The character of the water furnished to the Metropolis during the month of April was not found to differ appreciably from that observed during the previous month. Thus, taking the Thames-derived water for comparison, the mean proportion of organic carbon present in the supply for April was found to be 0.148 part in 100,000 parts of the water, as against a mean of 0.154 part in the supply of the previous month. Again, the mean amount of oxygen absorbed in the oxidation of the organic matter present in a gallon of the April water was found to be 0.039 grain, as against a mean of 0.041 grain for the water of the previous month; while the fraction indicating the mean degree of colour-tint of the April water was $\frac{1}{12.0}$, as against the fraction $\frac{1}{11.9}$ for the previous month; all these differences being insignificant, but the last named being in the opposite direction to the other two.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

SUMMARY OF USEFUL TESTS WITH
THE BLOWPIPE.*

By A. J. MOSES.

(Continued from p. 234).

NICKEL, Ni.

On Coal.—R. F., the oxide becomes magnetic.

With Borax.—O. F., violet hot, pale reddish brown cold.

R. F., cloudy and finally clear and colourless.

With S. Ph.—O. F., red hot, yellow cold.

R. F., red hot, yellow cold. On coal with tin becomes colourless.

* From the *School of Mines Quarterly*, vol. xi., No 1.

Interfering Elements.

General Method.—Saturate two or three borax beads with roasted substance, and treat on coal with a strong R. F. If a visible button results, separate it from the borax and treat with S. Ph. in the O. F., replacing the S. Ph. when a colour is obtained.

If no visible button results, add either a small gold button or a few grains of test lead. Continue the reduction, and—

With Gold.—Treat the gold alloy on coal with S. Ph. in strong O. F.

With Lead.—Scorify button with boracic acid to small size, complete the removal of lead by O. F. on coal, and treat residual button with S. Ph. in O. F.

Arsenic.—Roast thoroughly, treat with borax in R. F. as long as it shows colour, treat residual button with S. Ph. in O. F.

Alloys.—Roast and melt with frequently changed borax in R. F., adding a little lead if infusible. When the borax is no longer coloured, treat residual button with S. Ph. in O. F.

NITRIC ACID, HNO₃.

In Matrass with KHSO₄ or in Closed Tube with Litharge.—Brown fumes with characteristic odour. The fumes will turn ferrous sulphate paper brown.

PHOSPHORUS, P.

Flame.—Greenish blue, momentary. Improved by conc. H₂SO₄.

In Closed Tube with Dry Soda and Magnesium.—The soda and substance are mixed in equal parts and dried, and made to cover the magnesium. Upon strongly heating, there will be a vivid incandescence, and the resulting mass, crushed and moistened, will yield the odour of phosphoretted hydrogen.

POTASSIUM, K.

Flame.—Violet, except borates and phosphates.

Interfering Elements.

Sodium.—(a) The flame, through blue glass, will be violet or blue. (b) A bead of borax and a little boracic acid, made brown by nickel, will become blue on addition of a potassium compound.

Lithium.—The flame, through green glass, will be bluish green.

SELENIUM, Se.

On Coal, R. F.—Disagreeable horse-radish odour, brown fumes, and a volatile steel-grey coat with a red border.

In Open Tube.—Steel-grey sublimate, with red border, sometimes white crystals.

In Closed Tube.—Dark red sublimate and horse-radish odour.

Flame.—Azure-blue.

On Coal with Soda.—Thoroughly fuse in R. F., place on bright silver, moisten, crush, and let stand. The silver will be blackened.

SILICON, Si.

On Coal with Soda.—With its own volume of soda dissolves with effervescence to a clear bead. With more soda the bead is opaque.

With Borax.—Clear and colourless.

With S. Ph.—Insoluble. The test made upon a small fragment will usually show a translucent mass of undissolved matter of the shape of the original fragment.

When not decomposed by S. Ph., dissolve in borax nearly to saturation, add S. Ph., and re-heat for a moment. The bead will become milky or opaque-white.

SILVER, Ag.

On Coal.—Reduction to malleable white metal.

With Borax or S. Ph.—O. F., opalescent.

Cupellation.—Fuse on coal with 1 vol. of borax glass and 1 to 2 vols. of test lead in R. F. for about tw

minutes. Remove button and scorify it in R. F. with fresh borax, then place button on cupel and blow O. F. across it, using as strong blast and as little flame as are consistent with keeping button melted.

If the litharge is dark, or if the button freezes before brightening, or if it brightens but is not spherical, re-scorify it on coal with borax, add more test lead, and again cupel until there remains only a white spherical button of silver.

SODIUM, Na.

Flame.—Strong reddish yellow.

STRONTIUM, Sr.

On Coal with Soda.—Insoluble, absorbed by the coal.

Flame.—Intense crimson, improved by moistening with HCl.

With Borax or S. Ph.—Clear and colourless; can be flamed opaque.

Interfering Elements.

Barium.—The red flame may show upon first introduction of the sample into the flame, but it is afterwards turned brownish yellow.

Lithium.—Fuse with baric chloride, by which the lithium flame is unchanged.

(To be continued).

CORRESPONDENCE.

THE VOLUMETRIC ANALYSIS OF COPPER.

To the Editor of the Chemical News.

SIR,—As regards the use of a sodium carbonate solution of copper in titrating with KCy, it has been objected—

1. That sodium carbonate does not dissolve, but precipitates copper.

2. That a large quantity is necessary to effect solution.

3. That the quantity of sodium carbonate in the solution affects the amount of KCy used.

As regards 1, it is evident either that the experiment was not tried, or that the solution did not contain the free nitric acid stated in the previous note to be necessary. Sodium bicarbonate, however, contrary to what might be expected, does not give a solution under these circumstances.

In reference to 2 the same remarks apply, as on making the experiment it will be found that 20 to 30 c.c. is amply sufficient for any ordinary analysis, and this is but a few c.c. above that required to neutralise the excess of acid necessarily used in dissolving the copper sulphide. Moreover, the increased accuracy of the method permits the use of much smaller quantities of ore in assaying.

If the sodium carbonate is added, first to the copper and then the nitric acid (not sufficient, of course, to render the solution acid) a much larger quantity of sodium carbonate will be found necessary. In actual working, however, this order will never be followed.

To 3 I may say that no such disturbance has been noticed. To one of two copper solutions of equal strength and volume, and containing equal quantities of free nitro-sulphuric acid, was added 20 c.c. of sodium carbonate solution (saturated). This was just sufficient to redissolve the precipitated copper. To the other was added 250 c.c. of the same solution of sodium carbonate. On titration the amount of KCy used for each was identical.

It is true that when NaOH (or Na₂CO₃ in absence of free acid) is used to render the copper solution alkaline the amount of KCy used varies greatly: this for the following reason. When a small excess of NaOH is added a very unstable salt separates out, having a large molecular weight. As more alkali is added the precipitate becomes more simple, more stable, and therefore less

readily acted upon by the KCy. When, however, the alkali added forms a solution the case is not analogous.

The above reaction can also be made use of in the volumetric estimation of nickel.

REGINALD A. FESSENDEN.

Edison Laboratory, Orange, N.J.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 18, May 5, 1890.

Combustion-Heat of the Principal Nitrogenous Compounds contained in Living Beings and its Part in the Production of Animal Heat.—MM. Berthelot and André.—The authors have operated upon purified egg-albumen, purified blood fibrine, muscular flesh, hæmoglobine (obtained from a horse), caseine (from milk), osseine, purified chondrine, vitelline, yolk of egg, vegetable fibrine, crude gluten, isinglass, fibroine, wool, chitine, and tunicine. Under each was determined the composition of the specimen, the heat of combustion (referred to 1 gm. of carbon), the formation-heat from the elements, and the heat of combustion with formation of urea. The mean value of the combustion-heat for the albumenoid bodies capable of playing an alimentary part is, per gm., 5691 cal., and for a weight of the substance containing 1 gm. of carbon, 10,870 cal. The loss of heat due to the elimination of nitrogen in the form of urea is about one-sixth of the total combustion-heat of the substances.

Preparation and Properties of Carbon Tetrafluoride.—H. Moissan.—Of five different methods of preparing this compound the author gives the preference to the one which depends on the action of silver fluoride upon carbon tetrachloride. The operation must be conducted in a tube of brass. The tetrafluoride has the density 3.09 (theoretically 3.03). It liquifies at -15° under the ordinary pressure and 20° under a pressure of 4 atmospheres. It is sparingly soluble in water but dissolves freely in ether and especially in absolute alcohol. If heated in contact with glass it yields carbonic acid and silicon fluoride. If heated with sodium it is absorbed entirely, giving a deposit of carbon and sodium fluoride.

Reduction of Nitric Acid to Ammonia and a Method of Determining this Acid.—E. Boyer.—The solutions of nitrate to be reduced should contain at most 5 grms. of a pure nitrate in 100 c.c. The author takes a test-tube closed at one end, 0.30 metre long and 0.022 in diameter with a spout at its upper end, and introduces 5 grms. of zinc of the size of a pea, a quantity sufficient to cover the bottom of the tube. He takes, then, 10 c.c. of the solution, corresponding to 0.5 gm. of nitrate, and introduces it into the tube, keeping the lower end of the pipette near the bottom of the tube, so as not to splash the sides. He then introduces 5 c.c. of hydrochloric acid of sp. gr. 1.19, letting it run down the sides of the tube, and agitates it circularly. The hydrogen is given off at all points of the bottom of the tube and traverses the solution uniformly from bottom to top. When the escape of hydrogen has nearly ceased he adds again 5 c.c. of hydrochloric acid, which completes the reduction of the nitric acid to ammonia. In ten minutes the reduction is complete. The liquid contained in the tube then consists of a mixture of hydrochloric acid, ammonia, zinc chloride, and undissolved zinc. This mixture is distilled with caustic magnesia in Schloësing's apparatus, and the ammonia is collected and determined in the usual manner.

Molecular Refractive Powers of Salts in Solution.—E. Doumer.—This memoir cannot be usefully abridged.

Action of Oxygenated Water upon Permanganic Acid and the Permanganates.—A. Gorgeu.—Under the influence of hydrogen peroxide a solution of permanganic acid is gradually decolourised, whilst heat and oxygen are evolved and the peroxide is deposited. In contact with oxygenated water the alkaline permanganates are gradually decolourised, whilst there is precipitated a peroxide containing a large proportion of alkali.

Amethylcamphophenolsulphone and a Tetranitro Colouring-matter derived from the Same.—P. Cazeneuve.—The amethylcamphophenolsulphone yields the colouring-matter on treatment with fuming nitric acid. It dyes splend yellow and oranges on wool and silk without a mordant.

Archives Néerlandaises des Sciences Exactes et Naturelles.
Vol. xxiv., Part 1.

Molecular Theory of a Substance Composed of two different Matters.—J. D. van der Walls.—An elaborate mathematical paper not susceptible of useful abstraction.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 2.

Remarks on a Discourse by Mr. W. Crookes relating to the History of the Rare Earths.—Lecoq de Boisbaudran.—Already noticed.

Preparation of Capryl Chloride by Means of Caprylic Alcohol saturated with Hydrochloric Acid.—H. Malbot.—The alcohol above named is heated in a closed vessel with a large proportion of very strong hydrochloric acid. The etherification is very rapid and almost quantitative.

No. 3.

Combinations of Hydroxylamine with Metallic Chlorides.—L. Crismer.—The author has formed the bi-hydroxylamine compounds of zinc chloride, cadmium chloride, and barium chloride. Experiments with the corresponding salts of calcium, magnesium, iron, and cobalt gave no decided results.

Presence of Boric Acid in Plants.—E. Bechi.—The author denies the novelty of the observations of M. von Lippmann and M. Crampton on this subject.

A New Class of Diacetones.—A. Béhal and V. Auger.—Not adapted for useful abstraction.

MEETINGS FOR THE WEEK.

- TUESDAY, 27th.—Royal Institution, 3. "The Natural History of Society," by Andrew Lang.
Royal Medical and Chirurgical, 8.30.
WEDNESDAY, 28th.—Society of Arts, 8.
THURSDAY, 29th.—Royal Institution, 3. "Flame and Explosives," by Prof. Dewar, M.A., F.R.S.
FRIDAY, 30th.—Royal Institution 9. "Astronomical Telescopes," by A. A. Common, F.R.S., Treas. R.A.S.
SATURDAY, 31st.—Royal Institution, 3. "The Ballad Music of the West of England" (with musical illustrations), by Rev. S. Baring-Gould, M.A.

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AND
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THE CHEMICAL NEWS.

Vol. LXI. No. 1592.

NOTE ON THE
ESTIMATION OF RESIN BY GLADDING'S
METHOD.

By J. A. WILSON.

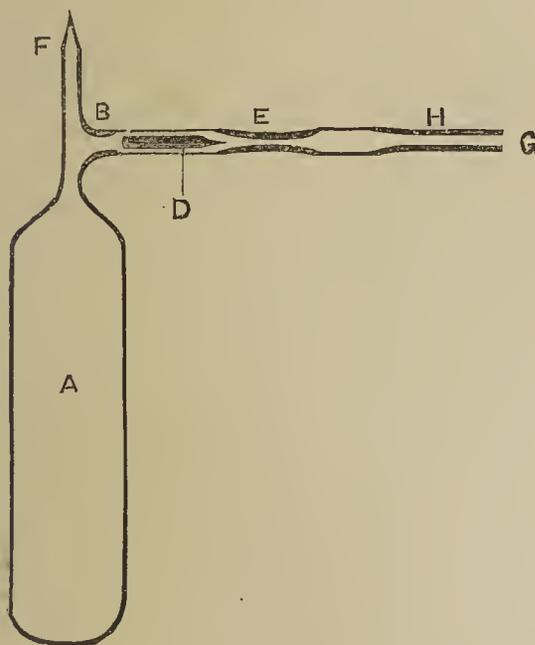
IN estimating resin in oils, fats, or soaps, it is very important that every trace of neutral fat be saponified. If this be not the case, it finds its way into the resultant ethereal layer, and, of course, vitiates the results to the extent named. In soaps where the cold, or semi-cold, process is used in their fabrication, it is especially necessary to guard against the above source of error.

ARRANGEMENT FOR SEALING TUBES UNDER
PRESSURE.

By A. RICHARDSON.

IN experimenting with gases under pressure I have found it necessary to seal tubes hermetically after gases have been admitted under pressure. In order to do this the following arrangement was employed with complete success:—

The experimental tube, A, is joined to a T-piece, B, the lateral limb of which is constricted as shown in the figure; a glass plug, D, is ground into the tube at E, and



serves the purpose of a valve opening inwards. When gas under pressure is allowed to enter the tube at G the valve opens, but, on removing the pressure from without, it at once closes; the escape of gas from A is thus prevented, and the tube may be sealed before the blowpipe at H. When the tube contains a liquid the plug should be moistened with it; this will prevent the escape of gas whilst the tube is being sealed, even though the plug does not fit very accurately; in the absence of any liquid greater care in grinding the plug is required. The tube, F, serves for the admission of liquid into the experimental

tube in the first instance; it is then closed, and at the end of the experiment it is opened and the contents of the tube removed. The rest of the apparatus is thus kept intact, and may be used repeatedly, especially if the tube is fairly long.

University College, Bristol,
May 17, 1890.

MANURE DRYERS.

By VINCENT EDWARDS, F.C.S.

(Concluded from p. 232).

IT would not be possible for me to give particulars of all substances used for the above purpose, so I merely select one or two which I know to be used to a considerable extent. I certainly think the results of my experiments go to prove that a careful analysis of all substances is necessary unless the quality of the manure is of no importance. I understand that soot is used to mix not only with superphosphates but special manures; the nitrogen and ammonia contained in it, of course, making it of particular value for the latter. I may here mention that consumers ought to know the ingredients of this class of fertilisers, as I have found in some cases the black colour covers a multitude of sins, most of them of omission. It is very doubtful, however, if the ammonia is of sufficient value to counterbalance the injury wrought by iron and alumina in some specimens, though they may not be the only cause of reduction of soluble phosphate. I think there is some obscure action at work which is not very well understood at present; an action which may be more mechanical than chemical.

EXPERIMENT No. 2.—*Soot*.—I procured a quantity from a local dealer who collects it largely, and which appears to contain a great variety of substances, brick dust, broken glass, stones, and other strange matters, which, if not rich and rare, are certainly wonderful results from the combustion of coal. They, of course, reduce the quantity of ammonia, which varies from 1 to 4 per cent. I found on testing it contained, soluble in HCl, 8.0 per cent Fe_2O_3 , 0.5 per cent Al_2O_3 . I made with this a mixture containing 80 per cent of the superphosphate and 20 per cent of the soot; this is rather more than would be added to dry superphosphate, but the iron being less than in the last experiment I increased the amount. I allowed this mixture to stand ten days, being anxious to conclude these experiments, though that is hardly time enough. On testing the mixture the result was 19.75 per cent of soluble phosphate. This shows a fall of 7.97 per cent instead of 5.544 per cent due to the addition of inert matter, or 2.426 per cent loss in ten days, owing to conversion of monocalcium phosphate into phosphate of iron and alumina; a considerable reduction of strength which is no doubt continuously at work, and which reduced special manures to the ridiculous figure of 5 or 6 per cent soluble phosphate.

EXPERIMENT No. 3.—*Flue Dust*.—This is a somewhat vague title for a number of substances which I am led to believe are added to manures. They are of various composition, according to H. A. Smith; some kinds of flue dust contain large quantities of arsenic, which is highly undesirable. I have analysed dust from different parts of vitriol plant, and find in all a considerable quantity of soluble iron together with a siliceous compound, insoluble in acids, which is not so injurious. I found in a recent sample 14.5 per cent soluble Fe_2O_3 , and made the following experiment with it, though I consider it better than some kinds of dust. I added 10 per cent of dust to the superphosphate and allowed the mixture to stand for ten days. On analysis, I found 21.85 per cent soluble phosphate; this shows a fall of 5.87 per cent instead of 2.772 per cent, a loss of 3.098 per cent in ten days, a loss which would become greater after a time as the iron is in a less

soluble state owing to the absence of water of hydration.

EXPERIMENT No. 4.—*Gypsum*.—I thought well to try an experiment with a good quality of gypsum, and obtained a quantity which came from a north of England firm; It was of a rose colour and very dry. On testing, I found it contained 1.5 per cent of Fe_2O_3 and Al_2O_3 , though there was more iron in a combined state with silica; this is not of much importance. I may note here that calcining gypsum, though it would render some iron less soluble, would drive off CO_2 from any carbonate of lime present, when the oxide left would reduce the soluble phosphate. I made a mixture of 10 per cent gypsum and 90 per cent superphosphate, which I allowed to remain for ten days; it did not dry the manure as well as the cinders. On testing, I found 24.7 per cent soluble phosphate, which is satisfactory, being a loss of only 0.3 per cent. This would have been otherwise with some bad kinds of gypsum. In all cases an analysis is desirable.

EXPERIMENT No. 5.—To prove that the reduction is due to soluble iron and alumina, I made a mixture of superphosphate with 10 per cent crystallised sulphate of iron; not having the pure at hand, I employed the commercial salt, which, however, does not make much difference. On analysis, I found but 11.4 per cent soluble phosphate, a loss of 13.548 per cent, which had been reduced to basic phosphate of iron.

I notice in Dr. Griffiths's recent book that a patent manure, "ferrous superphosphate," was not a success, due, no doubt to the precipitation of the phosphate in a very insoluble condition by the sulphate of iron. Of course, I am aware that the proportions of any of the mixings I have given are not as they might be made by a manufacturer, but I think I have shown enough to prove how injurious is the present method of adding anything almost to manures, and without knowing what it contains. Some substances are no doubt valuable for dressing and composts, but very hurtful to manure during manufacture. The use of Belgium phosphate and good gypsum as dryers would be the best plan and avoid much waste of good manure. The price would have to be raised by all makers, along with the quality, but this would enable farmers to use less, and thus save railway rates on stuff that is always at hand; both sellers and buyers would gain by improvement in quality and manufacture.

A SYSTEM OF CHEMICAL REAGENTS BASED ON THE EQUIVALENTS OF THE ELEMENTS.

By JOS. REDDOP, F.C.S., F.I.C.

(Concluded from p. 250).

Advantages of the System.

HAVING thus briefly described the proposed system of reagents, we will proceed to notice some of the advantages attending its employment in practical and analytical chemistry:—

1. It affords the most convenient method of expressing the *proportionate* strength or precipitating power of each reagent, and one which may be plainly indicated on each bottle.

2. It indicates, as near as can be practically attained, the *actual* strength of each reagent.

Thus:—36 E sulphuric acid contains 36 m.grm. equivalents in 1 c.c., and knowing this we can readily calculate the quantity of any constituent, e.g., the equivalent weight of sulphuric acid being 49, we have $49 \times 36 = 1764$ m.grms. = 1764 grms. of sulphuric acid present in 1 c.c. Similarly, each c.c. contains $1 \times 36 = 36$ m.grms. = 0.036 gm. of hydrogen, $16 \times 36 = 576$ m.grms. = 0.576 gm. of sulphur, and $32 \times 36 = 1152$ m.grms. = 1.152 grms. of oxygen.

3. By observing the quantity of a reagent employed in an analysis, we can calculate the quantity of by-product therefrom, a point of considerable importance in deciding upon the dilution of our solutions.

For example:—If, during a quantitative analysis, 10 c.c. of 36 E sulphuric acid is added and afterwards neutralised by sodium carbonate, we observe that 10×36 equivalents of sodium sulphate will be produced. Now, since the equivalent of sodium sulphate is 71, we have $71 \times 36 \times 10 = 25,560$ m.grms. = 25.56 grms. as the quantity of anhydrous sodium sulphate formed by the reaction. Knowing this, we are forewarned to dilute sufficiently before proceeding with the analysis.

4. In qualitative analysis we are able to form a better judgment of the amount of substance present than when using the reagents of indefinite strength hitherto employed.

5. The strength of reagents employed in chemical investigations may be most conveniently expressed on this system.

For example:—

Nitric acid sp. gr. 1.4268 at 15.5° C.	is exactly	16E	in strength
" " 1.1656	" "	5E	" "
" " 1.0345	" "	E	" "

Now it is evident that the latter mode of expression is far simpler, and gives a much more accurate idea of the strength of the acid than does its specific gravity. These equivalent numbers would be a valuable addition to sp. gr. tables.

6. Reagents may be most readily diluted to the various strengths required in chemical analysis.

For example:—Nitric acid sp. gr. 1.42 = 16 E approximately may be readily obtained by distillation. To make an acid of E strength, it is simply necessary to dilute 1 c.c. of 16 E acid with water to the volume of 16 c.c. To make 2 E acid, dilute 2 c.c. of 16 E acid to 16 c.c.; or to make 15 E acid, take 15 c.c. of 16 E acid and dilute to 16 c.c., and so on. This method of dilution, for which I am indebted to Mr. Harris, of Swindon, is applicable to all the reagents, and is theoretically exact. It is not usually necessary to take changes of temperature into consideration, except in the case of strong sulphuric acid.

7. This system affords the simplest method of calculating the theoretical quantity of reagent required to effect any chemical change.

For example:—If we wish to find the quantity of reagent necessary to precipitate 1 grm. of calcium from its solution; we already know that 1 c.c. of E reagent, say E ammonium carbonate, will precipitate 20 m.grms. (1 m.grm. equivalent); consequently, 50 c.c. of E reagent will be required to precipitate 1 grm. If preferred, 10 c.c. of 5 E ammonium carbonate may be used instead. In like manner we can calculate the quantity of acid theoretically required to *dissolve* a given quantity of metal or other substance. Thus, 1 grm. of zinc, containing 30.8 m.grms. equivalents, will theoretically require 30.8 c.c. of E acid or 6.16 c.c. of 5E acid to effect its solution. In the same way it may be shown that while to dissolve or precipitate 1 grm. of thallium theoretically requires only 4.9 c.c. of E reagent, to dissolve or precipitate 1 grm. of beryllium would require 217.4 c.c. of E reagent.

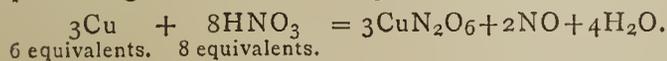
The following table gives the number* of m.grm. equivalents contained in 1 grm. of each of the more common elementary substances. This enables us to find at a glance the number of c.c. of E reagent theoretically required to effect the solution or precipitation of 1 grm. of each substance.

Should a secondary reaction occur, as for instance in the action of copper upon nitric acid, the quantity of re-

* This number is the reciprocal of the equivalent weight $\times 1000$; consequently a table of reciprocals would be applicable for all substances, and might be used for this purpose.

Symbol of Element.	Atomic weight.	Equivalent weight.	M.grm. equivs. per grm., or c.c. of E.
Al'''	27	9	III·I
Sb'''	120	40	25
Sbv	"	24	41·7
As'''	75	25	40
Asv	"	15	66·7
Ba''	137	68·5	14·6
Be''	9·2	4·6	217·4
Bi'''	210	70	14·3
Biv	"	42	23·8
B'''	11	3·67	272·5
Br'	80	80	12·5
Cd''	112	56	17·9
Ca''	40	20	50
C''	12	6	166·7
Civ	"	3	333·3
Cl'	35·5	35·5	28·2
Cl'''	52·5	17·5	57·1
Crvi	"	8·75	114·3
Co''	59	29·5	33·9
Co'''	"	19·67	50·8
Cu'	63·5	63·5	15·7
Cu''	"	31·75	31·5
F'	19	19	52·6
Au'	196·6	196·6	5·1
Au'''	"	65·53	15·3
H'	1	1	1000·0
I'	127	127	7·9
Fe''	56	28	35·7
Fe'''	"	18·67	53·6
Pb''	207	103·5	9·7
Li'	7	7	142·9
Mg''	24	12	83·3
Mn''	55	27·5	36·4
Mniv	"	13·75	72·7
Mnvi	"	9·17	109·1
Hg'	200	200	5
Hg''	"	100	10
Ni''	59	29·5	33·9
Ni'''	"	19·67	50·8
P'''	31	10·33	96·8
Pv	"	6·2	161·3
Pt''	197·1	98·55	10·1
Ptiv	"	49·28	20·3
K'	39·1	39·1	25·6
Siiv	28	7	142·9
Ag'	108	108	9·3
Na'	23	23	43·5
Sr''	87·5	43·75	22·9
S''	32	16	62·5
Siv	"	8	125
Svi	"	5·33	187·6
Sn''	118	59	16·9
Sniv	"	29·5	33·9
Tl'	204	204	4·9
Tl'''	"	68	14·7
Ti''	50	25	40
Tiiv	"	12·5	80
Zn''	65	32·5	30·8

agent required may be deduced from the equation representing the chemical change, as follows:—



Here we see that 6 equivalents of copper require 8 equivalents of nitric acid, or one-third more than the normal quantity; therefore $1\frac{1}{3}$ times the quantity of acid, as obtained from the table, will be required.

8. The system further affords a simple method of calculating the quantity of gas given off in chemical reactions.

Since 1 c.c. of an E reagent, in acting upon excess of metal, will liberate a m.grm. equivalent of hydrogen = 11·16 c.c., the volume given off by x c.c. of any E reagent will

be x 11·16 c.c. Conversely, we may calculate the quantity of acid required to produce a given volume of hydrogen.

9. In working with this system we have the most convenient method of expressing the precise acidity, &c., of chemical solutions intended for accurate titration, precipitation, &c.

For example:—In Margueritte's method of estimating

iron volumetrically by means of standard $\frac{N}{10}$

potassium permanganate, I recommend that the

solution for titration be acidified to E or $\frac{E}{2}$ sulphuric

acid, thus expressing the acidity at which it is preferred the reaction should take place.

An example of the application of these reagents to the separation of metals may be given. It is known that a solution of zinc chloride containing 1 grm. of zinc in 100 c.c. requires the presence of an appreciable quantity of free hydrochloric acid to prevent the precipitation of the zinc by hydrogen sulphide. It is also known that lead is not completely precipitated from its solutions by hydrogen sulphide if more than 2·5 per cent of free hydrochloric acid be present. The question arises how to acidify the solution so as to allow of the complete precipitation of the lead without the co-precipitation of the zinc. I have found that lead can be completely pre-

cipitated by hydrogen sulphide from an $\frac{E}{2}$ hydrochloric

acid solution without perceptible co-precipitation of zinc,

and now by acidifying the solution to $\frac{E}{2}$ hydrochloric

acid, I always secure the most favourable conditions for the separation of these metals.

As illustrating the application of this system to precipitation, I may mention the determination of lead as sulphate. It is well known that lead sulphate is soluble in strong sulphuric acid, and also in pure water, but that in dilute sulphuric acid it is practically insoluble. The strength of sulphuric acid corresponding to the least solubility does not appear to have been recorded. I have, however, found that lead sulphate is least soluble in E sulphuric acid, and now always adopt this strength in my analytical work.

As a final illustration we will take the precipitation of phosphoric acid by magnesia mixture.

David Lindo, in CHEMICAL NEWS, vol. xlvi, p. 217, has given the conditions under which he considers this precipitation can be best effected. I have calculated the quantities of reagent used in terms of E, and the conditions of precipitation may be stated as follows:—

1st. Solution to be neutral or slightly ammoniacal.

2nd. Dilution of P_2O_5 to be from $\frac{E}{5}$ to $\frac{E}{20}$, or about

1 grm. in from 200 to 800 c.c.

3rd. Dilution of AmCl to be from 0 to $\frac{E}{2}$.

4th. After precipitate has settled, add $\frac{1}{3}$ bulk of 5E ammonium hydrate.

5th. Wash with $\frac{3E}{2}$ ammonium hydrate.

6th. Magnesia mixture up to $\frac{E}{3}$ in excess does not

vitate result.

7th. Magnesia mixture counteracts solvent action of ammonium chloride.

It is now an easy matter, by means of the equivalent reagents, to ensure that the precipitation shall always take place under the conditions which have been found

to give the best results, and thus secure the highest possible degree of accuracy in our analytical work.

Having now described a system of reagents based on the chemical equivalents, which I have had in use with slight modifications for upwards of twelve years, I beg to recommend them to the attention of analytical chemists. The adoption of some uniform system by which a chemical experiment or method of analysis, once fully described, may be repeated under identical conditions in any laboratory, is a great desideratum. In conclusion, I venture to express the hope that the council of the Chemical Society or the Institute of Chemistry will, ere long, take this subject into consideration, and furnish us with a complete system for general adoption by all workers in chemical science.

Laboratory, L. and N. W. R.,
Crewe, April 4, 1890.

THE COMPOSITION OF BOILER SCALE.*

By THOS. B. STILLMAN.

THE results of an analysis of boiler scale usually represent the lime and magnesia as carbonates with a portion of the former as sulphate—on the general principle that the scale made continues to exist in the form in which it was precipitated. In those portions of the boiler where the direct heat does not come in contact with it, the scale remains unchanged after formation, but the conditions are altered where the scale is subjected to intense heat. In the latter case, while the deposition of the scale-forming material at first occurs as carbonate and sulphate, the gradual heating expels some of the carbonic acid, and the oxides of calcium and magnesium are formed.

That portion of the scale nearest the iron and to the heat loses more of its carbonic acid, and becomes caustic so long as the fire continues.

As soon, however, as the fires are drawn, the oxides of calcium and magnesium become hydrated by absorption of water.

If now a sample of the scale were taken for analysis, the water of hydration becomes an important factor in the analysis:—

A sample of scale from some boilers at Birmingham, Ala., recently submitted to me for analysis gave the following result:—

Silica and clay	11.70 per cent.
Fe ₂ O ₃ , Al ₂ O ₃	2.81 "
CaO	11.62 "
MgO	41.32 "
CO ₂	6.92 "
SO ₃	0.96 "
H ₂ O (of hydration)	21.78 "
H ₂ O (moisture at 212° F.)	0.69 "
Undetermined	0.20 "
Total	100.00 per cent.

An examination of this analysis shows an unusually small amount of carbonic and sulphuric acid, a large amount of water and of magnesia.

The great excess of the latter over the lime indicates that the water from which the scale was formed is a magnesia-water, but its presence in this amount does not in any way alter the conditions of the problem.

With less than 1 per cent of sulphuric acid and less than seven per cent of carbonic acid the oxides of calcium and magnesium could not exist in their entirety as carbonates or sulphates, for, combining the above acids to form carbonates and sulphates, the result indicated over 20 per cent lacking in the 100 parts.

The determinations of the carbonic and sulphuric acids

were in duplicate and in every way satisfactory, while no organic matter of any amount was indicated in the analysis.

The large percentage of the oxides of calcium and magnesium left after combination with the acids suggested water of hydration.

A sample of the scale (dried at 100° C.) was transferred to a platinum crucible and heated over the blast-lamp to a constant weight. The loss of weight was over 28 per cent, and, of course, included the carbonic, but not the sulphuric acid.

To check this result, a sample of the dried scale was ignited in a combustion-tube and the H₂O collected in a weighed chloride of calcium tube. The result was 21.78 per cent. of water of hydration.

This satisfied the conditions existing and the combinations gave as follows:—

Silica and clay	11.70 per cent.
Fe ₂ O ₃ , Al ₂ O ₃	2.81 "
CaSO ₄	1.69 "
CaCO ₃	5.45 "
MgCO ₃	7.35 "
Ca(OH) ₂	13.70 "
Mg(OH) ₂	56.37 "
H ₂ O (moisture at 212° F.)	0.69 "
Undetermined	0.20 "

Total 99.97 per cent.

A section of the scale was subjected to examination, layer by layer, and the following results confirm the above.

That portion of the scale next the iron and nearest the fire contained but traces of CO₂, and was principally the hydrated oxides. The middle portion of the scale was a mixture of CO₂ and the hydrated oxides, while the upper portion of the scale contained carbonates but no hydrated oxides. In other words, the composition of the scale will depend, in a great measure, upon what portion of the boiler the deposit is made. That deposited on the iron or shell not in contact with the flame or not subjected to extreme heat, will remain as deposited—as carbonates and sulphates—while that scale deposited upon the iron, subject to the flame or heat sufficient to drive out any carbonic acid from the scale, will vary in the amounts of CO₂ and water of hydration as indicated.

Scale formed in which the lime all exists as calcium sulphate and in which no magnesium carbonate is present will be subject to but little variation.

TWO METHODS FOR THE DIRECT DETERMINATION OF CHLORINE IN MIXTURES OF ALKALINE CHLORIDES AND IODIDES.*

By F. A. GOOCH and F. W. MAR.

(Concluded from p. 251).

THE colour of the ferric salt renders it impossible to tell by the appearance of the solution the exact moment when the iodine has been expelled, and starch paper loses its sensitiveness in hot vapours. We bestowed some attention, therefore, upon means for the detection of small amounts of iodine in hot steam in order to avoid the inconvenience of condensing the distillate and testing it for iodine. We found that red litmus, preferably wet, is a most sensitive agent for the detection of iodine under the circumstances, taking on, with exposure to traces of the vapour carrying that element, a distinct grey-blue, deepening with exposure to larger amounts into a

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xxxix., April, 1890.

Series I.

H ₂ SO ₄ [1 : 1]. C.m. ³ .	Fe ₂ (SO ₄) ₃ . Grms.	HNO ₃ . C.m. ³ .	KCl = HCl.		KI. Grm.	Initial volume. C.m. ³ .	Final volume. C.m. ³ .	Time in minutes.	AgCl	= HCl	Error. Grm.
			found. Grm.	found. Grm.							
IO	2*	—	0.4960	0.2425	—	400	300	40	0.9536	0.2425	0.0000
IO	2*	—	0.4970	0.2429	—	400	300	40	0.9534	0.2624	0.0005 -
IO	2*	—	0.4942	0.2416	—	400	300	30	0.9509	0.2418	0.0002 +
IO	2*	2	0.4969	0.2429	—	400	300	30	0.9559	0.2431	0.0002 +
IO	2*	3	0.4956	0.2423	I	400	350	30	0.9546	0.2428	0.0005 +
IO	2*	3	0.4969	0.2429	I	400	350	23	0.9662	0.2432	0.0003 +
IO	2†	3	0.4949	0.2419	I	400	300	27	0.9523	0.2422	0.0003 +
IO	2†	5	0.4970	0.2429	I	400	250	55	0.9559	0.2431	0.0002 +
IO	2†	5	0.4955	0.2429	I	400	300	30	0.9524	0.2422	0.0000
IO	2†	5	0.4967	0.2428	I	400	300	33	0.9546	0.2428	0.0000
IO	2†	6	0.4964	0.2427	I	400	300	30	0.9550	0.2429	0.0002

* The iron was added in the form of iron alum.
† The iron was added as FeSO₄ oxidised by HNO₃.

Series J.

H ₂ SO ₄ [1 : 1]. C.m. ³ .	NaNO ₂ used in generator. Grms.	KCl = HCl		KI. Grm.	Initial volume. C.m. ³ .	Final volume. C.m. ³ .	Time in minutes.	AgCl	HCl	Error, Grm.
		Grm.	Grm.					found. Grm.	found. Grm.	
IO	2	0.4953	0.2421	I	400	350	20	0.9524	0.2422	0.0001 +
IO	2	0.4975	0.2432	I	400	350	16	0.9573	0.2434	0.0002 +
IO	2	0.4956	0.2423	I	300	250	15	0.9530	0.2423	0.0000
IO	2	0.4973	0.2431	I	300	250	15	0.9550	0.2429	0.0002 -
IO	2	0.4964	0.2427	I	300	250	15	0.9550	0.2429	0.0002 +
IO	2	0.4969	0.2429	I	300	250	15	0.9567	0.2433	0.0004 +

lavender-blue. The addition of 0.005 gram. of iodine to 400 c.m.³ of boiling water produces immediately upon red litmus-paper the characteristic lavender-blue colour, and the test grows fainter and fainter as fresh test-papers are exposed, until at the end of five minutes, or thereabouts, when the litmus-paper shows no colour, the cooled solution yields no iodine to nitrous acid and chloroform. This reaction of litmus we found of great value, and in no case in which an exposure of two minutes' duration failed to develop the characteristic colour were we able to find iodine in the cooled liquid. To prevent mechanical loss of liquid we made use of the trap described in a previous paper from this laboratory consisting simply of an ordinary two-bulb straight drying tube cut off short and hung with the large end downward in the mouth of the Erlenmeyer flask. The residue in the flask after the expulsion of the iodine was treated with silver nitrate, and the precipitated chloride was determined similarly to that obtained in standardising the solution of potassium chloride.

Several determinations in blank—that is, experiments from which the iodine was purposely omitted—are included, for the sake of comparison, in the tabular statement (Series I).

These eminently satisfactory results prove the trustworthiness of the method.

The fact that nitric acid appears to affect so little the hydrochloric acid in the solution, suggested the possibility that nitrous acid itself might be turned to account and used in a similar process instead of a ferric salt and nitric acid. Some preliminary experiments were made, therefore, to test the behaviour of hydrochloric acid under the action of nitrous acid, and, as they gave favourable indications, the experiments of Series J were undertaken to test the action quantitatively. The general conduct of the test was similar to that followed in Series I. The solution of chloride and iodide containing 10 c.m.³ of sulphuric acid [1 : 1] was diluted to 400 c.m.³, and agitated while the gas developed by the action of sulphuric acid on 2 grms. of sodium nitrite was passed into it. With pure sodium nitrite at hand, there is probably no serious objection to introducing that substance directly into the solution, but impurities in the article at our disposal made it desirable to generate the gas outside the solution.

For a generator we used two straight drying tubes con-

nected by a rubber tube and set up after the fashion of the von Babo generator, and regulated the rapidity of the current to a rate of five or six bubbles to the second by changing the relative elevation of the generator tubes. The iodine separates immediately upon the introduction of the nitrous fumes and escapes upon boiling in dense fumes, leaving the solution colourless in a very short time. The litmus test was applied as an additional safeguard to indicate the completion of the removal of the iodine. The results of the experiments as given in the accompanying Table (Series J) are evidently satisfactory.

The modes of proceeding to the separation of iodine and the estimation of chlorine according to the processes which we have detailed may be briefly summarised as follows:—

First Method.—To the solution of the alkaline chloride and iodide diluted to about 400 c.m.³ in an Erlenmeyer flask capable of containing a litre, are added 10 c.m.³ of sulphuric acid of half strength, with 2 grms. of ferric sulphate (either in the form of iron alum, or ferrous sulphate oxidised in concentrated solution by about 0.3 c.m.³ of nitric acid), and 3 c.m.³ of nitric acid. A trap, of the form described, is hung in the neck of the flask, and the liquid is boiled until the steam which escapes no longer gives to red litmus-paper, after two minutes' exposure, the characteristic grey-blue due to traces of iodine. Then 1 c.m.³ more of nitric acid is added, and the test for iodine again made. When no iodine is found in the escaping vapour, silver nitrate is added in excess to the contents of the flask, the precipitate is settled, collected in a perforated crucible on asbestos, dried, and weighed as silver chloride.

Second Method.—The solution of the chloride and iodide contained in an Erlenmeyer flask is diluted to 400 c.m.³; 10 c.m.³ of sulphuric acid of half strength are added, and the vapour from 2 grms. of sodium nitrite acted upon by dilute sulphuric acid (preferably in a simple generator, such as is described above) is passed with reasonable rapidity into the agitated solution. The liquid is boiled until colourless, and still further until litmus paper placed in the steam gives no reaction for iodine after an exposure of two minutes. The contents of the flask are treated with silver nitrate, and the precipitated chloride is treated exactly as in the first method.

Both methods are convenient and precise.

SUMMARY OF USEFUL TESTS WITH
THE BLOWPIPE.*

By A. J. MOSES.

(Concluded from p. 253).

SULPHUR, S.

On Coal with Soda and a Little Borax.—Thoroughly fuse in the R. F., and either—

(a) Place on bright silver, moisten, crush, and let stand. The silver will become brown to black. Or

(b) Heat with dilute HCl (sometimes with powdered zinc); the odour of H₂S will be observed.

In Open Tube.—Suffocating fumes. Some sulphates are unaffected.

In Closed Tube.—May have sublimate red when hot, yellow cold, or sublimate of undecomposed sulphide, or the substance may be unaffected.

With Soda and Silica (equal parts). A yellow or red bead.

To Determine whether Sulphide or Sulphate.—Fuse with soda on platinum foil. The sulphide only will stain silver.

TELLURIUM, Te.

On Coal.—Volatile white coat with red or yellow border. If the fumes are caught on porcelain, the resulting grey or brown film may be turned crimson when moistened with conc. H₂SO₄ and gently heated.

On Coal with Soda.—Thoroughly fuse in R. F. Place on bright silver, moisten, crush, and let stand. The silver will be blackened.

Flame.—Green.

In Open Tube.—Grey sublimate fusible to clear drops.

With H₂SO₄ (conc.)—Boiled a moment, there results a purple violet solution, which loses its colour on further heating or on dilution.

TIN, Sn.

On Coal.—O. F., the oxide becomes yellow and luminous.

R. F., a slight coat, assisted by addition of sulphur or soda.

With Cobalt Solution. Moisten the coal in front of the assay with the solution, and blow a strong R. F. upon the assay. The coat will be bluish green when cold.

With CuO in Borax Bead.—A faint blue bead is made reddish brown or ruby-red by heating a moment in R. F. with a tin compound.

Interfering Elements.

Lead or Bismuth (Alloys).—It is fair proof of tin if such an alloy oxidises rapidly with sprouting and cannot be kept fused.

Zinc.—On coal with soda, borax, and charcoal in R. F. the tin will be reduced, the zinc volatilised; the tin may then be washed from the fused mass.

TITANIUM, Ti.

With Borax.—O. F., colourless to yellow hot, colourless cold, opalescent or opaque-white by flaming.

R. F., yellow to brown, enamel blue by flaming.

With S. Ph.—O. F., as with borax.

R. F., yellow hot, violet cold.

HCl Solutions.—If insoluble the substance may first be fused with S. Ph. or with soda and reduced. If then dissolved in dilute acid and heated with metallic tin, the solution will become violet after standing. Usually there will also be a turbid violet precipitate, which becomes white.

Interfering Elements.

Iron.—The S. Ph. bead in R. F. is yellow hot, brownish red cold.

TUNGSTEN, W.

With Borax.—O. F., colourless to yellow hot, colourless cold, can be flamed opaque-white.

R. F., colourless to yellow hot, yellowish brown cold.

With S. Ph.—O. F., clear and colourless.

R. F., greenish hot, blue cold. On long blowing or with tin on coal, becomes dark green.

With Dilute HCl.—If insoluble the substance may first be fused with S. Ph. The solution heated with tin becomes dark blue; with zinc it becomes purple and then reddish brown.

Interfering Elements.

Iron.—The S. Ph. in R. F. is yellow hot, blood-red cold.

URANIUM, U.

With Borax.—O. F., yellow hot, colourless cold, can be flamed enamel yellow.

R. F., bottle-green, can be flamed black, but not enamelled.

With S. Ph.—O. F., yellow hot, yellowish green cold.

R. F., emerald green.

Interfering Elements.

Iron.—With S. Ph. in R. F. is green hot, red cold.

VANADIUM, V.

With Borax.—O. F., colourless or yellow hot, greenish yellow cold.

R. F., brownish hot, emerald-green cold.

With S. Ph.—O. F., dark yellow hot, light yellow cold.

R. F., brown hot, emerald-green cold.

H₂SO₄ Solutions.—Reduced by Zn become successively yellow, green, bluish green, blue, greenish-blue, bluish violet, and lavender.

ZINC, Zn.

On Coal.—O. F., the oxide becomes yellow and luminous.

R. F., yellow coat, white when cold, assisted by soda and a little borax.

With Cobalt Solution.—Moisten the coal in front of the assay with the solution, and blow a strong R. F. upon the assay. The coat will be bright yellow-green when cold.

Interfering Elements.

Antimony.—Remove by strong O. F. or by heating with sulphur in closed tube.

Cadmium Lead or Bismuth.—The combined coats will not prevent the cobalt solution test.

Tin.—The coats heated in an open tube with charcoal dust by the O. F. may yield white sublimate of zinc.

ON SOME APPLICATIONS OF CAUSTIC
SODA OR POTASH AND CARBON IN THE
QUALITATIVE AND QUANTITATIVE
ANALYSIS OF MINERALS.*

By CHARLES A. BURGHARDT, Ph.D.

To those chemists who are brought much into contact with minerals and metallic ores, it has been for a long time a desire that the processes by which such minerals are made available for analysis should be rendered short, accurate, and simple. The minerals I refer to, of course, are those which are insoluble in acids. As is only too well known to chemists, a considerable expenditure of time and much patience is often required before the desired splitting up of the mineral and its solution is arrived at. There are, generally speaking, three kinds of fusing-mixtures or fluxes which the chemist has at his

* From the *School of Mines Quarterly*, vol. xi., No. 1.* From the *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, Vol. iii., Fourth Series, Session 1889-90.

disposal (for it is necessary to fuse the refractory mineral at a high temperature for a long time with one or more of these fusing mixtures), the commonest fusing mixture being one consisting of carbonate of sodium and nitrate of potassium, and most minerals can be eventually split up by its action. Some minerals are only acted upon by being fused with hydrogen potassium sulphate, it sometimes being necessary to split up partially with the first-mentioned fusing mixture, the process being finished by fusing the insoluble still refractory residuum with the hydrogen potassium sulphate. With many minerals these reactions are not complete even after several fusions at a long-sustained very high temperature. This entails much labour at the blowpipe table, and annoyance if the results obtained are not satisfactory. I am aware that many methods have been devised for arriving at satisfactory results by modifying, in various ways, the well-known fusion processes, but so far without very much real improvement.

I venture now to lay before you a general process which deals with all the refractory silicates, several refractory oxides and compounds of oxides, and some other insoluble mineral compounds. I am still occupied in ascertaining whether this process is applicable in the case of minerals where sulphur, arsenic, and antimony enter largely into their composition, and hope later on to lay the results obtained before this Society. After many experiments, I found that the best results were obtained by mixing the finely-divided mineral with about 10 per cent of its weight of finely-divided charcoal, and projecting the mixture carefully into a silver crucible containing fused hot caustic soda or potash, about six times the weight of the mineral powder taken for analysis. The crucible and its contents are then carefully heated over an ordinary Bunsen burner until the reaction arising has taken place, this point being easily ascertained by the fact that all further evolution of combustible gas has ceased, and the mass remaining in the crucible has become dry, and generally white or grey in colour. From the experiments which I have made I conclude that hydrogen gas is evolved from the caustic alkali, and possibly a small quantity of carbon monoxide, whilst undoubtedly carbon dioxide is largely produced by the combination of the carbon with the oxygen of the caustic alkali and the oxygen of the oxides present in the minerals taken for analysis. Further there is no doubt in my mind that metallic sodium or potassium is liberated during the course of the reaction, and these metals, whilst in the *status nascendi*, combine either with the metallic oxide (as in the case of oxide of zinc and oxide of tin) or with the acid present in the minerals. The latter conclusion will be more apparent after describing in greater detail the various experiments which I have made.

Quantitative Analysis of Tin Ore from Cornwall.

Two samples of roasted so-called black tin were powdered to an exceedingly fine powder and submitted to the process sketched out above. Black-tin is the technical term applied to tin ore which has been concentrated by washing away the lighter mineral impurities, drying, and afterwards roasting to free it from sulphur, arsenic, and antimony.

I took 0.5 grm. of the sample, mixed it carefully with sufficient powdered charcoal, and added the mixture carefully to the melted hot caustic alkali (soda was used in most cases) in the silver crucible. Heat was then gently applied with an ordinary Bunsen burner, and the mass heated until no further evolution of burning gas was observed; generally, thirty minutes heating being sufficient. The crucible and its contents were then placed in a porcelain basin, and the contents dissolved out with distilled water, and filtered from the insoluble oxides, undecomposed carbon, &c. I always submitted the residue to a second fusion, and found in most cases that every trace of mineral was completely decomposed after the

second fusion. In the solution were silicate of sodium, aluminate of sodium, and stannate of sodium, whilst in the insoluble residue were silica, bismuthic oxide, cupric oxide, ferric oxide, calcium carbonate, and manganese dioxide. The details of the method of analysis of the insoluble residue it will be unnecessary for me to enter into here, whilst the analysis of the soluble portion simply resolved itself into the elimination of the silica from the solution (previously treated with hydrochloric acid in excess) in the usual manner, the precipitation of the tin as sulphide, and its subsequent conversion into stannic oxide, in which form it was weighed.

The analyses resulted as follows, viz. :—

Sample.	No. 1.	No. 2.
Stannic oxide (SnO ₂)	66.04	82.84
Silica	14.80	4.20
Manganese dioxide	1.90	none
Ferric oxide	13.60	8.04
Cupric oxide	2.48	4.20
Calcium oxide	0.40	none
Bismuthic oxide	0.08	1.28
	<hr/>	<hr/>
	99.30	100.56

I found that 95 per cent of the total tin in the ore was taken up in the first fusion, which I consider a very satisfactory yield. By the old method of analysis the fusion would have to be performed over a blowpipe for an hour or more, and repeated at least three times in order to extract all the tin. *For success either by the old process or by my process an extremely fine state of division of the sample is necessary.*

Quantitative Analysis of Wolframite.

This mineral is practically tungstate of iron. It is a difficult mineral to analyse by the old methods, and much time is required to carry out the different processes. By my process the iron is entirely separated from the tungstic acid *at once*, and remains behind (after solution of the melt and subsequent filtration) on the filter-paper as ferric oxide and magnetic oxide. The greater portion of the manganese present in the mineral is also found on the filter-paper as manganese dioxide with the iron. In the solution there is tungstate of sodium, manganate of sodium, and silicate of sodium. The tungstic acid is thrown out of this solution (along with any niobic acid which may be present) by adding a slight excess of hydrochloric acid and boiling, when the tungstic acid, WO₃, is precipitated out as a yellow powder, dried, ignited, and weighed. Of course, if niobic acid is present, it must be separated from the tungstic acid.

A specimen of wolframite on analysis by the new method furnished the following result, viz. :—

WO ₃	64.00
FeO	17.51
MnO	11.67
SiO ₂	7.20
	<hr/>
	100.38

In this analysis I think the error is due to the silica being too high.

Quantitative Analysis of Chrome Iron Ore.

I have not had time to completely analyse the sample operated upon by the new process, but append the results, as below, the silica and alumina being obtained by difference. I varied the general method in this special instance by adding ammonium nitrate to the solid caustic soda *before* introducing the same into the silver crucible. This addition of the ammonium nitrate is to cause the chromic oxide liberated to be at once oxidised to chromic acid and combined with the excess of caustic soda present, thus forming sodium chromate. The method of working is briefly as follows :—

The finely divided levigated sample was mixed with

10 per cent of its weight (0.5 gm. of chrome iron ore was taken) of powdered charcoal and placed into the silver crucible, then five or six times the weight of caustic soda and about three times the weight of the substance taken of ammonium nitrate were placed upon the mineral in the crucible, and the whole heated gently at first, afterwards to redness for half-an-hour or so over the ordinary Bunsen burner. The cooled mass was afterwards extracted with water, filtered, and the solution evaporated down to dryness in a platinum basin, with ammonium nitrate to separate the alumina and silica, which were then filtered off. The filtrate from this treatment was rendered acid with hydrochloric acid, when *chromic chloride* was at once obtained without reduction by means of a reducing medium, and the chromium was precipitated out by means of ammonia, filtered off, the precipitate dried, ignited, and weighed as Cr_2O_3 . I cannot at present explain this remarkable reduction of the chromic acid, because in some experiments I had to employ a reducing medium as usual, such as boiling the acid solution with a little alcohol. I hope to investigate this reaction further. The results obtained are as follow, viz. :—

Cr_2O_3	43.40
FeO	19.44
MgO	8.86
Alumina and silica	28.30

100.00

After the fusion and extraction with water, the insoluble matter on the filter-paper was ferric oxide, magnesium carbonate, carbon, &c.

Qualitative Experiments.

Rutile (TiO_2) was at once decomposed and titanite of sodium produced, which, on being acidified with hydrochloric acid, gave the various reactions for titanium; for instance, a portion of the solution, on having a piece of metallic tin placed in it, gave a fine purplish-red coloured solution.

Titanite of Iron or Ilmenite gave the same reactions for titanium. It was easily attacked by the method.

Barytes (BaSO_4) gave insoluble carbonate of barium, which was then filtered off and dissolved in hydrochloric acid and tested with sulphuric acid, when it at once furnished a precipitate of barium sulphate. The filtrate from the barium carbonate, on being tested with hydrochloric acid, did not give off any sulphuretted hydrogen, proving the *absence* of sodium sulphide; therefore no *reduction* of the sulphuric acid had taken place. On testing the acidified solution, sulphuric acid was detected in large amount, consequently sodium sulphate had been found.

Simple silicates, such as kaolin (china-clay), talc, cyanite, &c., and double silicates such as tourmaline, hornblende, garnet, &c., are split up and rendered soluble just as easily as any of the other minerals mentioned above. I hope at some future time to lay before the Society a more extended series of analyses of metallic ores and silicates, also of some minerals containing fluorine, by the new method, and in concluding this communication I must express my thanks to my young assistant, Mr. Gilbert Rigg, who has carried out my instructions with great intelligence and enthusiasm.

A New Method of Chlorinisation in the Aromatic Series.—M. Petricou.—The author chlorinises benzene by means of tin chloride in the nascent state. He introduces into a flask terminating in an ascending condenser 400 c.c. of pure benzene and 90 grms. of granulated tin. He then introduces a current of tin and slightly heats the mass. After forty-nine hours of reaction the tin had disappeared and the benzene was become a mass almost solid at the common temperature.—*Bull. de la Soc. Chim. de Paris*, Vol. iii., No. 4.

PROCEEDINGS OF SOCIETIES

PHYSICAL SOCIETY.

May 16, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

PROFESSOR W. COLEMAN was elected a member of the Society.

Lord RAYLEIGH exhibited and described an arrangement of "*Huyghen's Gearing in Illustration of Electric Induction.*"

This gearing consists of two loose pulleys mounted on the same axle, with an endless cord laid over them, the loops or bights of which carry weighted pulleys whose planes are parallel to the axis on which the upper pulleys turn. If one of the latter pulleys be started to rotate, the other one turns in the opposite direction until such time as the speed of rotation of the first one becomes constant. Whilst this constant speed is maintained the second pulley remains stationary, one weight being raised and the other lowered; but, on retarding the motion of the first pulley, the second begins to turn in the same direction as the first. It will be noticed that the phenomena are analogous to those which occur in electric induction, where starting or increasing a current in one circuit induces an opposite current in a neighbouring circuit, whilst decreasing or stopping a current induces one in its own direction. Lord Rayleigh pointed out that in this apparatus there is nothing strictly analogous to electric resistance, for the friction does not follow the same law. The analogy, he said, was complete as regards there being no change of potential energy, and the mathematical equations for the kinetic energy of the system are precisely the same as those given by Maxwell for electric induction.

Dr. S. P. THOMPSON made a communication on "*Dr. Kœnig's Researches on the Physical Basis of Music,*" in the course of which Dr. Kœnig performed numerous novel and interesting experiments clearly illustrating the subject to a crowded audience.

After referring to the classical researches of the great mechanician, and to the remarkable precision with which his ingenious and unique acoustical apparatus is constructed, Dr. Thompson said the subject with which he wished to deal could be divided into two parts, the first relating to *Beats* and the second to the *Timbre* of sounds. On the question of beats, considerable discussion had taken place as to whether they formed independent tones if they were sufficiently rapid. Different authorities had come to different conclusions on the subject, the disagreement probably arising from the impure tones used in these investigations. Dr. Kœnig, however, had succeeded in making tuning-forks whose sounds are very nearly pure tones, and, by the aid of such forks, had conclusively answered the question in the affirmative. Before proceeding to show experimentally the truth of the conclusions arrived at, Dr. Thompson said it was necessary to define exactly the meaning of the term "harmonics." By this he meant tones whose frequencies are *true integral multiples* of their fundamental. This, he said, might seem to be identical with the "upper partial tones" of Helmholtz or the "overtones" of Tyndall; but such was not the case, as the upper partial tones of piano wires, &c., are not true integral multiples of the fundamentals, for the rigidity of the wire comes into play and prevents the sub-division being exact.

According to Helmholtz's theory, two tones harmonise when they do not produce beats of sufficient slowness to grate upon the ear, and the frequency of the two sets of beats were supposed to be equal to the difference and the sum of the frequencies of the two fundamental tones. In investigating the subject, Kœnig finds it necessary to distinguish between primary and secondary beats, and also

that primary beats belong to two categories. These categories he calls inferior and superior respectively, and the frequencies of the two sets correspond respectively to the positive and negative remainders obtained by dividing the number representing the number of vibrations in the tone of lowest pitch into the corresponding number for the higher tone. For example, two forks of 100 and 492 vibrations produce beats having 92 and 8 as their vibration frequencies for—

$$492 = 100 \times 4 + 92$$

$$\text{and also } 492 = 100 \times 5 - 8$$

A set of "superior" beats of 8 per second and an inferior beat tone of 92 per second may be heard when two such forks are sounded together. These primary beats or beat tones act as independent tones, and produce secondary beats. Tertiary ones may also be obtained.

To demonstrate the existence of beats to the large audiences assembled, Dr. Kœnig had provided two large tuning-forks with resonators about four feet long. One of the forks gave 64 vibrations per second and the other 128, but the latter had sliding weights whereby its frequency could be made anything between 128 and 64. Adjusting the weights so as to give 72, and bowing both forks, the beats of about 8 per second were distinctly heard at the extremity of the room. By varying the weights so that the fork gave 80, $85\frac{1}{2}$, 96, $106\frac{2}{3}$, 112, 120, and 128 vibrations successively, beats of various frequencies were produced, and it was remarkable to note that tones of 64 and 120 produced 8 beats a second, exactly like 64 and 72. When the forks made 64 and 96 vibrations, *i.e.*, at an interval of a fifth, then the inferior and superior beats agree in frequency, *viz.*, 32, and by careful observation a low tone of about this pitch can be heard. If the tones sounded simultaneously differ by more than an octave, the same law for the number of beats holds good, whilst Helmholtz's difference and summation tone law is inapplicable. This was shown by sounding a fork and its double octave slightly mistuned by weighting; slow beats were quite evident, although the difference in the frequencies of the primary notes was large. Similarly, forks vibrating approximately at rates in the proportions 1 : 5 and 1 : 6 gave slow beats.

Coming to the main question, as to whether beats, when sufficiently rapid, blend into tones, just as primary shocks do, Dr. Thompson briefly recalled the various arguments for and against such an effect; and then Dr. Kœnig proceeded to experimentally prove the affirmative. Taking two forks, tuned to 2048 and 2304 vibrations respectively (ratio 8 : 9), and sounding them simultaneously, the middle C of the piano (256) was distinctly heard. The same beat tone resulted from forks having frequencies in the ratio of 8 : 15, whose negative remainder was 256. Various other tones were sounded simultaneously in pairs, and in all cases the corresponding beat tone was quite distinct. In these experiments the existence of nodes and loops in the air was distinctly noticeable, for as Dr. Kœnig turned the tuning forks in his hand the intensity of the beat tones heard at a particular spot varied enormously. The experiments were carried a step further by impressing vibrations of different frequencies on one and the same body; the beat tones in this case were quite perceptible. In carrying this out Dr. Kœnig had constructed steel bars of approximately rectangular section, whose periods of vibration were different in two directions at right angles: striking one face of the bar a certain note resulted, whilst a blow on an adjacent face produced a different one. When the bar was struck on the edge adjoining the two faces both of the notes could be heard as well as the beat tone produced therefrom. The experimenter had gone still further and made such bars so short that neither of the fundamental notes are within the limits of audition, but the resulting beat tones can be heard quite distinctly. In all cases, the frequency of the beats agree with that calculated from Dr. Kœnig's formula, and secondary beats follow the same law.

It was then pointed out that not only beats, but the maxima of a series of pulsations varying in intensity will, if isochronous and sufficiently rapid, give tones just as a series of primary shocks do. This was illustrated by tuning forks and by directing a stream of air issuing from a slit against a notched rim of a rotating disc. A further modification was given by a modified disc siren; in this the holes, instead of being of the same size all round a circle, increase to a maximum and then decrease again, there being several sets of such holes in one circumference. When this was put in operation, notes corresponding in pitch to the number of holes, and also to the number of sets of holes, could be heard. A wave siren was also used to illustrate the same facts. The matter was further illustrated by moving a tuning fork towards a wall or other reflecting surface at various velocities. According to Doppler's principle, as the fork recedes from the observer and approaches the wall the frequency of the direct waves is less and that of the reflected waves greater than that of the fork, and these two series of waves produce beats. By sufficiently increasing the velocity and using a fork of high pitch, the beats blend into tones.

Coming to the second half of Dr. Kœnig's researches, Dr. Thompson said that Helmholtz contended that the "timbre" of musical sounds was not affected by differences of phase amongst the component tones; on this point, however, Kœnig had come to the opposite conclusion. To illustrate graphically why phase should affect timbre, a number of diagrams were exhibited, some showing the resultant wave form produced by combining a tone with its harmonics of equal intensity, when the differences of phase between them were 0, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ respectively, while others represented the wave-forms when the harmonics and the fundamental were of different intensities. The effect of phase on the shape of the wave-form was very marked. The subject was treated experimentally by means of a wave-form against which a stream of air issuing from a slit could be directed. By inclining the slit to one side of the radius or the other, the phases of the component waves could be altered, and this had a marked effect on the character of the sound produced. Illustrations of Kœnig's multiple wave-sirens, both of the cylinder and disc forms, were next shown, and the results of investigations made with the apparatus described. From these results it appears to be impossible to produce the timbre of instruments such as trumpets, clarionets, &c., by any combination of a tone and its pure harmonics. This led to the investigation of impure harmonics. By plotting and combining curves it was shown that the wave-form obtained from a tone and impure harmonics changes in successive periods, and this peculiarity was observed to exist in a record taken from a vibrating string. Various discs with wavy edges of different forms were spun before an air slit, and the varying character of the resulting sounds as the slit was turned, demonstrated.

Before concluding, Dr. Thompson remarked the word "timbre" required to be re-defined, for the rigidity of strings, wires, &c., and the interference of the wood and metal parts of organ pipes and other wind instruments generally, prevent the formation of pure harmonics. A model, consisting of vibrating strips placed vertically or inclined, was exhibited to show the different kinds of timbre. The difference between mixtures and compounds of tones was pointed out, and the inability of the ear to distinguish between pure and impure sounds referred to.

Lord RAYLEIGH thought more information was required on the important subjects brought forward, and asked in what class of musical sounds are the overtones strictly harmonious. He could admit that in piano wires they may not be so, but he was not quite so clear about organ pipes. He said he was filled with admiration with the perfection of the apparatus displayed, and expressed a wish that such mechanical acousticians could be found on this side of the channel.

Mr. BOSANQUET said he had been carefully over the

ground investigated by Dr. Koenig. He believed Dr. Koenig was the first to get at the facts concerning beats, but it was difficult to admit all that had been said about them. However, the chief difference between authorities seemed to be one of language. Owing to the lateness of the hour he could not discuss the question fully, and so asked to be allowed to reserve his opinion on the matter. As regards "timbre" he thought the experiments on the effects of phase were not conclusive. The sounds of wind instruments, such as trumpets, he said, depended greatly on who produced them. It was no easy matter to bring out their full sweetness, and it was comparatively few persons who could ever attain perfection. He ventured to think that in a properly used instrument none of the harmonics are out of tune.

Mr. BLAICKLEY agreed with Lord Rayleigh about piano wires, and, as regards wind instruments, he would hardly think that the overtones were so inharmonious as Dr. Thompson would have him believe. In fact, Mr. Stroh had obtained wave-forms for him from various instruments, but in none of them was there any discontinuity such as shown on one of the diagrams exhibited. However, he was of opinion that there is something in "timbre" not accounted for by the ordinary theory.

The PRESIDENT said that in view of the production of audible sounds by the beats from notes beyond the range of audition, it might be possible to demonstrate that insects produce sounds inaudible to the human ear by putting several together in a box and listening for beat tones.

Dr. KÖENIG acknowledged the most cordial vote of thanks accorded to himself and Dr. Thompson.

CORRESPONDENCE.

TAR ACID IN VINEGAR.

To the Editor of the Chemical News.

SIR,—A few days back a sample of malt vinegar was submitted to me for examination. Analysis gave the following results per cent:—

Solid matter	1.20
Acetic acid	4.46
Ash	0.14
Sp. gr.	1.0119

No free sulphuric acid—no injurious metals. These results are in fair accordance with those of a genuine malt vinegar, and I felt justified in regarding it as such.

Out of curiosity, and luckily, I tasted the vinegar, and noticed after a time, when the pungent taste of the acetic acid had disappeared, a lingering flavour strongly resembling tar acid. On distilling I then obtained a distillate which readily yielded tribromocresol with bromine-water. The iron reaction was not distinct, nor could the smell of tar acid be detected, probably on account of the presence of acetic acid. I do not remember reading anywhere of vinegar containing such a foreign substance as cresolic acid, and it is just a question whether, in the present case, its existence was accidental or purposed. The probability of it being overlooked, when present in small quantity, in carrying out the ordinary analysis of vinegar, renders it, I venture to think, worthy of the notice of your numerous readers.—I am, &c.,

S. ARCHD. VASEY.

Chandos Street, London, W.C.,
May 20, 1890.

Action of Sulphuric Acid upon Tribromo-phenol.—M. Georgesco.—The author finds, in opposition to Hertzig, that sulphuric acid does not destroy tribromo-phenol, but transforms all the bromo-derivative into franceins.—*Bull. de la Soc. Chim. de Paris*, Vol. iii., No. 4.

NOTICES OF BOOKS.

The Chemistry of Paints and Painting. By A. H. CHURCH, M.A., F.R.S., Professor of Chemistry in the Royal Academy of Arts in London. London: Seeley and Co., Limited.

WE have much pleasure in welcoming a work on this subject from the pen of a distinguished chemist, who has made it his special study.

Our first emotion on examining Prof. Church's treatise was surprise at finding some of the colours recognised by the dyer and tissue-printer as "fast," such as indigo and madder, here regarded as untrustworthy. But it must be admitted that the conditions in the two cases are totally different. A tinctorial masterpiece is exposed to the light, perhaps for a few days or weeks. At the end of that time the pattern or the shade or the garment goes "out of fashion," and whether the colour has proved permanent or not no one cares to inquire. The works of the artist are much more severely tested. They are exposed to light continuously, perhaps, for half a century, and if their colours are not absolutely permanent they cease to be "things of beauty," and become rather an eye-sore than "a joy for ever."

The author, in his strictness, is guided not merely by theoretical considerations or even by prolonged experiments, but by the careful study of the changes which have taken place in pictures by the most eminent masters. Hence the advice which he gives should be taken to heart by every artist who aims at something more than transitory effects. Thus he says:—"Beautiful and rich as are the colours prepared from cochineal, not one of them should ever find place upon the palette of the artist. They all become brownish, and ultimately almost disappear after a short exposure to sunlight. Ultimately, a greenish grey or a faint sepia-like brown is the sole residue." The madder-colours are said to be "much less affected by light than are the pigments from cochineal, yet it cannot be affirmed that any of them are absolutely permanent when continuously exposed."

Indigo is "unfortunately gradually oxidised and browned when exposed to light." Hence Prof. Church does not recommend it, and suggests that it may be advantageously replaced by ultramarine or by a good prussian blue, either being associated with a little ivory black.

Guignet's green, otherwise known as vividian, is pronounced to be in every respect a safe pigment. Unfortunately, it is sold in France under the name of "vert émeraude," one of the synonyms of Schweinfurt green, and, what is still worse, vile mixtures of chrome yellow and prussian blue are sometimes sold in its place.

Among yellows, cadmium sulphide, when genuine and properly prepared, seems to take the first rank. Vanadium yellow, though in every other respect admirable, loses its beauty if exposed to light for a few hours only.

Among whites must be noticed a curious novelty—lead sulphate prepared by a special process. It is said to be less readily acted upon by sulphuretted hydrogen than is ordinary white lead. Zinc white (sulphide) is objected to from its injurious action upon many other colours.

It is quite natural that the vermilion heightened by an admixture of eosine, geranium red (mercuric iodide), and the aniline lakes should be excluded. But we regret that there is no mention of "mineral lake," a stannic chromate, described by Gentele as very similar in its colour to rose madder, whilst perfectly fast.

It is interesting to find that certain choice madder-pigments for artists have still to be prepared from the plant in preference to artificial alizarin. Were this not the case the cultivation of *Rubia tinctorum* would be "wholly extinguished."

Among the most important features of this work is a selection—or rather several selections—of pigments

which may be regarded as, under ordinary circumstances, fully permanent. The work concludes with a notice of a long and somewhat acrimonious discussion on the stability of water-colour drawings, which raged in 1886 in the *Times* and in several other papers.

Artists and lovers of art will the better appreciate Prof. Church's book if they reflect that its chief rival is a treatise in which vermilion is described as a "sulphide of arsenic," and in which, when testing for lead in cadmium red, the operator is advised first to add white lead to the sample. It is to be regretted that the modern rage for apparent cheapness will oppose a barrier to the selection of suitable pigments and the elimination of such as are untrustworthy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 19, May 12, 1890.

Iridium and Phosphorus Double Chloride.—H. Geissenheimer.—The author uses as his material the hydrated dioxide. He heats 1 grm. of this hydrate for thirty hours in a sealed tube with 10 grms. phosphorus perchloride and 15 grms. of phosphorus trichloride. He obtains light yellow crystals of the formula $\text{Ir}_2\text{P}_3\text{Cl}_{15}$, which, if kept for half an hour between 70° and 80° , are converted into $\text{Ir}_2\text{Cl}_3 \cdot 2\text{PCl}_3$. At temperatures between 120 and 125 the product is $\text{Ir}_2\text{Cl}_{13} \cdot 3\text{PCl}_3$. If the temperature is gradually raised to 190° , the chloride becomes brick-red, and corresponds to the formula $\text{Ir}_3\text{Cl}_{13} \cdot 3\text{PCl}_3$.

A New Characteristic Reaction of Hydrogen Peroxide.—G. Denigès.—An aqueous solution of ammonium molybdate (10 per cent) to which an equal volume of concentrated sulphuric acid is added gives, on the addition of a few drops of oxygenated water, an intense yellow colouration resembling that of the alkaline dichromates. It enables us to detect 1-10th m.grm. of hydrogen peroxide.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 4.

Researches on the Sulphines.—G. Patein.—The author has obtained four double cyanides of sulphines and silver, which he here describes.

New Chemical Properties of the Alcoholic Extract of Beer Yeast.—J. de Rey-Pailhade.—The author, on stirring up beer-yeast, previously washed and pressed, in an equal weight of alcohol at 86° , and filtering, obtains a liquid of a light yellow colour, clear, and having a slightly acid reaction. This liquid he names *philothion*. If shaken up with washed sulphur or with ether saturated with sulphur it gives off sulphuretted hydrogen. One litre of the liquid recently prepared yields about 10 m.grms. of H_2S . The alcoholic extract of yeast, if exposed to the air for a few days, loses this property of combining with or taking up sulphur.

Speed of Dissolution of Certain Mineral Carbonates in Acids.—W. Spring.—All the carbonates tried (arragonite, witherite, cerusite, azurite, dolomite, smithsonite, and malachite) dissolve with equal speed in hydrochloric and nitric acids. The rate of solution is independent of the chemical nature of the inorganic monobasic acids, or the rate of solution is a constant magnitude for each species of carbonate. The phenomenon depends on physical and not chemical factors. The rate of solution increases rapidly with the temperature, but in an un-

equal manner in different carbonates. Hence a comparison of the rates of solution of the carbonates at given temperatures cannot yield any result of a general scientific value.

Rate of the Solution of Iceland Spar in Hydrochloric Acid.—W. Spring.—The rate of the solution of spar in an acid does not merely depend on the chemical nature of the mineral, but is also a simple function of the elasticity, and varies with the temperature according to an exponential.

Action of Fuming Nitric Acid upon Hexachloric Benzene.—M. Istrati.—The author has succeeded in causing nitric acid to act upon hexachlorobenzene. He concludes that chlorine, though intimately connected to the molecule, may be partially expelled by nitric acid and replaced by oxygen. During the attack there is produced a gaseous mixture of nitrous vapours, and probably carbon dioxide, free oxygen, and nitrogen.

Transformation of Paradichlorobenzene into its Meta-Isomer.—M. Istrati.—Not suitable for useful abstraction.

New Method for the Preparation of Non-saturated Acids of the Aromatic Series.—L. Edeleano and M. Budishteano.—The authors have sought to combine the methods of Bertagnini and of Perkin. They heated benzoic aldehyd with acetyl chloride in the proportion of 1 mol. with 3 mols. sodium acetate, heating for twenty-four hours to 160° in a flask with an ascending condenser.

Melting and Solidification-Points of Certain Fatty Bodies and of their Mixtures.—A. Terreil.—The author's results are given in the form of tables.

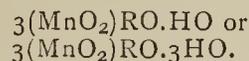
The Refractive Molecular Powers of Salts in Solution.—E. Doumer.—Already noticed.

On Azocumyl Chloride.—P. Alexeyeff.—The chlorides of the azo-acids give us not merely a means of preparing their derivatives, but also of purifying the azo-acids and of establishing their molecular weights.

Vol. iii., No. 5.

Physiological Action of Selenious Acid.—C. Chabrié and L. Lopicque.—A dose of selenious acid a little above two-thousandths is needed to hinder the fermentation of meat-broth under the action of the ordinary microbes of the air. With smaller proportions fermentation is set up and the selenious acid is reduced. Sulphites injected into the blood of an animal are converted into sulphates, which has no poisonous action. The selenites are not oxidised under similar conditions. In the higher animals selenious acid has a very considerable poisonous action. Dogs die when they have received 3 m.grms. of neutral sodium selenite per kilo. of their weight. There is intense congestion of all the viscera. The heart is arrested in systole.

Natural Manganese Oxides. Psilomelanes and Wads.—A. Gorgeu.—Among the minerals known as "wads," some affect a crystalline form, and there is no warrant for considering them as alteration-products. They are true acid hydrated manganites answering to the formulæ:—



Researches on Dispersion in the Aromatic Compounds.—Ph. Barb'ér and L. Roux.—This paper requires the accompanying diagram and tables.

Vol. iii., No. 6.

Determination of Total Nitrogen in Manures.—E. Aubin and J. Quenot.—This paper will be inserted in full.

The Synthesis of Ethyl α - β -Diacetylpropionate.—Iw. Ossipoff.—The author has obtained this product by setting out from sodium ethyl acetyl acetate, which is treated with monochloro acetone.

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

Recent Progress of the Electro-Metallurgy of Aluminium and the Influence of this Metal upon Siderurgic Products.—R. van Langenhove.—The author calls attention to the extraordinary fact that when aluminium is once deoxidised it becomes difficultly oxidisable, even at the highest temperatures. He concludes that in forming ferro-aluminium alloys only small proportions of the latter metal should be introduced. Aluminium acts upon iron in the same manner as carbon, increasing its hardness and tenacity at the expense of ductility. In augmenting fluidity and ensuring the absence of blowholes its action is similar to that of silicon. Phosphorus, like silicon and copper, occasions more or less serious perturbations in castings containing aluminium.

Vol. viii., No. 3.

Resistance of Aluminium-Bronze and Brass.—M. Tetmayer.—As the proportion of aluminium rises from 5.5 to 11.5 per cent in bronzes, the resistance to rupture per m.m. rises from 44 to 80 kilos. In the case of brass, as the percentage of aluminium increases from 1 to 4 per cent the resistance rises from 40 to 69 kilos. per m.m.

Vol. ix., No. 1.

Chemical Industry at the Paris Exhibition of 1889.—Jean Kruitweg.—The author expresses his regret at the "indifference" of Switzerland and Britain and the "abstention" of Germany. He, consequently, in estimating the progress of the chemical arts, recognises merely what was to be seen in Champ-de-Mars.

Preliminary Study on a Bridge over the Straits of Dover.—MM. Schneider and Hersent.—The total cost of this gigantic undertaking—which is not open to the grave objections existing against the proposed tunnel—is estimated at 860 million francs.

Fractionation of Simple Bodies.—An abridgment of the Presidential Address of Mr. Crookes, delivered before the Chemical Society in March, 1889.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. v., No. 51.

This issue contains no chemical matter.

MEETINGS FOR THE WEEK.

- MONDAY, June 2nd.—Society of Chemical Industry, 8. "Some Considerations on the Chemistry of Hypochlorite Bleaching," by Messrs. Cross and Bevan.
Royal Institution, 5. General Monthly Meeting.
- TUESDAY, 3rd.—Royal Institution, 3. "The Natural History of Society," by Andrew Lang.
Institute of Civil Engineers, 8. (Anniversary).
- WEDNESDAY, 4th.—Geological, 8.
- THURSDAY, 5th.—Royal Institution, 3. "Flame and Explosives," by Prof. Dewar, M.A., F.R.S.
Chemical, 8. "Note on the Preparation of Pure Crystalline Copper," by C. C. Duncan.
Royal, 4 30.
- FRIDAY, 6th.—Royal Institution 9. "The Search for Coal in the South of England," by Prof. W. Boyd Dawkins, M.A., F.R.S.
Physical, 8. "The Effect of Change of Temperature on the Villari Critical Point of Iron," by Herbert Tomlinson, F.R.S. "The Diurnal Variation of the Magnet at Kew," by W. G. Robson and S. W. Smith.
Geologists' Association, 8.
- SATURDAY, 7th.—Royal Institution, 3. "The Ballad Music of the West of England" (with musical illustrations), by Rev. S. Baring-Gould, M.A.

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THE CHEMICAL NEWS.

Vol. LXI. No. 1593.

NOTES ON VALENCY, BASICITY, COMPLEX ACIDS, AND CHEMICAL NOTATION.

By T. STERRY HUNT.

1. IN the now obsolescent electro-chemical hypothesis of Berzelius certain chemical relations between different elements or their oxygen or sulphur compounds were distinguished by the terms electro-negative and electro-positive, or by the corresponding signs of *minus* and *plus* ($- +$). As synonymous with these the names of acidic and basic or basylous, or of chlorous and zincous, have been employed. While none of these terms are free from objections, we may perhaps employ the words negative and positive (without the Berzelian prefix), while occasionally making use of acidic and basylous as synonymous with them when speaking of oxidised compounds.

2. When, in accordance with the discovery of Newlands, the chemical elements are arranged in successive series according to their equivalent weights and their valency, and when, moreover, as shown by Mendeleeff in his table of the periodic law, the even and the odd series of the first seven groups are each divided into two sub-groups, it is very apparent, as pointed out by the latter chemist, that the elements in most of the odd series of these seven groups are more markedly negative than those of the corresponding even series. If we except the second series, which is anomalous in other respects, we note evidences of this predominance of negative relations in the odd sub-groups of VIII.*b* in ClBrI, of VI.*b* in S Se Te of V.*b* in P As Sb, of IV.*b* in Si Ge Sn Pb, and of III.*b* in Al Ga In.

Farther inspection, moreover, shows that in passing from the second series, in which the relations of negative and positive between the two sub-groups are, as it were, confounded, a loss of negative and a gain of positive characters appears as we proceed to higher series. Thus, in II.*a* the comparatively feeble positive relations of the oxide of Be led Berzelius and others after him to regard it as a sesquioxide nearly related to alumina. It is, however, clearly a diad oxide, and is followed by those of Ca Sr Ba with increasing equivalent weights and augmented positive characters. Again, in II.*b* the action of heat on the hydrous chlorides of Mg and Zn shows these elements to be less positive than Cd, while the strongly basylous HgO not only decomposes a solution of ZnCl, but separates potassium hydroxide from a solution of KI to form a double potassio-mercuric iodide. In III.*a* the negative B is followed by the positive Sc, and by Tl La and Yb, which are strongly basylous. In III.*b* Al₂O₃ is at once negative to oxides of groups I. and II., with which it forms compounds known as aluminates, and positive to the strongly negative or acidic oxides of groups V., VI., and VII., forming with them salts which, when soluble, are not very stable. The basylous or positive character augments progressively in Ga and In. In IV.*a* the strongly negative character, seen in CO₂, is less marked in TiO₂, and ZrO₂, while negative to many oxides, sustains to others positive relations, playing the part of a salifiable base. The positive character is still more marked in CeO₂, while ThO₂ is strongly basylous, its hydroxide, like those of Tl La Ba Ca and Cd, absorbing carbonic dioxide from the atmosphere. In V.*b*, where negative characters are strongly marked in the triad and pentad oxides of P and As, the triad oxide of Sb is feebly and that of Bi is strongly basylous. While in VI.*a* the hexad oxides of Cr, Mo, and W are more or less

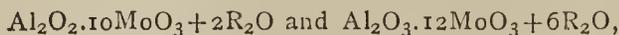
strongly negative, that of U is positive. The negative energies of VI.*b* and VII.*b* progressively diminish with the increased equivalent weight, and in the former sub-group FeO₂ is already feebly basylous, uniting like Al₂O₃ both with positive and with negative oxides. Too little is yet known to permit similar comparisons in VIII., and I may perhaps offer exceptions, but for all the other groups it may be said that the positive or basylous energy varies directly and the negative or acidic energy inversely as the equivalent weight of the element.

3. Half a century since, when the doctrine of valency was unknown, all basylous oxides were divided into protoxides (or suboxides) on the one hand and sesquioxides on the other. At that time Ga, In, and Tl were undiscovered, and the sesquioxides were chiefly represented to the chemist by alumina and the corresponding oxides of Cr, Mn, and Fe, to which might be added the rare oxides of Bi and U, and also that of Be erroneously reckoned in the same category. Certain chemical analogies led Berzelius, to whom we owe our first accurate knowledge of zirconia, to regard it also as a sesquioxide, Zr₂O₃, and this view was henceforth generally accepted by chemists (with the exception of Gmelin, who wrote it ZrO), until the determination of the vapour-density of the volatile zirconia chloride showed that zirconia, like silica (which Berzelius made SiO₃), was to be regarded as a tetrad oxide, ZrO₂. In those days also Sc and Yb were yet unknown, and Y and La, together with the corresponding oxides of Ce and Di, were universally regarded as protoxides. Hence alumina, with the so-called peroxides of chromium, manganese, and iron, which replace it in alums (together with the rare beryllic and zirconic oxides), became to chemists the type of sesquioxides. The contrast between these and other basylous oxides was such as to influence strongly the chemical classification of natural silicates, into so many of which alumina enters. It was in accordance with these views, further impressed upon chemical mineralogy by the authority of Rammelsberg, that the writer attempted, in 1885, the division of all such silicates into three parts:—(1) protosilicates or non-aluminous silicates, like chrysolite; (2) protopersilicates or silicates of alumina, and protoxides like orthoclase; (3) persilicates or silicates of alumina without protoxides. At the same time the sesquioxides of Cr, Mn, and Fe were rightly and zirconic oxide wrongly regarded as in certain cases more or less completely replacing alumina. The oxide of beryllium was, however, reckoned as a protoxide.

Apart from the erroneous position thus assigned to zirconia, the fallacy underlying this time-honoured distinction between protoxides and sesquioxides will be apparent when it is considered that it is not the sesquioxide or triad character of alumina which determines its relations in these silicates, and in other combinations, but its position intermediate between negative and positive triad oxides, which makes it acidic to monad and diad basylous oxides, on the one hand, and basylous to the more strongly negative oxides on the other. Alumina is positive to the negative pentad and hexad oxides, but its relations to SiO₂ demand further and special consideration.

4. Those silicates in which alumina occurs, together with other and more distinctly basylous oxides, are, in accordance with known chemical analogies, to be regarded as salts of a composite aluminosilicic acid, belonging to the class designated as "compound inorganic acids" by Wolcott Gibbs, whose generalisations on the subject constitute a most important contribution to theoretical chemistry. These composite mineral acids may be defined as combinations of two or more negative or acidic oxides, often of different groups, frequently attaining very high equivalent weights, and often of comparatively small saturating power. For the purposes of illustration it may be well to note some of these acids and their salts, in which we shall follow the notation adopted for them by Gibbs. The borotungstates of Klein are represented

respectively by $B_2O_3 \cdot 7WO_3 + 2R_2O$, $B_2O_3 \cdot 9WO_3 + 2R_2O$, $B_2O_3 \cdot 12WO_3 + 4R_2O$, and $B_2O_3 \cdot 14WO_3 + 3R_2O$. In the complex molybdates described by Struve and by Parmentier are two aluminomolybdates,—



besides corresponding chromic and ferric compounds and a manganomolybdate, $Mn_2O_3 \cdot 16MoO_3 + 5R_2O \cdot H_2O$. These same sesquioxides may also, according to Gibbs, unite at the same time both with phosphoric and molybdic oxides to form still more complex bodies. We have, moreover, silicotungstates, phosphotungstates, vanadotungstates, arsenotungstates, antimoniotungstates, and even stannophosphomolybdates and stannophosphotungstates of various degrees of complexity in which the negative or acidic member is made up of tetrad, pentad, and hexad oxides united. Besides the tetrad oxides SiO_2 and TiO_2 , other tetrad forms, as VO_2 , MoO_2 , and WO_2 , and moreover, in addition to the pentad oxides named, triad oxides of P and As. Portions of the oxygen in molybdic and tungstic hexad oxides may be replaced by fluorine, while hydrocarbon radicles like ethyl, methyl, and phenyl appear also to be capable of entering into these compounds. In the case of the silico-tungstates of Marignac, two types are known in which SiO_2 is united respectively with $10WO_3$ and $12WO_3$, while in the phosphotungstates, according to Gibbs, we have a homologous series, the extreme terms of which, so far as known, are $P_2O_5 \cdot 6WO_3 + 6H_2O$ and $P_2O_5 \cdot 24WO_3 + 6H_2O$, the common difference being $2WO_3$. As example of still greater complexity he gives us as the formula of a phosphotungstate—



All of the above described salts are soluble and crystallisable, while the anhydrous, dense, insoluble, and quasi-metallic tungsten-bronzes are regarded as salts of analogous constitution.*

The consideration of these salts of complex mineral acids will help us to understand better the problems presented by the native silicates, and their relations to boric and aluminic oxides on the one hand and to TiO_2 , the various pentad and hexad oxides, and fluorine and chlorine on the other. The analogies of the borotungstates and the aluminotungstates lead us to admit the existence of borosilicates, boraluminosilicates, and aluminosilicates in which the oxides of boron, aluminum, and silicon alike play the part of negative or acidic elements. The importance of clearly defining these relations is rendered more evident by the fact that over one-half of all the native silicates known to mineralogy (without counting the small number of simple aluminous silicates, hydrous and anhydrous) contain alumina together with some more distinctly basylous oxide. The sesquioxides of Cr, Mn, and Fe (and even of Ti) may occasionally replace alumina, not in virtue of their triad constitution, but because of their relatively negative characters, which bring them near to it chemically. It will be found that the markedly basylous triad oxide, like those of Y, La, Ce, and Di, do not replace Al_2O_3 , but, on the contrary, take the place of diad oxides.

5. Among native oxidised aluminous species, besides the compounds of alumina with pentad and hexad oxides, may be distinguished:—(1) *Aluminates*, including non-silicated compounds of negative alumina with other more basylous oxides; (2) *Aluminosilicates* in which a complex aluminosilicic acid is combined with one or more basylous or positive oxides; (3) Simple silicates of alumina into which Al_2O_3 may be supposed to enter, as in its phosphates and sulphates, as a positive or basylous element, but which it may also be permitted to regard as generated by the more or less complete elimination of H_2O from normal aluminosilicic hydrates, which are thereby at last converted into anhydride of these complex acids.

* Gibbs, *Amer. Chem. Journal*, vii., 392–417; also Hunt, "Mineral Physiology, &c.," pp. 386–389.

An examination alike of the variations in the relative proportions of alumina and silica, and in the basicity of the native aluminosilicates soon suffices to show that a great multiplication of formulæ would be necessary to include all the known types, and furthermore, that attempts to unite them with Al_2O_3 and SiO_2 would make their notation inconveniently cumbersome. While the constitution of these aluminosilicates is probably as complex as that of any of the borotungstates, aluminomolybdates, silicotungstates, phosphomolybdates, and phosphotungstates already noticed, it has long seemed desirable to the writer to devise for these silicates and for mineral species in general a notation as near as may be monadic, and one in which the valencies alike of negative and positive elements should be made apparent. These ends it is sought to attain by employing for all monads and diads the ordinary chemical symbols in small ordinary roman letters; for all triads and for the hexad uranic oxide, small italic letters; and for all tetrads, small black-faced roman letters. Those elements which yield basylous oxides at once monad and diad or triad, are distinguished in their monad forms by duplicating the initial letter, as *ccu*, *hhg*, *aau*, *ttl*. The equivalent weight of diads is divided by 2, that of triads by 3, and that of tetrads by 4, to correspond in each case with monadic oxygen = $O \div 2 = o = 8$, and with monadic fluorine = $f = 19$. For the pentad and hexad negative oxides, however, we employ diad symbols, conjoined, however, with monad oxygen. The symbols of the elements are in all cases followed by the coefficient, even though this should be unity.

In illustration of this system as applied to certain well-known aluminosilicates, we give the ordinary and the monadic notations side by side.

Anorthite ..	$Al_2O_3 \cdot 2SiO_2 + MO$	$= al_3o_3si_4\ 04 \cdot m_1o_1$
Leucite ..	$Al_2O_3 \cdot 4SiO_2 + MO$	$= al_3o_3si_8\ 08 \cdot m_1o_1$
Albite ..	$Al_2O_3 \cdot 6SiO_2 + MO$	$= al_3o_3si_{12}o_{12} \cdot m_1o_1$
Meionite ..	$3Al_2O_3 \cdot 6SiO_2 + 4MO$	$= al_9o_9si_{12}o_{12} \cdot m_4o_4$
Garnet ..	$Al_2O_3 \cdot 3SiO_2 + 3MO$	$= al_3o_3si_6\ 06 \cdot m_3o_3$
Zoieite ..	$4Al_2O_3 \cdot 9SiO_2 + 6MO$	$= al_2o_2si_3\ 03 \cdot m_1o_1$

These monadic formulæ may be further condensed by uniting in one term the oxygen of the different oxides. Albite will then become $al_3si_{12}m_1o_{16}$, and meionite $al_9si_{12}m_4o_{25}$. In this notation andalusite and cyanite are $al_3si_2o_5$, and topaz $al_3si_2(o_4f_1)$.* The new formulæ, in which $m = a$ monadic portion of a monad or a diad base, corresponding to 8 parts of oxygen, will suffice to show the simplicity of the monadic notation here proposed, which gives at once the oxygen ratios, and distinguishes between the monads and diads on the one hand and the triads and the tetrads on the other. The numerical value calculated for the formula ($o_1 = 8$) divided by the sum of the oxygen coefficients gives the mean value = p of the oxide unit, which, in its turn divided by the specific gravity = d (water being unity) gives the reciprocal of the coefficient of condensation of the species = N . This datum enables us to compare different species as to their relative condensation, upon which, as we have elsewhere shown, their hardness and their chemical indifference depend.

New York, April 27, 1890.

ON THE PRESENT CONDITION OF THE PHILADELPHIA WATER SUPPLY.†

By SAMUEL C. HOOKER.

SINCE my third report was presented to this Section a great deal of space has been devoted in the daily papers

* Such a notation, with the exception of the use of unlike kinds of letters for diads, triads, and tetrads, was employed by the writer in 1885 in his essay on "The Classification of Silicates, Mineral Physiology, &c.," pp. 320–370.

† *Proceedings of the Chemical Section of the Franklin Institute*, May, 1890.

to the discussion of our water supply, and while one cannot but regret that much has been said which is both exaggerated and untrue, it is a matter for congratulation that the subject has once again been brought prominently before the public.

During a large portion of last summer, the water supplied to all parts of the city, without exception, was almost uninterruptedly muddy. Under these circumstances it is scarcely to be wondered that there should have been a disposition to make the worst of a condition of affairs certainly bad enough without the least exaggeration. It is too much to expect that the newspaper should possess in all or even in most cases the necessary knowledge to discriminate between facts which have and others which have no weight, between arguments and opinions which are or are not entitled to consideration, and the result has been that an immense amount of misleading information, a vast number of positively incorrect and worse than valueless statements have been distributed broadcast to the public. Facts have been dwelt upon which have no weight, self-constituted authorities have been quoted whose statements have been remarkable for their inaccuracy, positively ridiculous for their scientific absurdity.

While, however, there has been unquestionable exaggeration in the arguments used against the water, there has also been a deplorable exhibition of bias and misinformation, and a positive disinclination to admit facts on the part of certain gentlemen, who appear to regard the present condition of our water supply as all that can be desired.

For three months, after the publication of my third report, I continued the laborious investigation, the early results of which have been already communicated to you. The publication of the numerous analyses has, however, been purposely delayed, because it was thought probable that they would be more fairly and impartially considered after the excitement created by the newspaper agitation had subsided. My analyses did not justify me in speaking as badly of the water as several of the newspapers were able to do, and any less vehement protest against its condition would have failed at that time to have attracted the attention which I hope will now be given to this paper.

In the following Table will be found, as the condensed result of my investigation, average figures for the water collected at different parts of the city during six months of last year:—

Samples collected March to September, 1889.	Free Chlorine.	Albumenoid ammonia.	Nitrogen of nitrates.
West Philadelphia, Forty-fourth and Chestnut Streets (24 samples) ..	0'233	0'0015	0'0080
Sixteenth and Locust Streets (23 samples)	0'254	0'0014	0'0081
Twentieth Street and Columbia Avenue (23 samples)	0'266	0'0024	0'0097
Front and Bainbridge Streets (23 samples)	0'265	0'0013	0'0076
Average of 93 city samples	0'254	0'0016	0'0083

For purposes of comparison several samples of water were taken from Schuylkill, at Phoenixville, in order that some idea might be formed of the extent of the pollution occurring within about 25 miles of the city. The samples from Phoenixville were furnished to me through the courtesy of the Water Department. For the other samples I am indebted to the kindness of several gentle-

men residing in the various neighbourhoods in which they were collected, who most cheerfully undertook the troublesome task of drawing the water for analysis at stated times.

Deferring for a moment the consideration of the Phoenixville samples, and judging the water by such standards as are universally adopted, when the history of the water examined is entirely unknown, we are compelled to acknowledge that the above analyses do not in any way condemn the water, but, on the contrary, we must admit that the chlorine, free and albumenoid ammonias, and the nitrates are present in quantities less than they are known to exist in many absolutely unpolluted waters.

By comparing the water at Phoenixville, however, with that supplied for city use, we are able to detect in the city water a slight increase in the quantity of the substances estimated, indicating that the sewage pollution, which we know exists, has occurred to an extent sufficient to appreciably influence the composition of the water.

The following Table gives the average results of analyses of five samples of water obtained from each of the points named at nearly corresponding dates:—

	Free Chlorine.	Albumenoid ammonia.	Nitrogen of nitrates.
Phoenixville (average of 5 samples)	0'196	0'0039	0'0079
West Philadelphia, Forty-fourth and Chestnut Streets (average of 5 samples)	0'227	0'0022	0'0101
Sixteenth and Locust Streets (average of 5 samples)	0'264	0'0017	0'0099
Twentieth Street and Columbia Avenue (average of 5 samples) ..	0'242	0'0027	0'0126
Front and Bainbridge Streets (average of 5 samples)	0'260	0'0012	0'0078

Passing on to the discussion of each of the impurities determined, we may at once dismiss the nitrates from consideration, as the quantities present in the various samples of water examined differed only slightly from each other. It will be observed that the chlorine in the water drawn at all points in the city is greater than that found in the samples from Phoenixville.

Similarly, the albumenoid ammonia in three out of the four localities in the city is distinctly greater than in corresponding samples from Phoenixville. With regard to the free ammonia a decrease in quantity is observed in the city water, but in spite of this, in view of the figures for albumenoid ammonia, we are compelled to regard the quantity of the organic substances discharged into the river after leaving Phoenixville as somewhat greater than the combined action of the natural processes of purification and the subsiding reservoirs has been able to dispose of. During the six months covered by my investigation these impurities were almost entirely mechanically suspended, and by a suitable system of filtration could have been readily removed, leaving the water remarkably free from organic matter.

That most of the organic substances reaching the city should be pumped from the river in an insoluble form is not, after all, extraordinary. A considerable proportion of the organic matter of sewage exists, of course, in solution, but as many varieties of waste from as many factories, &c., are discharged into the river, it is probable that these substances, by acting and reacting on each other, give rise to the formation of precipitates, which in some cases may consist essentially of organic matters formerly in solution, in others which may mechanically enclose them. However this may be, the fact remains

that the organic matter of the Schuylkill water, during the six months of last year that I investigated the subject, was almost and entirely in suspension and the condition of the water, deprived of its suspended matters, was entirely satisfactory, and often of a very high degree of purity.

Mud, whether wholesome or unwholesome, has obviously no place either in drinking water or in water to be used for household or industrial purposes, and to show, therefore, that the mud of the Schuylkill water is accompanied by precipitated organic matters derived from sewage, seems to me to add little to the many emphatic arguments which can be already urged with unquestionable force against its presence being tolerated. But, on the other hand, by showing that practically the entire amount of the substances which can be considered objectionable are present in suspension and can be readily removed, leaving a water of a high degree of purity, how strong an argument we have for carrying out such purification.

In order that Schuylkill water may be filtered satisfactorily on a large scale, it is necessary to use a so-called "coagulant," and whether this be alum or iron, it is probable that the result will be much the same. Economical and mechanical considerations will have to be carefully weighed in choosing between them. The beneficial action of both these substances depends upon the formation of precipitates, which, in the act of separation, entrap and enclose the microbes and suspended particles, so that they can be arrested during subsequent filtration through sand. If the filtration be attempted without the addition of the coagulant, the very minute particles to which the turbidity of the water is due pass through the interstices of the filter-bed unchecked, but by first entrapping them in the precipitates derived from the coagulant used, they are virtually increased in size and can be arrested by the sand bed.

There is so much prejudice against alum that it is desirable to discuss its use in the purification of water somewhat in detail. Alum is a double sulphate of aluminium and potassium, and contains a large proportion of water of crystallisation. Its percentage composition is as follows:—

Sulphate of aluminium	36.07
Sulphate of potash	18.35
Water of crystallisation	45.58
	100.00

The sulphate of aluminium is the active portion of the alum and may be substituted for it if desired.

As soon as the alum is added to the water the carbonates present in solution react with the sulphate of aluminium, becoming themselves converted into sulphates with the formation of unstable carbonate of aluminium. The latter gives off carbonic acid gas and alumina separates. It is evident, therefore, that the separation of the alumina is not attended by the formation of free sulphuric acid, as has been alleged. The addition of alum to the water slightly increases the quantity of sulphates present, and a small quantity of carbonate of lime is usually converted into sulphate of lime. The aluminium is entirely precipitated as alumina, and unless a considerable excess has been used, none whatever remains in solution.

I have dwelt upon the action of alum at so great a length (1) because I have been much impressed by the results which can be obtained by its use; (2) because it forms an essential feature of the American system of filtration; and (3) because I am convinced that the objections which have been urged against it are based upon an erroneous conception of its mode of action.

If it is the presence of microbes which is to be mainly feared in drinking-water, there can be, aside from boiling the water, no surer way of getting rid of them than by

the use of a coagulant. The efficiency of iron for this purpose has been amply demonstrated at Antwerp and elsewhere; and in the United States, Dr. Prudden, a well-known bacteriologist, of New York, has stated that he has found water purified by sand and alum filtration practically sterile. It has been frequently stated that microbes cannot be removed by filtration, that they will even pass a thousand abreast through the interstices of an ordinary sand-bed. In answer to this it may be said that while it is useless to look for good results by simple filtration at any speed which may be considered practical through clean sand alone, the matter is entirely changed by the use of a coagulant, and the smaller the particles, the more minute the microbes, the more surely are they entrapped in, surrounded, and held by the precipitate formed.

The albumenoid ammonia in Schuylkill water, purified by sand and alum, has been often determined in my laboratory, and has always fallen below 0.0050 part per 100,000.

There is scarcely a day when the water of Philadelphia does not reflect discreditably upon the city, its officials, and its citizens. If we had but the one alternative, the use of the Schuylkill in its present condition or the expenditure of 20,000,000 dol. to get water from elsewhere, we might possibly be excused for hesitation. But there are other ways of solving the difficulty. Water, considerably worse than that taken from the Schuylkill, has been successfully purified elsewhere, and why should not Philadelphia adopt a similar system of purification. It is evident that additional subsiding basins alone are impracticable for the work required. The enormous East Park reservoirs and the comparatively small amount of work they accomplish must have convinced all who have impartially considered the matter that some other method of purification must be adopted. The suspended matters of the Schuylkill water are mostly so minute and are deposited so slowly that very many times our present storage capacity would be necessary to render the condition of the water at all times uniformly clear and satisfactory. The large number and large size of the reservoirs required to do this and the immense outlay which their construction would involve would seem to be sufficient reason for looking to other methods of purification.

In conclusion, I desire to acknowledge my indebtedness to a gentleman who wishes to be nameless, not only for the interest he has taken in the progress of this investigation, but also for liberally sharing the expenses connected with it.

SOME POINTS IN THE DETERMINATION OF SILICA IN SILICATES BY FUSION WITH ALKALINE CARBONATES.*

By JAMES P. GILBERT, S.B.

THE usual method of determining silica in silicates—that of fusion with the alkaline carbonates, decomposition with hydrochloric acid, and subsequent evaporation to dryness—does not always give satisfactory results. This method is universally described in the text-books as being accurate, with the occasional caution that the filtrate should also be examined for any silica which may not have been rendered insoluble by evaporation to dryness. But one looks in vain for any intimation of what may be the amount of the error in the determination of silica as usually carried out if one neglects to examine the filtrate. There is no doubt that many chemists have had trouble with this method, and some have given it up, preferring to volatilise the silica with hydrofluoric and sulphuric acids, and, after a careful analysis of the residue, to calculate the silica by difference. A recent writer† makes the statement that he

* *Technology Quarterly*, vol. iii., No. 1.

† George Craig, *CHEM. NEWS*, vol. lx., No. 1563.

TABLE I.

Analyses of Blast-Furnace Slag (containing 46 per cent lime) by Fusion with Alkaline Carbonates.

I.	II.	III.	IV.
Residue insoluble in hydrochloric acid after evaporation to dryness. Per cent.	Weight of residue obtained from treating Column I. with hydrofluoric acid. Grm.	Weight of silica found in alumina. Grm.	Total silica. Per cent.
1.	41.25	0.0003	41.26
2.	41.34	0.0024	41.17
3.	41.39	0.0012	41.33
4.	41.32	0.0020	41.18
5.	41.22	0.0012	41.19
6.	41.43	0.0021	41.23
7.	41.40	0.0014	41.32
8.	41.48	0.0017	41.35
9.	41.33	0.0013	41.25
10.	41.71	0.0036	41.42
11.	41.53	0.0028	41.27
12.	41.89	0.0031	41.35
13.	41.79	0.0032	41.41
14.	41.65	0.0027	41.43
15.	41.90	0.0028	41.48

Nos. 1 to 3 inclusive were dehydrated on the water-bath.

Nos. 4 to 6 inclusive were dehydrated at 125° C.

Nos. 7 to 9 inclusive were dehydrated on iron plate over Bunsen burner.

Nos. 10 to 15 inclusive were dehydrated in air-chamber at 280° C.

All evaporations were made in porcelain.

TABLE II.

Analyses of a Blast-Furnace Slag (containing 35 per cent lime and 15 per cent magnesia).

I.	II.	III.	IV.
1.	33.65	0.0032	33.61
2.	33.90	0.0014	33.18
3.	33.46	0.0013	33.29
4.	33.71	0.0027	33.40
5.	33.42	0.0021	33.24
6.	33.75	0.0031	33.36
7.	33.49	0.0032	33.24
8.	33.85	0.0045	33.27
9.	33.90	0.0042	33.30
10.	33.65	0.0062	33.62
11.	33.83	0.0046	33.80
12.	33.95	0.0088	33.60

Nos. 1 to 3 inclusive were dehydrated on the water-bath.

Nos. 4 to 6 inclusive were dehydrated at 120° C.

Nos. 7 to 9 inclusive were dehydrated on iron plate over Bunsen burner.

Nos. 10 to 12 inclusive were dehydrated at 280° C.

TABLE III.—Analyses of a Sample of Orthoclase.

I.	II.	III.	IV.
1.	64.80	0.0018	64.52
2.	64.13	0.0018	64.30
3.	64.03	0.0026	64.20
4.	64.35	0.0020	64.52
5.	64.98	0.0050	64.45
6.	64.62	0.0035	64.36
7.	64.83	0.0068	64.45
8.	64.97	0.0083	64.35

Nos. 1 and 2 were dehydrated on the water-bath.

Nos. 3 and 4 were dehydrated at 120° C.

Nos. 5 and 6 were dehydrated on iron plate over Bunsen burner.

Nos. 7 and 8 were dehydrated at 280° C.

has never been able to obtain more than 97.5 per cent of the total silica in highly siliceous bodies by the fusion method. The following work was undertaken in the hope of discovering some of the sources of error in the fusion process.

The influence of the temperature at which the silica is dehydrated was first investigated. Most authorities say that evaporation on the water-bath to complete dryness, or until no more hydrochloric acid is given off, is sufficient to dehydrate the silica, but a few recommend subsequent heating in an air-chamber to a temperature of 110° C. A higher temperature than 110° C. is said by Fresenius to be inadmissible, since there is liability of the silica re-combining with the bases present to form silicates partially decomposable with hydrochloric acid.

To test the influence of temperature on the amount of silica obtained, the following determinations of silica were made in a blast-furnace slag containing about 46 per cent of lime, 10 per cent of alumina, and less than 1 per cent of magnesia. The silica was dehydrated at various temperatures, but in all other respects the process was carried out exactly as Fresenius directs. What is generally called silica, that is, the mass insoluble in hot hydrochloric acid after evaporation to dryness, is given in Column I. of Table I. This was treated with hydrofluoric acid, and the weight of the residue is given in Column II. In the filtrate from the silica the alumina was precipitated by ammonia, dried, ignited, and then fused with potassium bisulphate. The residue left on treating the fused mass with water (and correcting for the impurities of the bisulphate used) is given in Column III. The total silica in Column IV. is calculated by subtracting the weight of the residue left after treatment with hydrofluoric acid from the weight of the silica as given in Column I., and adding that found with the alumina in Column III.

In this series of results it will be seen that the silica was practically all rendered insoluble even at the temperature of the water-bath, and that there was no gain in this respect in using a higher temperature. But the amount of foreign matter in the silica was, in general, perceptibly higher at the higher temperature of dehydration. This is probably due to the alumina being rendered partially insoluble in acid. From the fact that very little silica was found in the alumina, it would seem as if there were no tendency for the silica to re-combine with the lime and alumina even at a temperature of 280° C. Nos. 13, 14, and 15 were digested, after dehydration, with hot acid for one hour, in the expectation of dissolving out all the alumina and other bases, but this treatment did not give smaller residues after the volatilisation of the silica with hydrofluoric acid than in Nos. 10, 11, and 12, which were treated only thirty minutes with acid.

The general uniformity of the results in this series suggested the possible influence of the calcium chloride present in dehydrating the silica on evaporation to dryness. This led to the second point considered, namely, the influence of the salts present on the determination of silica. It is not unreasonable to suppose that some salts, such as calcium chloride, may have a beneficial influence, while others, as, for example, magnesium chloride, which is decomposed when its solution is evaporated, may vitiate the silica determination by forming a silicate which will be subsequently decomposed by hydrochloric acid with solution of the silica. To test the effect of magnesium chloride, determinations of silica were made in a slag containing about 35 per cent of lime, 15 per cent of magnesia, and 15 per cent of alumina. (See Table II.).

This series differs from the first mainly in the large amount of impurity in the silica and the large amount of silica in the alumina when the dehydration is effected at a temperature of 280° C. The best results were obtained at a temperature of 120° C. The increase of silica in the alumina as the temperature is increased would seem to be due to the magnesia, for the conditions were, in all other respects, the same as in the analyses of the other slag. The above results indicate that there is no danger

of the silica combining with the magnesia at 120° C., and that at this temperature the silica is almost completely dehydrated, the calcium chloride probably assisting in the dehydration.

A series of analyses was next made on orthoclase, practically free from lime and magnesia. (See Table III.).

This series differs from the previous one in that the higher temperature is not accompanied with an increased amount of silica in the filtrate. This would seem to be a confirmation of the idea that there was a re-combination of the silica and the magnesia at the temperature of 280° C. in the magnesia slag; and the fact that the amounts of silica found in the alumina are (with one exception) uniformly higher than those in the lime slag indicates, I think, the beneficial effect of the calcium chloride in the dehydration of the silica.

The third point considered was the influence of temperature on the dehydration of the silica when no bases other than the alkalis were present. From the last three series of analyses it would seem that some silica always fails to be rendered insoluble by heat alone, so that, if a definite amount of pure silica were taken and subjected to alternate fusions and dehydrations, we should expect that the amount of silica obtained would diminish at each successive treatment. To ascertain if this were so, two determinations of silica were made in the lime slag, and the silica thus obtained repeatedly treated by fusion with alkaline carbonates in the usual way. The per cent of silica recovered in each case is given below. The silica obtained from the slag by the first fusion and dehydration is taken as 100 per cent.

	I. Per cent.	II. Per cent.	
1.	42.02	41.81	Silica in slag obtained by heating to 280 C.
2.	97.24	97.79	
3.	96.04	96.70	Percentage of the above obtained in four successive fusions by heating to 120° C.
4.	95.17	95.96	
5.	94.19	95.45	

The large difference between the results of the first and second fusions is probably due to impurities in the silica, which was heated to 280° C.; but the variations in the other cases can only be due to loss of silica by incomplete dehydration. Still, these are better results than Craig obtained, who does not, however, mention the temperature he used in dehydrating the silica.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 15th, 1890.

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

MR. JAMES HAMILTON was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Charles F. Branson, Kenley Lodge, Macaulay Road, Clapham Common; John Hutchinson Edward, 117, Stockport Road, Manchester; Arthur R. Haslam, Ph.D., 64, Rathgar Road, Dublin; John Robert Johnson, 16, Oxford Street, Liverpool; Patrick Kelly, 43, Lennox Street, Dublin; Thomas Parker, M.I.C.E., Wolverhampton; Richard James Redding, Royal Laboratory, Woolwich Arsenal; Frederick Smith, Johannesburg, Transvaal, South Africa.

The following were elected Fellows of the Society:—

James Robert Appleyard; William Henry Blake; James

Kear Colwell; S. Sydney Monckton Copeman, M.A., M.B.; Andrew Fairgrieve; G. H. Finlay; John Archyll Jones; Oliver Kirk; Robert Walter Oddy; William Tate.

The following papers were read:—

36. "Diethylphosphorous Acid." By T. E. THORPE, F.R.S., and BARKER NORTH, Associate of the Normal School of Science.

The authors describe the mode of preparing this compound and its properties. It is obtained by adding alcohol, drop by drop, to phosphorous oxide contained in a vessel surrounded with ice and salt. It is a colourless mobile liquid, possessing a peculiar penetrating alliaceous smell. Its vapour is poisonous, and even small quantities produce headache and nausea. It boils at 184—185°, and has the relative density 1.0749 at—

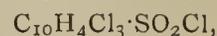
$$\frac{15.5^{\circ}}{4}$$

It interacts with water, forming alcohol and phosphorous acid, and is converted by bromine into ethyl bromide and metaphosphoric acid.

37. "The Homonuclear Trichloronaphthalenes." By HENRY E. ARMSTRONG and W. P. WYNNE.

1 : 2 : 3-Trichloronaphthalene.—The compound prepared by Faust and Saame from α -chloronaphthalene tetrachloride has been shown by Widman to be this modification, the proof being that it affords nitrotrichlorophthalic acid on oxidation with nitric acid; the authors have obtained it from a novel source—by the action of phosphorus pentachloride on Zincke and Kegel's $\alpha\beta$ -dichloro- β -naphthol (*Berichte*, 1888, 3385). This naphthol derivative is found to crystallise in aggregates, such as Zincke and Kegel describe, of long prismatic needles springing from a common centre—m. p. 76—77°; also (a) in fairly large aggregates composed of characteristic short stumpy prisms—m. p. 76—77°; and (b) in very long, slender, flat, transparent needles melting at 66° and, on re-fusion, at 74°. In no case was a higher melting-point than 77° observed. Zincke and Kegel, however, give 81° as the melting-point of the substance; and it is noteworthy, therefore, that the authors find the melting-point of trichloronaphthalene to be 92—93°, instead of 96°, and that one of them, in conjunction with Mr. Rossiter, has found that the various chloro-derivatives of β -naphthol described by Zincke and Kegel uniformly melt at temperatures about 4° lower than stated by these chemists; it may also be mentioned that a similar discrepancy is to be noted in the case of a recent paper of Clausius (*Berichte*, 1890, 517), who specially calls attention to the fact that he finds the melting-point of 2 : 2'-dihydroxynaphthalene to be 4° higher than previously observed.

$\alpha\beta$ -Dichloro- β -naphthol exchanges its hydroxyl for chlorine when distilled with the theoretical quantity of phosphorus pentachloride at 240—250°. The resulting trichloronaphthalene crystallises from alcohol, in which it is sparingly soluble in the cold, either in long, very slender needles or in radiate aggregates of flat needles; it melts at 81°. It is but little acted on when heated at 100° with H₂SO₄, but is readily sulphonated when digested at 100° for an hour with four times its weight of acid containing 10 per cent SO₃. The barium salt of the acid, (C₁₀H₄Cl₃SO₃)₂Ba + 3½ OH₂, crystallises in small spherical aggregates, and is sparingly soluble in water; the potassium salt, C₁₀H₄Cl₃SO₃K, is very soluble in water, but sparingly soluble in alcohol, from which it crystallises in minute anhydrous needles. The chloride,—



crystallises from benzene, in which it is very soluble, in small prismatic needles; from petroleum spirit, in which it is sparingly soluble, in small, flat, slender needles; and from acetic acid in white aggregates of very small needles; it melts at 182°. The amide could not be obtained crystalline; it melts at 296°. The chloride was hydrolysed by prolonged heating with concentrated muriatic

acid at 260°; the regenerated trichloronaphthalene crystallised from alcohol in long slender needles melting at 81°.

1 : 2 : 4-Trichloronaphthalene.—This modification was first prepared by Cleve, who most accurately described its properties (*Berichte*, 1888, 893), from dichloro- α -naphthol; the authors prefer to prepare it from dichloro- α -naphthylamine. It melts at 92°. When sulphonated, either by means of the theoretical quantity of SO_3HCl or by heating with twice its weight of H_2SO_4 at 100° for one hour, it yields an acid which, when dissolved in water, forms a viscid solution—in this respect resembling the acid obtained by sulphoning 1 : 4-dichloronaphthalene. The *barium* salt of the acid, $(\text{C}_{10}\text{H}_4\text{Cl}_2\text{SO}_3)_2\text{Ba} + 3\text{H}_2\text{O}$, is very sparingly soluble in water, and crystallises in fluffy masses of very small slender needles; the *potassium* salt $\text{C}_{10}\text{H}_4\text{Cl}_2\text{SO}_3\text{K}$ is extremely soluble in water, but sparingly soluble in alcohol, from which it crystallises in anhydrous, short, slender needles. The *chloride* $\text{C}_{10}\text{H}_4\text{Cl}_2\text{SO}_2\text{Cl}$ crystallises from benzene in tufts of long slender needles; from petroleum spirit, in which it is sparingly soluble, in long slender needles; and from acetic acid in slender flat needles; it melts at 157–158°. The *amide* crystallises from alcohol in tufts of short slender needles, and melts at 235°. The chloride was hydrolysed with considerable difficulty, requiring prolonged heating at 260–265° with concentrated muriatic acid; the resulting trichloronaphthalene crystallised from alcohol in tufts of slender flat needles melting at 92°.

38. "The Ten Isomeric Dichloronaphthalenes and the Sulphonic Acids and Trichloronaphthalenes Derived therefrom." By HENRY E. ARMSTRONG and W. P. WYNNE.

Whereas theoretically only *ten* dichloronaphthalenes are possible, *twelve* have actually been described. Nine of these are already proved to be definite substances, and their constitution may be regarded as well established (*Proc. Chem. Soc.*, 1888, 104; 1889, 34, 48); these nine include the three possible $\alpha\alpha$ -, the four possible $\alpha\beta$ -, and the two possible hetero- $\beta\beta$ compounds. Of the remaining three, one—the so-called α -dichloronaphthalene (m. p. 38°)—has been shown by the authors to be non-existent, and to consist of the 1 : 3- (m. p. 61°) and 1 : 4- (m. p. 63°) modifications (*Proc. Chem. Soc.*, 1888, 106). A second is undoubtedly also non-existent, viz., the " κ -dichloronaphthalene" (m. p. 94°), which, according to Claus (*Ber.*, 1882, 314) is obtained by the action of phosphorus pentachloride on the α -naphtholsulphonic acid prepared by sulphoning α -naphthol dissolved in acetic acid. The several monosulphonic acids formed from α -naphthol, however, correspond to one or other of the nine recognised dichloronaphthalenes, and on this ground alone the production of the tenth, and—it is to be supposed—only possible, modification in such a manner appears impossible, even if the fact be left out of account that homo- $\beta\beta$ -dichloronaphthalene—the only modification required in addition to the nine above specified in order to complete the list—cannot be prepared from α -naphthol. α -Naphthol is converted, with exceptional facility, into the 1 : 2 : 4-disulphonic acid, and the corresponding trichloronaphthalene melts at 92°, which is very nearly the melting-point of Claus's compound; the authors, therefore, have little doubt that the substance described by Claus as κ -dichloronaphthalene was in reality 1 : 2 : 4-trichloronaphthalene.

The only remaining modification to be considered is the ι -dichloronaphthalene (m. p. 120°), first prepared by Leeds and Everhard by heating naphthalene tetrachloride with silver oxide, and which was subsequently separated by Widman from the product of the action of alcoholic potash on the tetrachloride. Until it was discovered that α -dichloronaphthalene was a mixture of the 1 : 3 and 1 : 4 compound, the authors were inclined to think that perhaps this modification was impure ϵ -dichloronaphthalene (*B. A. Report*, 1888); but the necessity for this assumption, occasioned by the existence of the α -compound, having

been removed, it appeared highly probable that the ι -compound was the homo- $\beta\beta$ -modification—and this proves to be the case, the authors having succeeded in obtaining a substance with all the properties ascribed by Leeds and Everhard and by Widman to ι -dichloronaphthalene by a novel method, which places its constitution beyond all doubt, viz., by partially reducing 1 : 2 : 3-trichloronaphthalene.

The existence of a complete series of ten isomeric dichloronaphthalenes may, therefore, now be regarded as established. No fewer than eight of these have been discovered by Cléve and his pupils; all who study the subject must be led to admire the work of the Swedish chemists, and to recognise the influence which it has exercised.

In order to characterise the various dichloronaphthalenes, and also to determine the manner in which constitution affects the course of chemical change in the case of naphthalene derivatives, the authors have sulphonated the ten modifications, and have converted the resulting sulpho-acids into trichloronaphthalenes. A brief account of the results is now given, details with reference to the composition of the salts, &c., being reserved for a full communication.

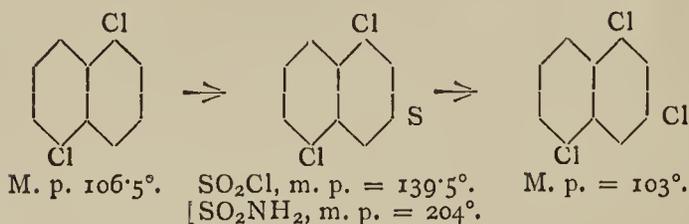
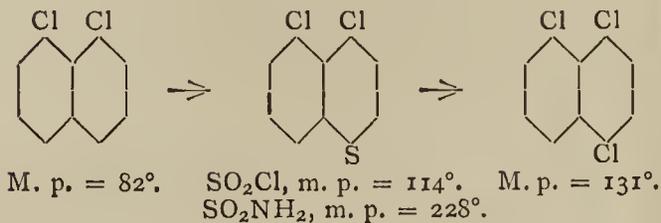
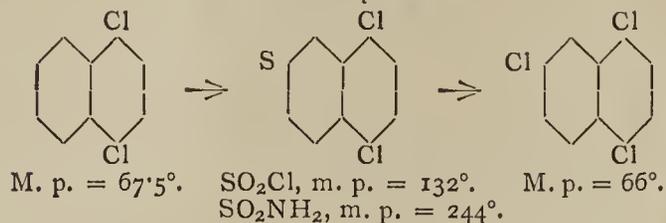
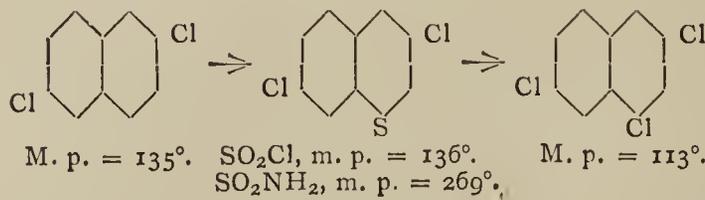
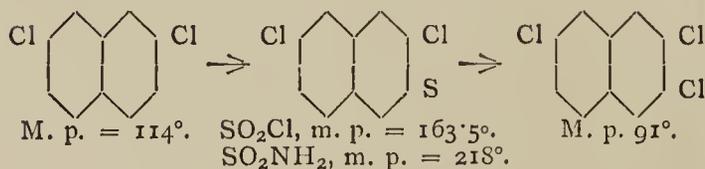
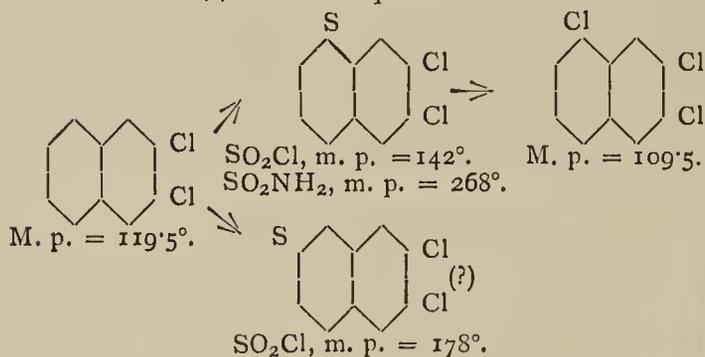
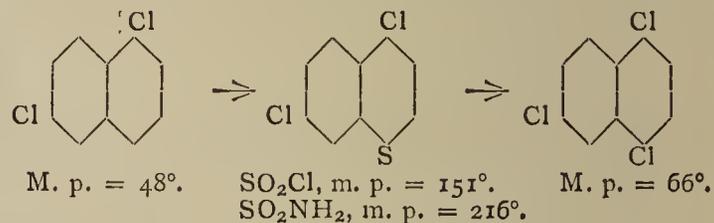
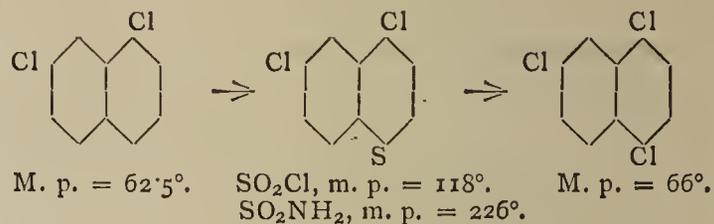
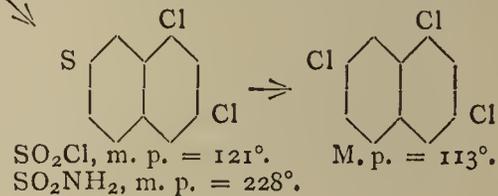
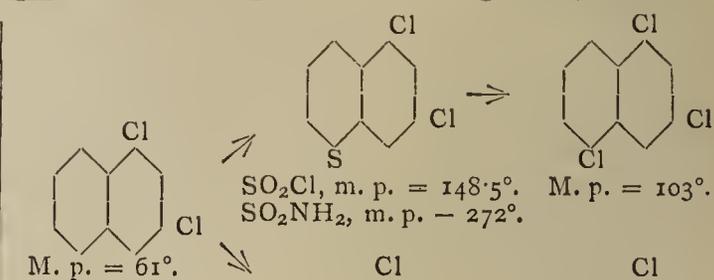
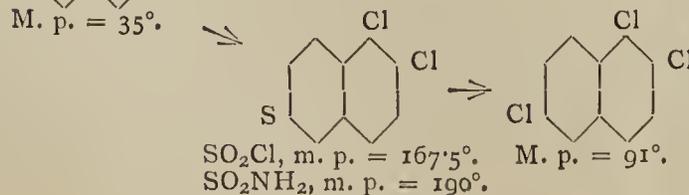
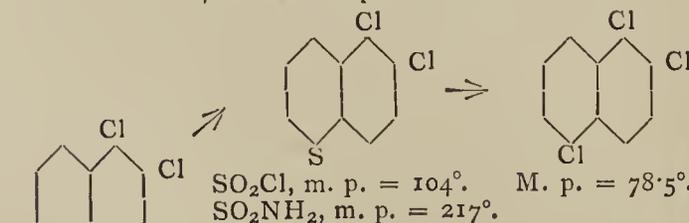
To avoid the possibility of the occurrence of secondary changes induced by the presence of water, chlorosulphonic acid was throughout employed as the sulphoning agent instead of sulphuric acid, and sulphonation was effected by adding slightly less than the theoretical quantity of this agent to a 10 per cent solution of the dichloronaphthalene in dry carbon bisulphide; the carbon bisulphide was subsequently removed by distillation on a water-bath, the acid dissolved in water, and the solution steam-distilled to free it from unattacked dichloronaphthalene and traces of carbon bisulphide, and finally filtered to remove the small proportion of insoluble non-volatile compound (sulphochloride or sulphone) always formed.

$\alpha\alpha$ -Dichloronaphthalenes.

1. 1 : 4-Dichloronaphthalene.—On sulphonation, this yields a practically uniform product, a very small proportion of an isomeric acid of undetermined constitution being simultaneously formed. The *chloride* of the acid, $\text{C}_{10}\text{H}_5\text{Cl}_2\text{SO}_2\text{Cl}$, crystallises from benzene in aggregates of slender prismatic needles melting at 132°, identical with the chloride of Widman's dichloronaphthalene- β -sulphonic acid; the *amide* is sparingly soluble in cold alcohol, and crystallises in tufts of very slender long needles melting at 244°. The corresponding *trichloronaphthalene* crystallises in tufts of slender needles, which, on standing, undergo conversion into opaque, white aggregates melting at 66° (*Proc. Chem. Soc.*, 1890, 18). The sulphochloride undergoes hydrolysis when heated with concentrated muriatic acid at 260–265°; the pure dichloronaphthalene thus obtained crystallises from alcohol in long, narrow, slender ribbons melting at 67.5°.

2. 1 : 1'-Dichloronaphthalene was prepared by Atterberg's method (*Ber.*, 1876, 1732) from β -dinitronaphthalene. The sulphonation product consists of a single acid, the *chloride* of which crystallises from petroleum spirit in minute aggregates melting at 114°; the *amide* crystallises from alcohol in tufts of small slender needles melting at 228°. The corresponding *trichloronaphthalene* crystallises from alcohol in very long slender needles melting at 131°.

3. 1 : 4'-Dichloronaphthalene yields two acids on sulphonation; of these, one is formed in small quantity only, and has not been completely examined. The chief product yields a *chloride*, which crystallises from benzene in aggregates of long, flat, thin, narrow plates melting at 139.5°; the *amide* crystallises in small prismatic aggregates melting at 204°. The corresponding *trichloronaphthalene* crystallises from alcohol in long slender needles melting at 103°. On hydrolysing the acid at 260–265° with concentrated muriatic acid, pure 1 : 4-dichloronaphthalene was obtained, which crystallises from alcohol in short flat thin scales melting at 106.5°.

αα-Dichloronaphthalenes.*ββ-Dichloronaphthalenes.**αβ-Dichloronaphthalenes.**αβ Dichloronaphthalenes.*

4. 1 : 2-Dichloronaphthalene is found to yield a mixture of an α - and a β -sulphonic acid, the former constituting about two-thirds of the product.

The chlorides of the two acids require to be mechanically separated after crystallisation from benzene.

α-Acid.—The chloride crystallises from benzene, in which it is very soluble, in large prismatic forms melting at 104°; the *amide* crystallises from alcohol in tufts of small slender needles, and melts at 217°. The corresponding *trichloronaphthalene* crystallises from alcohol in short flat needles melting at 78.5°. On hydrolysis with concentrated muriatic acid at 230°, the chloride gave pure 1 : 2-dichloronaphthalene melting at 35°.

β-Acid.—The *chloride* of the β -acid is less soluble in benzene, and crystallises in aggregates of small prisms melting at 167°; the *amide* crystallises from dilute alcohol in short slender white needles melting at 190°. The corresponding *trichloronaphthalene* crystallises from alcohol in slender needles and melts at 91°. On hydrolysis with concentrated muriatic acid at 260–265°, the β -chloride gave pure 1 : 2-dichloronaphthalene melting at 35°.

5. 1 : 3-Dichloronaphthalene.—On sulphonation this yields a mixture of an α - and a β -acid, the former constituting about four-fifths of the product.

The *chloride* of the α -acid crystallises from benzene in well-defined prisms melting at 148.5°, and crystallographically identical with those of the chloride of Widman's dichloronaphthalene- α -sulphonic acid; the *amide* is sparingly soluble in alcohol and crystallises in flocks of microscopic needles melting at 272°. The corresponding *trichloronaphthalene* crystallises from alcohol in long slender flat needles melting at 103°. On hydrolysis with concentrated muriatic acid at 230°, the α -chloride gave pure 1 : 3-dichloronaphthalene, which crystallised in long slender ribbons melting at 61°.

The β -acid, although the minor product of sulphonation, constitutes the sole product when the sulphonation product is heated in a dry atmosphere at 160° for eighteen

hours. Its *chloride* is very soluble in benzene and crystallises best from a mixture of benzene and petroleum spirit in long narrow four-sided prisms melting at 121° ; the *amide* crystallises from alcohol in tufts of short, very slender needles, and melts at 228° . The corresponding *trichloronaphthalene* is sparingly soluble in hot alcohol, and crystallises from benzene in slender needles melting at 113° . On hydrolysis with concentrated muriatic acid at $260-265^{\circ}$, the β chloride gave pure 1:3-dichloronaphthalene melting at 61° .

6. 1:2'-*Dichloronaphthalene* yields an almost uniform product on sulphonation, the proportion of isomeric acid formed being very small. The *chloride* of the chief product crystallises from benzene in transparent, slender, flat needles which rapidly became opaque on exposure to the air, and then melt at 118° ; the *amide* is sparingly soluble in alcohol, and crystallises in narrow slender ribbons melting at 226° . The corresponding *trichloronaphthalene* crystallises from alcohol in slender flat needles which, on standing in the solvent, became opaque and melted at 66° . On hydrolysis with concentrated muriatic acid at 230° , the chloride gave pure 1:2'-dichloronaphthalene, which crystallises from alcohol in small crystalline aggregates melting at 62.5° . The synthetic 1:2'-dichloronaphthalene, prepared by Erdmann's method, was found to melt slightly higher, viz., at $63-63.5^{\circ}$.

7. 1:3'-*Dichloronaphthalene* yields a uniform product on sulphonation. The *chloride* of the acid crystallises from benzene in magnificent prisms and melts at 151° ; the *amide* crystallises from alcohol in long slender needles melting at 216° . The corresponding *trichloronaphthalene* crystallises from alcohol in slender flat needles which become opaque on standing in the solvent and melt at 66° . On hydrolysis with concentrated muriatic acid at 230° , the chloride gave pure 1:3'-dichloronaphthalene, which crystallised from alcohol in long slender ribbons melting at 48° .

$\beta\beta$ -Dichloronaphthalenes.

8. 2:3-*Dichloronaphthalene*. To prepare this modification a solution of 1:2:3-trichloronaphthalene in alcohol heated at $60-70^{\circ}$ is treated with one-and-a-half times the theoretical quantity of 2 per cent sodium amalgam during one hour; the α -dichloronaphthalene is purified by fractional steam-distillation and fractional crystallisation from alcohol. It crystallises in the manner described by Leeds and Everhard and by Widman, in thin lustrous scales and melts at about 120° . On sulphonation it yields a product containing an α -acid and probably a β -acid, the former constituting the chief product. The α *chloride* crystallises from benzene in lustrous slender narrow ribbons melting at 142° ; the *amide* is sparingly soluble in alcohol and crystallises in aggregates of small slender needles melting at 268° . The corresponding *trichloronaphthalene* crystallises from alcohol in long and very slender needles, and melts at 109.5° . On hydrolysis with concentrated muriatic acid at 230° , the α -chloride was found to yield pure 2:3-dichloronaphthalene, which crystallised from alcohol in the characteristic thin scales melting at 119.5° .

Isomeric Acid.—The salts of this acid have not yet been obtained in quantity sufficient for analysis. The *chloride* is very soluble in benzene and crystallises in opaque hemispherical aggregates melting at 178° ; on hydrolysis with concentrated muriatic acid at $260-265^{\circ}$ it gave 2:3-dichloronaphthalene melting at 119.5° . There can be little doubt that this acid has the constitution $[\text{Cl}_2 : \text{SO}_3\text{H} = 2 : 3 : 2']$.

9. 2:2'-*Dichloronaphthalene* yields an almost uniform product on sulphonation, the proportion of isomeric acid formed being very small. The *chloride* of the chief product crystallises from benzene in well-formed elongated prisms, and melts at 163.5° ; the *amide* crystallises from dilute alcohol in tufts of long slender needles, and melts at 218° . The corresponding *trichloronaphthalene* crys-

tallises from alcohol in minute plates and melts at $90.5-91^{\circ}$. On hydrolysis with concentrated muriatic acid at $260-265^{\circ}$, the chloride gave pure 2:2'-dichloronaphthalene, which crystallised from alcohol in large thin laminae melting at 114° .

10. 2:3'-*Dichloronaphthalene* affords an almost uniform sulphonation-product, the proportion of isomeric acid formed being small. The *chloride* of the chief product crystallises from benzene in radiate groups of long slender prismatic needles melting at 136° ; the *amide* is sparingly soluble in alcohol and crystallises in small aggregates of prismatic needles melting at 269° . The corresponding *trichloronaphthalene* is sparingly soluble in alcohol and crystallises in small slender needles melting at 113° . On hydrolysis with concentrated muriatic acid at 230° , the chloride gave pure 2:3'-dichloronaphthalene crystallising from alcohol in long narrow ribbons melting at 135° .

It is noteworthy that the chlorides of the β sulphonic acids require prolonged heating at a higher temperature than those of the α acids to effect their hydrolysis; and that on distillation with phosphorus pentachloride they give a smaller yield of trichloronaphthalene.

In the accompanying table the formulæ of the dichloronaphthalenes are given in first column, those of the acids into which they are converted on sulphonation are given in the second, and the third comprises the trichloronaphthalenes obtained from the dichloronaphthalene-sulphonic acids. The evidence on which the constitution of the tri-derivatives here given is based has been incidentally given in previous papers (*cf. Proc. Chem. Soc.*, 1889, 48; 1890, 11), and will be summarised in a forthcoming account of the trichloronaphthalenes.

(To be continued.)

NOTICES OF BOOKS.

Gems and Precious Stones of North America. A Popular Description of their Occurrence, Value, History, Archæology, and of the Collections in which they Exist; also a Chapter on Pearls, and on Remarkable Gems Owned in the United States. Illustrated with Eight Coloured Plates and numerous Minor Engravings. By GEORGE FREDERIC KUNZ. New York: The Scientific Publishing Company.

THIS beautifully got up and richly illustrated volume is not easy to characterise. It is not a monograph of the precious stones of North America, including, as it does, much matter of which the mineralogist can take no account. Still, he will find here abundant valuable information on the North American localities in which such stones have hitherto been found. The author is of opinion that, *e.g.*, the daily yield from the South African diamond mines would exceed in value the entire yearly out-put of precious stones in the United States. He gives an account of alleged valuable gems which when they came into qualified hands were found to be nearly worthless. An instance of this kind is the supposed "Blue Ridge Sapphire," which, after being paraded as the "Georgia marvel," and valued at 50,000 dollars, proved to be a water-worn piece of rolled blue bottle-glass. A stone weighing nine ozs., found in North Carolina, was thought to be a genuine emerald, containing, curiously enough, a number of small diamonds! This treasure, on examination, proved to be merely "a greenish quartz crystal filled with long hair-like crystals of green byssolite or actinolite on which were series of small liquid cavities that glistened in the sun and led to the enclosed diamond theory." A supposed ruby of six ozs. in weight was merely a garnet of poor quality.

The author gives some hints which may save prospectors from much disappointment, at least as far as diamonds

are concerned. He explains the error—one of the many delusions contained in the writings of Pliny—that a diamond will not break if struck with a hammer. It is suggested that good specimens may have been destroyed by this rough and fallacious test. As the simplest criterion, the finder is advised to try if a specimen will scratch corundum. If it does so, and if it is not scratched by a diamond, it may safely be assumed to be a diamond. This subject naturally leads to the much disputed question of the origin of diamonds. The rocks in various parts of the United States where diamonds have been occasionally found have been compared with those of Kimberley, which are much more recent formations. Itacolumite, like that of Brazil, has been found in North Carolina, but no diamonds have actually been discovered in this formation. It has been recently contended that the diamond is not of terrestrial, but of cosmic formation. This theory receives some confirmation from the facts that diamonds have occurred in meteorites. In 1884, Sir H. E. Roscoe, as here quoted, stated in a paper read before the Literary and Philosophical Society of Manchester, that on digesting some of the "blue" soft diamond earth of South Africa in ether he obtained a small quantity of an aromatic crystalline body.

A singular fraud in connection with diamonds was carried out in New Mexico and Arizona about twenty years ago. A company was started for collecting the diamonds, rubies, &c., which were there plentiful. An agent of the projectors had made extensive purchases of rough diamonds in Hatton Garden, and with these the selected locality was "salted." A diamond weighing 108 carats was said to have been found, and 80,000 carats of rubies; but the rubies were merely garnets, the 108-carat diamond was a piece of quartz, and the smaller stones were found to have the peculiarities of African and Brazilian diamonds. The promoters are said to have realised 750,000 dollars.

The United States are richer in the varieties of corundum than in diamonds, and some beautiful specimens are here represented in their natural colours.

Turquoise is very abundant in New Mexico, and appears to have been valued as an ornament by the aborigines. The American specimens, however, like the Egyptian, do not retain their full blue colour, like the genuine Persian stones, but turn to a green.

A singular phenomenon is shown in the plate opposite p. 138. A tree which has been fossilised forms a natural bridge over a dell 45 feet in width. Fully fifty feet of the tree rests on the rock on one side, so that the trunk is visible for 100 feet. It is found to belong to the genus *Aracaria*, of which the Norfolk Island pine (*A. excelsa*) is a living specimen.

We find here an extensive chapter on pearls, and on nautilus shells, which have, of course, no other connection with gems beyond their being prized as ornaments. There is a curious figure of a pearl having a nucleus of clay. It seems that a company was formed for pearl-fishing by means of a submarine boat. The project seems very feasible, but it was not successful, as the company soon ceased to exist.

The fugitive character of the beauty of the opal is fully noticed. Of all its varieties, the fire-opal is most readily injured by moisture or sudden atmospheric changes. Specimens "have been known to lose their brilliancy whilst in a jeweller's safe or in a collector's cabinet." They not only lose their colour but become filled with flaws and cracks. The Mexican and Central American opals are said to be more liable to such changes than the Hungarian specimens. Concerning the Queensland opals the author says nothing.

A large portion of the fourteenth and fifteenth chapters is devoted to anthropology—a science which in the United States is cultivated with surprising zeal. We find here representations of polished figures executed by the aborigines in obsidian knives and mirrors of the same material, a mirror of iron pyrites, a "banner-stone" of

ferruginous quartz, &c. The author remarks that many of the aboriginal stone objects found in North America are marvels of skill in chipping, drilling, grinding, and polishing," and adds that no modern lapidary "could make anything more graceful in form and general outline than are some of the quartz discoidal stones found" in North Carolina.

In the last chapter the author takes up the commercial and statistical phase of his subject. To define precious stones he finds difficult. "Strictly speaking," he says, "the only precious stones are the diamond, ruby, sapphire, and emerald, though the term is often extended to the opal, notwithstanding its lack of hardness, and to the pearl, which is not a mineral but an animal product."

The term "gem" is limited to minerals hard enough to scratch quartz, and by archæologists it is applied only to engraved stones.

The work before us is unique in its plan, no less than in its accurate and splendid illustration, and will be welcomed by all lovers of precious stones.

The Journal of the Royal Agricultural Society of England.
Third Series, Vol. i., Part 1. London: Murray.

THIS issue contains very much valuable matter, not all of which, however, can legitimately fall under our notice.

The "Disposal of Sewage in Small Towns and Villages," by Mr. Clare Sewell Read, contains some sensible and appropriate remarks, mixed with utterances showing that the sewage question is not the writer's forte.

For cottages he prefers the dry-closet system, but his confidence in the removal of all dangerous impurities from sewage by a passage through 20 feet of soil seems very overstrained. He admits that "the curse of most sewage farms is that they have to deal with the largest volume of sewage when they want it least." His commendation of osiers as the best crop for irrigation beds is quite justified by facts.

"The Evolution of the Horse," by Prof. W. H. Flower, is a most valuable addition to biological literature, but it cannot be brought within our purview.

Prof. E. Kinch contributes a paper on basic cinder, otherwise known as Thomas slag, and its uses in agriculture. It appears that the make of steel in this country by the Thomas-Gilchrist process was last year nearly half a million tons, and in the whole world over 2½ million tons. The yield of basic slag was 700,000 tons, containing on an average 36 per cent of the basic calcium phosphate. The caution is given to farmers who use this manure never to mix it with ammonium sulphate, as it causes an escape of ammonia. The slag is pronounced a good phosphatic manure, especially on heavy clays, peats, and soils deficient in lime. On calcareous soils it is less efficient.

Twenty-Fifth Annual Report of the Alumni Association of the Philadelphia College of Pharmacy, for the Years 1888—1889. Philadelphia.

WE find in this Report a selection of papers which, if not exclusively devoted to chemistry, are not without a profound interest. In one entitled "Life in an Almshouse" we find the sad remark: "If you want anything done, no matter how intricate—if you want talent of any description you can find it in the almshouse."

The "Liabilities of the Profession of Pharmacy" contains some of what has been called the most hateful of vices for the especial benefit of the "Alumni." The speaker draws a novel distinction between trades and professions. In the former the object is money, or perhaps fame; in the latter it is the welfare of man, the advancement of knowledge, or the attainment of an ideal.

Action of Lime upon Raffinose.—L. Lindot.—In comparison with calcium saccharate, raffinose is insoluble.

CORRESPONDENCE.

MEDICAL OFFICERS OF HEALTH AND
PUBLIC ANALYSTS.

To the Editor of the Chemical News.

SIR,—A short time since the Town Council of one of the largest towns in Lancashire met for the purpose of selecting a gentleman to fill the joint position of Medical Officer of Health and Public Analyst. The advisability of keeping these two offices quite distinct has recently been suggested in the CHEMICAL NEWS—a suggestion with which I most cordially agree—as so few medical men are competent to perform a public analyst's duties satisfactorily.

In the *Proceedings of the Institute of Chemistry*, Part 2, 1890, p. 48, attention is called to the desirability of urging upon those who have at their disposal the appointment of analysts to various official positions that "membership of the Institute should be an indispensable qualification." This is a step in the right direction, and if the Council of the Institute could see their way to take even more decisive action upon this point it would be for the benefit of the entire chemical profession.—I am, &c.,

ROWLAND WILLIAMS.

Laboratory and Assay Office,
28, Pall Mall, Manchester,
June 2, 1890.

CHEMICAL NOTICES FROM FOREIGN
SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 20, May 19, 1890.

The Isomeric States of Chromium Sesquibromide.
—A. Recoura.—The author has previously shown that chromium sesquichloride differs from the other salts of chromium by the fact that it may assume two distinct isomeric states, but presenting this character in common, that the oxide precipitated from both their solutions by alkalis is the sesquichloride of the violet series. He obtained the green sesquibromide by mixing a saturated solution of chromic acid with a solution of hydrobromic acid at about 50 per cent, employing it in large excess. The solution, evaporated down with heat, gives, when cold, fine green needles, having the composition $\text{Cr}_2\text{Br}_3\cdot 12\text{HO}$. They are extremely soluble in water and very deliquescent. The dilute solution passes in about an hour from a splendid green to a bluish shade, and in twenty-four hours to a violet. This change is accompanied by the liberation of heat. The sesquioxide precipitated from the solutions, whatever their state, is always that of the violet salts of chromium.

The Existence of a Crystalline Hydrate of Ferric Oxylchloride, and on its Transformation into a Dimorphous Variety of Goethite.—G. Rousseau.—The decomposition of dilute solutions of ferric chloride was first pointed out by Senarmont. The study of this phenomenon was resumed by Debray, who found that very dilute solutions of ferric chloride are split up at about 70° into hydrochloric acid, and colloidal sesquioxide precipitable by sodium chloride. At 100° Graham's oxide is gradually converted into the modification of ferric oxide discovered by Saint Gilles. If very concentrated solutions of ferric chloride are operated upon, crystals are obtained of the formula $\text{Fe}_2\text{Cl}_3\cdot 2\text{Fe}_2\text{O}_3\cdot 3\text{HO}$.

Certain New Double Chromates.—M. Lachaud and C. Lepierre.—The authors have obtained double chromates of lead and of the alkaline metals, *i.e.*, of potassium in a brick-red, a yellow, and an orange modification, of sodium in a yellow and an orange form. With lithium they were less successful. Their experiments with barium, strontium, and calcium chromates have not led to results of importance.

Crystallisation of Alumina and of other Oxides in Gaseous Hydrochloric Acid.—P. Hautefeuille and A. Perrey.—Alumina prepared by the limited decomposition of the oxalate, if exposed to the action of hydrochloric acid at a pressure of three atmospheres and at a temperature below incipient redness, is converted into corundum. Amorphous titanate acid crystallises in the form of anatase and zirconia in rhombic tables.

Bouquet of Wines and Brandies.—A. Rommier.—The author, referring to his communication made to the Academy June 24, 1889, finds that active ellipsoidal ferment, if introduced into grapes when crushed at temperatures below $21-22^\circ$ multiplies more rapidly than the spores of the ferments found on the skins of the grapes; the action of the latter is paralysed. If a small quantity of an ellipsoidal ferment is added to grapes at temperatures above $21-22^\circ$, the ferment added develops along with the natural ferment and modifies the bouquet of the wine. M. Martinand has made an *experimentum crucis* which seems to confirm the author's theory. He divided the grapes of one and the same vine into five lots, and added to each a different ferment; to (1) that of a must of cherries in full fermentation; (2) of Beaujolais; (3) of Burgundy; (4) of Champagne; (5) of Bordeaux. All these wines presented distinct flavours.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. iv., No. 48.

This number contains no chemical matter.

Vol. v., No. 49.

Report by M. Le Chatelier on the Manganese-Steel of Mr. Hadfield.—The Committee consider manganese steel well adapted for agricultural machinery, wagon wheels, horse shoes, the axles of rotation of a great number of machines, and in general for articles exposed to wear by friction or to fracture by shocks.

Report given in by H. Le Chatelier on behalf of the Committee of Chemical Arts on M. Henry's Slag Cement.—This cement is obtained by mixing blast-furnace slags of suitable composition previously soaked in water and finely ground with a certain proportion of slaked lime. The new product cannot be placed in the same rank as Portland cements of good quality, but its cost is less by at least one-half.

Vol. v., No. 50.

This number contains no chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 6.

The Blue Flame of Common Salt, and the Spectroscopic Reaction of Copper Chloride.—G. Salet.—The well-known blue flame produced when salt is thrown upon a coke fire is due to traces of copper present in the fuel. The spectrum of the flame shows the bands of copper chloride.

Remarks on Formic Fermentation.—M. Berthelot.—The author has studied this phenomenon in the case of dung. He finds that the total heat given off is greater than that liberated in alcoholic fermentation.

Combustion- and Formation-Heats of Urea.—MM. Berthelot and Petit.—A thermo-chemical paper not adapted for abridgment.

Heat Developed by the Action of Oxygen upon the Blood.—M. Berthelot.—The absorption of oxygen tends to raise the temperature of the blood in the lungs, whilst the production of carbonic acid and of watery vapour tends to lower it.

On the different States of the Graphite Carbons, and on the Corresponding Chemical Derivatives.—M. Berthelot and P. Petit.—The authors have analysed and studied the graphite of cast-iron, pyrographitic oxide, amorphous graphite, and electric graphite.

Combustion- and Formation-Heat of the Graphitic and Pyrographitic Oxides.—M. Berthelot and P. Petit.—A thermo-chemical supplement to the foregoing memoir.

No. 7.

A Bichloric-propionic Aldehyd.—W. Spring and E. Tait.—By the direct action of chlorine, propylic alcohol only yields one bichloro-derivative of propionic aldehyd, accompanied by secondary products. The introduction of a third atom of chlorine into the molecule demands special consideration.

Thermo-chemical Researches on Silk.—Leo Vignon.—The author has undertaken to ascertain if the absorbent power of silk, raw or ungummed, in presence of different reagents, gives rise to phenomena which may be measured thermally.

The Use of Tannins to Prevent Crock in Steam Boilers.—Leo Vignon.—Free tannins attack the boiler plates. Tannins associated with an excess of sodium carbonate present the same inconvenience. The influence of sodium carbonate is sensibly nil, and it is to be recommended.

Detection of Benzoic Acid in Alimentary Substances.—E. Mohlor.—This process will be given at some length.

Certain Derivatives of Erythrite.—E. Grimeaux and Ch. Cloez.—An account of hydrofurfuran, and the bromhydrines of erythrite.

On the Dispersion of Watery Solutions.—M. Barbier and L. Roux.—This memoir cannot be usefully reproduced without the accompanying diagrams and tables.

Remark on the Specific Dispersive Power of Aqueous Solutions.—MM. Barbiér and Roux.—The specific dispersive power for a given substance varies very slowly with the concentration. This variation is, according to the cases, sometimes increasing and sometimes decreasing, but always very slight. Its mean value is common to all the substances examined.

Justus Liebig's Annalen der Chemie.
Vol. ccliv., Part I.

The Alkyloxalic Acids, the Dichlorglycolic Ethers, the Alkyloxalic Chlorides, and the Tetra-alkyl or Semiorthoxalic Ethers.—R. Anschütz.—Not susceptible of useful abridgment.

Formulæ for Calculating the Molecular Volumes of Organic Compounds.—W. Lossen.—This memoir does not admit of abridgment.

Communications from the Chemical Institute of the University of Geneva.—These comprise memoirs by S. Levy and F. C. Witte on symmetric tetrachloro-diacetyl, and by S. Levy and A. Curchod on symmetric tetrachloroacetone.

Communication from the Organic Laboratory of the Royal Technical High School at Aachen.—This includes a second treatise by A. Michaelis on syntheses effected by means of sodiumphenylhydrazine, and a memoir by O. Burchard on ethylenphenylhydrazine.

MEETINGS FOR THE WEEK.

- TUESDAY, 10th.—Royal Institution, 3. "The Natural History of Society," by Andrew Lang.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8.
- WEDNESDAY, 11th.—Microscopical, 8.
- THURSDAY, 12th.—Royal Institution, 3. "Flame and Explosives," by Prof. Dewar, M.A., F.R.S.
— Royal, 4.30.
— Mathematical, 8.
— Society of Arts, 8. "The Rationale of Indian Railways," by Sir Theodore C. Hope.
- FRIDAY, 13th.—Royal Institution 9. "The Physical Foundation of Music," by Prof. Silvanus P. Thompson.
— Astronomical, 8.
— Quekett Club, 8.
- SATURDAY, 14th.—Royal Institution, 3. "The Ballad Music of the West of England" (with musical illustrations), by Rev. S. Baring-Gould, M.A.

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BRITISH ASSOCIATION FOR THE
ADVANCEMENT OF SCIENCE, 22, Albemarle Street,
London W.

The NEXT ANNUAL GENERAL MEETING will be held at LEEDS, commencing on Wednesday, September 3.

President Elect—
Sir FREDERICK AUGUSTUS ABEL, C.B., D.C.L., D.Sc.,
F.R.S., V.P.C.S.

NOTICE to CONTRIBUTORS of MEMOIRS.—Authors are reminded that, under an arrangement dating from 1871, the acceptance of Memoirs and the days on which they are to be read are now as far as possible determined by Organising Committees for the several Sections before the beginning of the Meeting. It has, therefore, become necessary, in order to give an opportunity to the Committees of doing justice to the several Communications, that each Author should prepare an Abstract of his memoir of a length suitable for insertion in the published Transactions of the Association, and the Council request that he will send it, together with the original Memoir, by book-post on or before August 6, addressed thus:—"General Secretaries, British Association, 22, Albemarle Street, London, W. For Section —." Authors who comply with this request, and whose papers are accepted will be furnished before the Meeting with printed copies of their Reports or Abstracts. If it should be inconvenient to the Author that his paper should be read on any particular day, he is requested to send information thereof to the Secretaries in a separate note.

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THE CHEMICAL NEWS

Vol. LXI. No. 1594. 14 JUN 90

A NEW AND EFFICIENT APPLIANCE FOR
THE DETECTION OF HYDROCARBONS
AND OTHER COMBUSTIBLE GASES WHEN
IN ADMIXTURE WITH THE ATMOSPHERE.

By H. N. WARREN, Research Analyst.

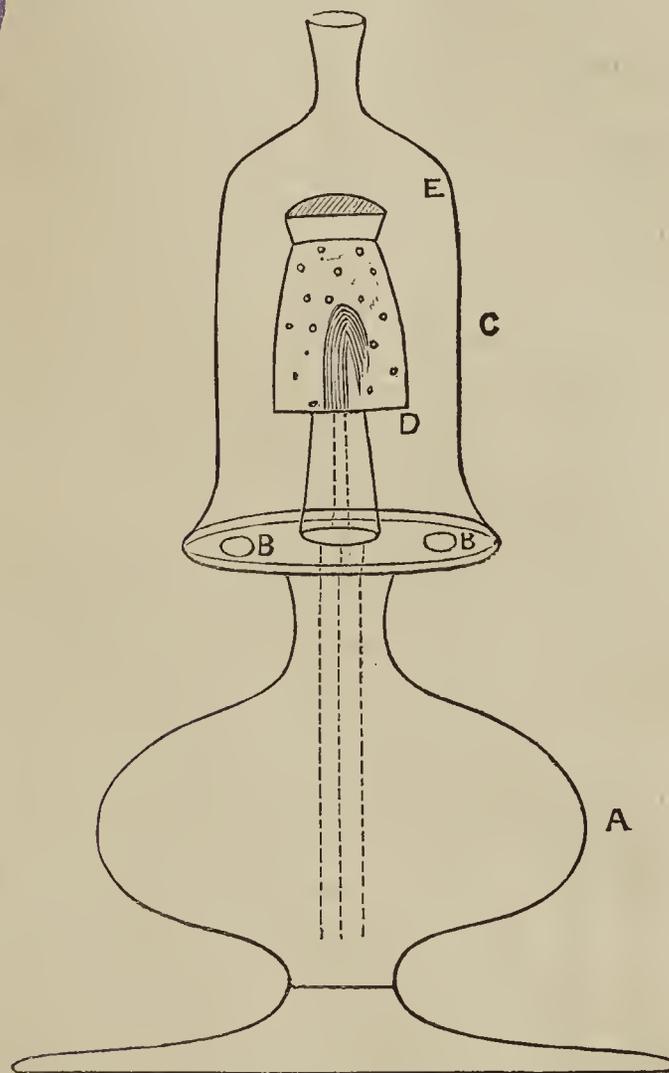
THIS peculiar form of gas-testing apparatus was introduced by the author at the commencement of the year, and is intended chiefly for the detection of suspected escapes of coal-gas when in confined spaces, such, for instance, as private houses, laboratories, &c.

Experiments with a view of studying more closely the condensing action of platinum when in various forms of division were the chief motor which led to the construction of the same. Thus, if asbestos (for convenience sake in the form of yarn) be introduced into a solution of platonic chloride, and, after drying, ignited in a closed crucible, the substance, as is well known, has conferred upon it the property of condensing gases upon its surface, due to the impregnation of what is known as platinum black. This method of rendering asbestos sensitive is, however, attended with several inconveniences, both on account of the disengagement of acid during ignition, thus rendering the texture rotten, and at the same time retarding surface-action by the formation of magnesium salts. To obviate these difficulties the writer has substituted with advantage for the chloride that of platonic oxalate, and by so doing has obtained a modified action of peculiar sensitiveness. This compound is readily procured by saturating asbestos yarn of finest quality with a strong solution of platonic oxalate, obtained by dissolving the hydrate of that metal in oxalic acid and, after drying, igniting the same in a porcelain crucible. If a sample of so-prepared asbestos be now introduced into a mixture of hydrogen and oxygen gases combination at once takes place, accompanied by the usual phenomenon; but if the said mixture be now substituted by one of coal-gas replacing the hydrogen, no action is the result. Withdraw now the sensitive wick and heat to 80° F. and replace the same in the mixture, quite a different result is at once obtained, the wick being quickly raised to incandescence, and continues as long as the slightest mixture of gas remains; so sensitive, in fact, is the reaction that 0.5 per cent by volume of coal-gas or other hydrocarbons, when in admixture with the atmosphere, is at once readily detected.

The subjoined figure, representing a section of the apparatus when in use, will perhaps serve to more clearly demonstrate the same, A serving as the basis or reservoir of the lamp, and containing petroleum spirit, which is employed as a fuel for the same, and surmounted by a gallery running round the upper part and pierced with two apertures at B B, intended to collect the air desired when applying the chimney, C. In using the apparatus the wick, consisting of platinised asbestos, is first inserted in its holder and a light applied to the same. The flame caused by the combustion of the petroleum spirit may be now conveniently extinguished, leaving the uppermost part of the wick red-hot, which continues to glow while any petroleum spirit remains in the reservoir. While the wick is still glowing there is placed over it the copper thimble, D, which is perforated with numerous small holes, and containing a further coil of platinised asbestos, E, in close proximity.

The reaction may thus be readily explained:—The heated asbestos, fed by the petroleum spirit, naturally produces sufficient heat to maintain the secondary coil at

to a temperature required for producing effects when in contact with hydrocarbons. If the so-prepared lamp be now introduced into a room where an explosive atmosphere is prevalent, the glass chimney at once samples



the atmosphere by causing an upward draught, the which, passing over the heated coil immediately raises the same to incandescence.

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

A METHOD FOR THE DETERMINATION OF
IODINE IN HALOID SALTS.*

By F. A. GOOCH and P. E. BROWNING.

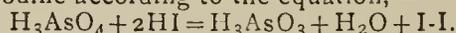
FEW problems of analysis have been more discussed than the estimation of iodine accompanying chlorine and bromine in haloid salts; and yet the constant succession of new processes is sufficiently indicative that the solution of the question is not generally regarded as satisfactorily settled. The method of Fresenius, according to which iodine is liberated by nitrous acid, collected in carbon disulphide, and titrated by sodium thiosulphate, finds ready acceptance for the determination of small amounts of iodine; but when the quantity of iodine to be estimated is considerable, the method is unwieldy. Probably the process most generally in use is that based upon the liberation of iodine by means of a ferric salt, and the titration of the distillate by one or other of the well-known iodometric methods. The latter method is fairly

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xxxix., March 1890

accurate, but the requirement of special apparatus for properly condensing the distillate is detrimental to rapidity and ease of execution. In this process the amount of iodine set free should be measured exactly by the reduction of the ferric salt, and were the ferrous salt produced in the course of the action sufficiently stable, the determination of its amount might be substituted for the titration of the iodine, and so the collection and further treatment of the distillate might be dispensed with; but ferrous salts are too sensitive to atmospheric influence to preserve under the conditions of this process their own degree of oxidation, and the amount of iron found in the ferrous condition cannot be made to serve as a trustworthy indication of the reducing action which actually takes place in the separation of the iodine. The advantage of replacing the collection and examination of the distillate by treatment of the residue is, however, so great as to constrain us to search for some substitute for the ferric salt, which, by virtue of easy reducibility, may act as a liberator of iodine from hydriodic acid, and, at the same time, by reason of stability after reduction, shall register accurately the quantity of iodine set free in the reducing process. The results of our experience are contained in the following account:—

Strong sulphuric acid, as is well known, acts upon an iodide in a way to liberate iodine at the cost of its own loss of oxygen, though by simple dilution of the mixture thus formed the action is reversed, the iodine going back into the form of hydriodic acid, and the products of the reduction of sulphuric acid again taking back their oxygen and re-forming the acid. In the presence of any substance easily reducible by the deoxidation products of sulphuric acid the liberation of iodine, by the action of that acid upon iodides, should take place without interference, and even more easily and completely than in the absence of such a substance, while the sulphuric acid should remain at the end of the process in its original form. If the products of reduction which appear in such a case in the place of those of the sulphuric acid should be neither readily oxidisable nor easily volatilisable, it ought to be possible to remove by heat the iodine set free in the action without disturbing the record kept of its amount by the reduced substance remaining in the residue.

The qualities of arsenic acid suggest it as a substance likely to possess just these qualities; for, though arsenious acid is converted into arsenic acid by the action of iodine in alkaline solution, in acid solution the reverse is true to at least a limited extent, and arsenic acid liberates iodine according to the equation,—



In company with sulphuric acid of such strength as to liberate the iodine from hydriodic acid, the reduction should fall in the end upon the arsenic, and the arsenious oxide produced should, under proper conditions, preserve the record of the iodine liberated and removed by volatilisation. We therefore undertook experimentation upon this line, and the accompanying table shows the results of a preliminary investigation of the mode of action of a mixture of sulphuric and arsenic acids upon an alkaline iodide. In making these tests a standard solution of potassium iodide was put into a test-tube, a solution of potassium arseniate was added, sulphuric acid mixed with its own volume of water was introduced, the volume of the liquid was adjusted, a film of kerosene 3 m.m. thick was placed upon the surface of the liquid, and the whole was gently heated and agitated. Kerosene was chosen in preference to other solvents of iodine on account of its lightness, which makes it float upon the mixture, and its high boiling-point, which permits the application of heat to hasten and complete the reaction. Its disadvantage is the persistency with which it adheres to the walls of the test-tube, so that washing with alcohol (or other solvent) after the completion of each test is necessary to prevent the transfer of the iodine of one test to the test next succeeding. The data of these experiments are indicated in the headings.

It will be noted that in Series A, in which the absolute amount of iodine employed, its proportion to the entire volume, and the amount of the arsenic salt remained the same, the proportion of sulphuric acid being the variable element, it is shown that the proportion of sulphuric acid should reach at least twelve parts by volume in one hundred of the solution in order that the maximum distinctness of the test may be developed. An excess of sulphuric acid beyond this proportion is not disadvantageous.

In Series B the proportion and absolute amount of iodine vary as well as the proportion of acid, while the quantity of arsenic remains invariable. The results of this series confirm those of the previous series as to the proper proportion of sulphuric acid to be used, and the sensitiveness of the test is shown to reach (in round numbers) one part by weight of iodine in six hundred thousand parts of the solution.

The tests of Series C indicate plainly that it is the sulphuric acid which is the potent agent in liberating the iodine, the experiment in which acetic acid was substituted for sulphuric acid being particularly noteworthy in this connection. The presence of arsenic acid increases the sensitiveness of the reaction, but its addition beyond a very moderate amount does not appear to be necessary or advantageous. The presence of a chloride or bromide does not impair the delicacy of the test.

The quantities of iodine taken in the experiments just described were necessarily small, and the question arises naturally as to whether the course of action would be similar in the presence of larger amounts of that substance and the correspondingly greater amount of arsenious oxide which is produced with its tendency to reverse the reaction according to which the elimination of iodine proceeds. The solution of this question was reached in the following experiments:—

To 50 c.m.³ of liquid containing 10 c.m.³ of sulphuric acid [1 : 1], and 1 c.m.³ of a decinormal solution of iodine in potassium iodide (0.001265 gm. of the former in 0.0018 gm. of the latter) was added 1 c.m.³ of a decinormal solution of arsenious oxide (0.00495 gm.), an amount ten times as much as would be necessary to convert the iodine into hydriodic acid were the solution alkaline. The colour of the iodine vanished gradually under the action of the arsenious acid, but was restored by the addition of 1 gm. of hydrogen potassium arseniate, and again dispelled by another portion of arsenious acid equal in amount to that introduced at first. Heat was applied at this point with the result that the colour of the iodine showed again faintly, and upon boiling the liquid until its volume decreased to 25 c.m.³ it became colourless and yielded no iodine when agitated with nitrous acid and chloroform.

An experiment differing from the last in that thirty times as much arsenious oxide and iodine were taken, gave similar results.

It is plain, therefore, that the arsenious acid and arsenic acid exert opposite effects under the conditions of these experiments, and that one or the other prevails according to the proportionate composition of the solution, the degree of dilution, and the temperature.

The experiments detailed in the following statement were intended to determine the conditions best adapted to eliminate the iodine from such quantities of potassium iodide as would ordinarily be dealt with in the course of analysis.

A solution of potassium iodide was placed in an Erlenmeyer beaker of 300 c.m.³ capacity, followed by a solution of potassium arseniate and by dilute sulphuric acid [1 : 1], and the volume of the liquid was diluted to about 100 c.m.³. A mark was put upon the beaker to indicate the level to which the liquid was to be reduced, a spiral of platinum wire was placed in the solution to prevent explosive ebullition, and the contents of the flask were boiled until the desired degree of condensation was reached. Colourlessness of the liquid at this point,

Series A.

KI. Grm.	Grms. of iodine to c.m.s. of solution.	H ₂ KAsO ₄ . Grm.	H ₂ SO ₄ [1 : 1]. C.m.s.	H ₂ SO ₄ (strong) in 100 parts by volume	NaCl. Grm.	KBr. Grm.	Total vol. C.m.s.	Reaction or iodine.
0'0001	1 : 132000	1	2	10 : 100	—	—	10	Faint.
0'0001	1 : 132000	1	2	10 : 100	—	—	10	Faint.
0'0001	1 : 132000	1	2.5	12.5 : 100	—	—	10	Faint.
0'0001	1 : 132000	1	2.5	12.5 : 100	—	—	10	Distinct.
0'0001	1 : 132000	1	3	15 : 100	—	—	10	Distinct.
0'0001	1 : 132000	1	4	20 : 100	—	—	10	Distinct.
0'0001	1 : 132000	1	4.5	22.5 : 100	—	—	10	Distinct.
0'0001	1 : 132000	1	5	25 : 100	—	1	10	Distinct.

Series B.

0'0005	1 : 26400	1	2.5	12.5 : 100	—	—	10	Distinct.
0'000133	1 : 99000	1	2.5	12.5 : 100	—	—	10	Distinct.
0'0001	1 : 198000	1	3	10 : 100	0'007	—	15	Faint.
0'000067	1 : 198000	1	2.5	12.5 : 100	—	—	10	Faint.
0'000067	1 : 198000	1	2.5	12.5 : 100	—	1	10	Faint.
0'0001	1 : 198000	1	5	16.6 : 100	0'005	—	15	Distinct.
0'0001	1 : 198000	1	5	16.6 : 100	0'005	—	15	Distinct.
0'0001	1 : 264000	1	2.5	6.25 : 100	—	—	20	Invisible.
0'0001	1 : 264000	1	2.5	6.25 : 100	—	—	20	Faint.
0'0001	1 : 264000	1	5	12.5 : 100	—	—	20	Faint.
0'000033	1 : 396000	1	2.5	12.5 : 100	—	—	10	Faint.
0'000033	1 : 396000	1	2.5	12.5 : 100	—	—	10	Faint.
0'000033	1 : 594000	1	5	16.6 : 100	0'005	—	15	Faint.

Series C.

0'0020	1 : 8000	1	None. Acetic acid 1.5 gm. (absolute).	—	—	—	12	Invisible.
0'0010	1 : 13200	—		5	25 : 100	—	—	10
0'0002	1 : 66000	—	5	25 : 100	—	—	10	Faint.
0'0010	1 : 13200	0.2	5	25 : 100	—	—	10	Marked.
0'0001	1 : 132000	0.2	5	25 : 100	—	—	10	Distinct.
0'000033	1 : 198000	0.5	1.25	12.5 : 100	—	—	5	Faint.
0'000033	1 : 198000	0.5	1.25	12.5 : 100	—	—	5	Faint.
0'0001	1 : 264000	2.0	4	10 : 100	—	—	20	Faint.
0'0001	1 : 264000	2.0	6	15 : 100	—	—	20	Faint.

though a fair indication of the absence of free iodine, is no indication that the hydriodic acid has been completely decomposed, and so, in the event of finding the liquid colourless, it was first cooled and shaken with chloroform to prove or disprove the absence of free iodine, and then tested for the presence of hydriodic acid by shaking with nitrous acid and chloroform.

An inspection of these results shows at once that when the larger amounts of iodine are to be eliminated the proportion of sulphuric acid to the final volume after boiling needs to be increased somewhat beyond that which is necessary to set free very small portions, such as were dealt with in the experiments of the earlier series.

(To be continued).

SOME POINTS IN THE DETERMINATION OF SILICA IN SILICATES BY FUSION WITH ALKALINE CARBONATES.*

By JAMES P. GILBERT, S.B.

(Concluded from p. 272).

THE fourth point considered was the possibility of obtaining the silica in a purer state, that is to say, to decrease the amount of the residue left after treatment with hydrofluoric acid. This residue may be due to imperfect washing, or to the fact that alumina has been rendered insoluble

in hydrochloric acid by prolonged heating to a high temperature. The higher residues obtained in the cases in which the silica was heated to 280° C. point to the latter possibility. But it is not improbable, as will be mentioned later on, that under certain conditions the silica may enclose alkaline salts so that it is impossible to remove them completely by washing.*

In an interesting article by Lindo,† on the analysis of glass, I met the recommendation that the watery solution of the fusion be diluted to a very large bulk, so that on acidifying with hydrochloric acid there shall be no precipitation of silica. In this way he obtained, on evaporation, what he called "vitreous silica," in distinction from the ordinary "amorphous silica." This vitreous silica, he says, is so easily washed that time is gained in the analyses to compensate for that lost in the evaporation of the solution. Lindo takes it for granted that one cannot get all the silica by the ordinary process of dehydration, and that the last traces of it cannot be got out of the filtrate unless there is sufficient iron oxide or alumina present to effect its complete precipitation. In the analysis of glass, he added a known amount of ferric chloride to the filtrate from the alumina, and by precipitating this iron with ammonia the last traces were obtained.

The following analyses of glass were made according to his directions. The powdered glass, about 1 gm., was

* In this connection it is interesting to note that all the residues left on treatment with hydrofluoric acid, in the two slags analysed, contained manganese, which may point to an insoluble compound of manganese with the alkaline salts.

† CHEMICAL NEWS, vol. lx, No. 1546.

fused with 5 grms. of sodium and potassium carbonates, and the mass treated with about 400 c.c. of boiling water until it was thoroughly disintegrated. On acidifying with hydrochloric acid, a clear solution was obtained. This was evaporated to dryness on a water-bath, heated to 125° C., and, as recommended by Lindo, the silica thus obtained again fused and treated as before. This silica obtained from the second fusion was weighed, and then treated with hydrofluoric acid. The two filtrates were combined and evaporated to dryness, heated to 125° C. for one hour, and the residue, insoluble in hydrochloric acid and water, filtered off; this is given in the third column. The first three analyses are of German "half-white" glass; the last two, of Bohemian white glass.

TABLE IV.—*Determinations of Silica in Glass. (Lindo's Method).*

	I. Silica obtained after two fusions. Per cent.	II. Residue from Column I. with hydro- fluoric acid. Grm.	III. Silica ob- tained from the filtrates. Grm.	IV. Total silica. Per cent.
1.	73.03	0.0003	0.0058	73.58
2.	71.81	0.0008	0.0125	73.06
3.	72.50	0.0004	0.0084	73.22
4.	71.96	0.0000	0.0051	71.43
5.	71.25	0.0007	0.0060	71.70

In this case it is seen that a considerable portion of the silica fails to be dehydrated by one evaporation and heating to 125° C. The silica obtained in this way is very compact, and the washing, as claimed by Lindo, is very easily done. The purity of the silica thus obtained (shown by the small residue left on treatment with hydrofluoric acid) is doubtless in part due to the facility with which the silica is washed; for it is conceivable that, when the silica is separated from a concentrated solution of alkaline salts, it may enclose particles of the liquid which may not be easily washed out. But this high purity, as compared with the silica obtained from the slags and the felspar, may be due to the absence of any large amount of alumina in the glass.

To see what would be the character of the silica obtained from the first slag by large dilution of the solution of the fused mass before acidifying, the following determinations were made:—

TABLE V.—*Amount of Foreign Matter in Silica obtained from Lime Slag. (Lindo's Method).*

	I. Weight of silica obtained from slag. Grm.	II. Residue from Column I. with hydrofluoric acid. Grm.	
1.	0.2755	0.0008	Silica obtained by evaporation to dry- ness on water-bath.
2.	0.2610	0.0010	
3.	0.2871	0.0008	Silica obtained by evaporation to dry- ness and heating to 125° C.
4.	0.2683	0.0012	
5.	0.2506	0.0036	Silica obtained by evaporation to dry- ness and heating to 280° C.
6.	0.3113	0.0043	

These figures would seem to justify the inference that in the presence of considerable alumina it is not possible, even by large dilution, to get as pure silica as is easily obtained when only salts of the alkalies or alkaline earths are present.

The foregoing determinations confirm the statement that the ordinary process of fusion with alkaline carbonates and evaporation to dryness cannot always be relied on to render all the silica insoluble. No experiments were made to determine the effect of repeated evaporations to dryness with hydrochloric acid.

When the evaporation is carried out in the presence of free sulphuric acid the results are more satisfactory, but, as Craig says, the amount of alkaline sulphates introduced seriously interferes with the determination of the bases present.

A comparison of results obtained from a sample of quartz by evaporation with hydrochloric and sulphuric acids is given below.

Silica by evaporation to dryness with hydrochloric acid and heating to 120°. Per cent.	Silica by evaporation to dryness with sulphuric acid. Per cent.
98.95	99.43
98.60	99.67
98.79	99.51
	99.70

In these determinations I followed Lindo's recommendation of diluting largely before acidifying, and the residue left, on treatment with hydrofluoric acid, was very small. The first two determinations by sulphuric acid were done by decomposing the dilute watery solution of the fusion with hydrochloric acid, evaporating to dryness, and then adding strong sulphuric acid in excess and heating on an iron plate until copious fumes of sulphuric acid were given off for several minutes. The silica was in appearance the same as obtained by Lindo's method with the aid of hydrochloric acid only. But in the last two the watery solution of the fusion was decomposed directly by sulphuric acid in considerable excess, and then evaporated as before. The silica obtained in this way was very bulky and gelatinous.

These results seem to justify the recommendation that has been made; namely, that in the analysis of silicates the silica is best determined by dehydration with sulphuric acid (in cases where it is not inadmissible by the presence of lime, barium, lead, &c.), and that the bases should be determined, after the decomposition of the silicate, by hydrofluoric acid.

THE ELECTROLYSIS OF METALLIC PHOSPHATES IN ACID SOLUTION.*

By EDGAR F. SMITH.

SOME experiments on the action of the current upon metallic phosphates have been published by Moore,† and more recently Brand‡ has communicated his experience with the pyrophosphates dissolved in an excess of sodium pyrophosphate and also in ammonium hydroxide or carbonate. The experiments in this paper relate wholly to the deposition of metals from the solutions of their phosphates in normal phosphoric acid. The course pursued in the preparation of the solutions for electrolysis was to first precipitate the metals with an excess of disodium phosphate, dissolving the compound obtained in a measured volume of free phosphoric acid (sp. gr. 1.347), and then exposing this liquid to the action of currents of known strength. When operating upon mercuric solutions, prepared in the manner indicated, the deposition of the metal in the early part of the experiment was perfectly satisfactory, but as the decomposition advanced, a heavy white precipitate appeared in the solution, and, although it gradually suffered reduction, the metal that separated was so fluid-like that it mechanically carried down impurities, hence was unfit for electrolytic determinations, and the experiments in this direction were consequently suspended. Mercurous phosphate proved to be insoluble, or nearly so, in phosphoric acid. This is also the case with bismuth and lead phosphates, therefore neither of these metals was available in the proposed experiments.

* *American Chemical Journal*, xxii., No. 5.

† *CHEM. NEWS*, liii., 209.

‡ *Zeit. für Anal. Chem.*, xxviii., 581.

Copper.

To a solution containing 0.0996 gm. metallic copper, as sulphate, 10 c.c. Na_2HPO_4 (sp. gr. 1.0358) and 3½ c.c. H_3PO_4 (sp. gr. 1.347) were added. The precipitated copper phosphate, dissolved in ½ c.c. of acid, so that the deposition of metal occurred in the presence of 3 c.c. of free phosphoric acid. The total dilution with water amounted to 125 c.c. The current employed gave 0.15 c.c. oxyhydrogen gas per minute. The copper deposit weighed 0.0997 gm. The metal precipitation was allowed to continue through the night. Later, two additional experiments were arranged in every respect similar to the one just described, increasing the current, however, to 0.5 c.c. oxyhydrogen gas per minute. The copper found was in (a) 0.0990 gm., and in (b) 0.0994 gm. The addition of an excess of ammonium hydroxide to the filtrates did not produce the slightest blue colouration. The metallic copper from the above experiments showed a rich red colour. The metallic lustre observed upon the metal deposited from solutions containing other free acids, e.g., HNO_3 , was not noticed here. That the conditions of the preceding depositions will answer for the separation of copper from other metals is evident from the results recorded below. Strong currents deposit metallic iron and other metals from their phosphates in phosphoric acid solution, while they are unaffected by the feebler currents.

Copper from Iron.

A solution containing 0.0996 gm. metallic copper, 0.1700 gm. metallic iron, 30 c.c. Na_2HPO_4 (sp. gr. 1.0358), and 4½ c.c. H_3PO_4 (sp. gr. 1.347) were diluted to 125 c.c. with water and exposed to the action of a current generating 0.6 c.c. oxyhydrogen gas per minute. The deposited copper weighed 0.0996 gm. Additional experiments verified this result. The filtrates contained no copper.

Copper from Aluminium.

Here the quantity of copper was the same as before, while the aluminium metal was 0.1000 gm., 20 c.c. Na_2HPO_4 (sp. gr. 1.0358) with 3 c.c. H_3PO_4 (sp. gr. 1.347). The total dilution was 100 c.c. The current gave 0.3 c.c. oxyhydrogen gas per minute. The copper deposited weighed 0.0995 gm.

Copper from Chromium.

Both metals were added as sulphates, the quantity of metallic chromium being in excess of that of the copper. The volume of alkaline phosphate was 20 c.c., and that of the phosphoric acid 3 c.c. The final dilution and current strength were the same as in the separation of copper from aluminium. The deposition was made during the night. The metal obtained equalled 0.0994 gm. It was brilliant red in colour, similar to that noticed frequently by chemists in the separation of these two metals from each other. The chromium was oxidised to chromic acid. The filtrate gave no indication of unprecipitated copper. A duplicate experiment afforded a similar result.

Copper from Zinc.

In this separation there were present 0.1500 gm. metallic zinc and alkaline phosphate and free phosphoric acid in the same quantities as with aluminium and chromium. The dilution was 100 c.c., while the current gave but 0.15 c.c. oxyhydrogen gas per minute. The deposited copper weighed 0.0993 gm. The filtrate gave no colouration upon the addition of an excess of ammonium hydroxide.

Copper from Cobalt.

With 0.0968 gm. cobalt and conditions similar to those just given under copper and zinc, except that the current had increased to 0.22 c.c. oxyhydrogen gas per minute, the deposited metal was found to be 0.0995 gm.

Copper from Nickel.

The nickel (0.1105 gm.) was present as chloride, while the conditions of experiment were similar to those in the preceding example. The deposit of copper weighed 0.0996 gm.

In all of the experiments given above the copper deposited rapidly from the cold solutions. Before interrupting the current the acid liquid was syphoned off and replaced by water. The deposits were washed with cold and hot water. Alcohol and ether were not used. The drying was done upon a warm iron plate. The current employed was obtained from ten ordinary "crowfoot" cells. In each experiment the poles of the battery were about ¾ inch apart.

Cadmium.

As this metal deposits from solutions containing free sulphuric acid,* it was expected that the same would occur in the presence of free phosphoric acid. This is proved by the following experiments:—10 c.c. cadmium sulphate (=0.1827 gm. Cd) were precipitated by an excess of Na_2HPO_4 (sp. gr. 1.0358) and the phosphate dissolved in 1½ c.c. H_3PO_4 (sp. gr. 1.347). Total dilution, 100 c.c. The current gave 0.6 c.c. oxyhydrogen gas per minute. Two determinations were made in this way. The found metal was in (a) 0.1839 gm., and in (b) 0.1820 gm. The (a) deposit showed a little sponginess, and this doubtless caused it to give a higher result than required by the theory. The filtrates from these deposits gave no cadmium reactions upon applying the usual tests for that metal. In two other determinations, where the only change made in the conditions of experiment was the reduction of the current to 0.40 c.c. gas per minute, the deposited cadmium weighed in (a) 0.1828 gm. and in (b) 0.1833. These figures indicate complete deposition, and that the method is reliable. Cadmium does not, however, deposit as rapidly as copper under like circumstances. It was also found advisable towards the close of the experiment to increase the current strength. The acid liquid should always be removed from the dish in which the deposition occurs before the current is finally interrupted. The deposits were washed and dried as described with copper.

Cadmium from Zinc.

0.1827 gm. cadmium and 0.1500 gm. zinc (both as sulphates) were precipitated by 40 c.c. disodium phosphate, dissolved in 3 c.c. H_3PO_4 (sp. gr. 1.347) and acted upon in the cold for twelve hours with a current giving 0.35 c.c. oxyhydrogen gas per minute. The cadmium deposit weighed 0.1820 gm. The entire dilution was 125 c.c. With a second cadmium solution (=0.1057 gm. Cd) together with the same quantity of zinc as before, 20 c.c. Na_2HPO_4 (sp. gr. 1.0358), 3 c.c. H_3PO_4 (sp. gr. 1.347), and 100 c.c. water, 0.1060 gm. cadmium was obtained. This deposit was crystalline, but in spots slightly spongy, which may account for its being somewhat higher than the theoretical. Two more separations of these metals were made, with a reduction of the phosphoric acid from 3 c.c. to 2 c.c., otherwise the conditions remained as before, and the cadmium obtained was in (a) 0.1057 gm. and in (b) 0.1051 gm. The current strength in these depositions was 0.37 c.c. oxyhydrogen gas per minute in each dish. *b* is low; its filtrate gave a trace of cadmium sulphide upon testing with hydrogen sulphide. My experience has been that in experiments such as these it should never be omitted to increase the current for about one hour previous to the final disconnection.

Cadmium from Nickel.

Only two experiments were made with these metals. They were conducted in the same manner as those with zinc and cadmium. The cadmium found was in (a) 0.1059 gm., and in (b) 0.1051.

* *American Chemical Journal*, ii., 41.

Cadmium from Iron.

The quantities of the metals were 0.1700 grm. iron and 0.1057 grm. cadmium. The alkaline phosphate and phosphoric acid were the same as with cadmium and zinc. Total dilution, 100 c.c. Current, 0.37 c.c. oxyhydrogen gas per minute. The deposited cadmium weighed in (a) 0.1058 grm. and in (b) 0.1062 grm.

Cadmium from Chromium.

In this separation the conditions were the same as with the preceding metals. Found cadmium was 0.1055 grm. The deposit was spongy, and the reduction of the strength of the current seemed not to remove this undesirable feature.

Cadmium from Aluminium.

The quantity of cadmium present was 0.2120 grm., while the aluminium was in equal amount. The alkaline phosphate, free phosphoric acid, total dilution, and current strength were the same as with zinc and iron. The results obtained were in (a) 0.2122 grm. Cd and in (b) 0.2120 grm. Cd.

The separation of copper from the metals mentioned in connection with it was not attended by any difficulty whatever, but with cadmium, compliance with the conditions mentioned was absolutely required, otherwise the results varied. In solutions containing free phosphoric acid, cadmium is unusually inclined to sponginess, so that concentration of liquid should be avoided, and the poles of the acting battery should not approach too closely to each other. The most favourable separation was found to be $1\frac{1}{2}$ inches and the proper dilution of the liquid 100—150 c.c. Such, at least, was the case in the separations just described.

Copper from Cadmium.

These metals have been separated from each other in the presence of free nitric acid,* and also in the presence of free sulphuric acid.† From the results about to be given, their separation in the presence of free phosphoric acid is also possible. Two experiments were conducted under the following conditions:—0.2452 grm. copper as sulphate, 0.1827 grm. cadmium as sulphate, 20 c.c. Na_2HPO_4 (sp. gr. 1.0358), and 10 c.c. H_3PO_4 (sp. gr. = 1.347), with a total dilution of 125 c.c., were exposed to the action of a current generating 0.10 c.c. oxyhydrogen gas per minute for a period of twelve hours, when the following amounts of metallic copper were obtained:—in (a) 0.2451 grm. and in (b) 0.2452 grm. In a third experiment, with double the amount of copper present, the current was allowed to act through the night, and the deposited metal weighed 0.4904 grm. Again, with a current liberating 0.2 c.c. oxyhydrogen gas per minute, conditions in all other respects similar to those previously mentioned, the found copper was 0.2451 grm. Cadmium was not detected in these deposits. The filtrates showed no trace of copper.

Silver phosphate is readily dissolved by phosphoric acid, but from such solutions even the feeblest currents deposit the metal in a spongy condition, so that it was useless in the quantitative work. But from an ammoniacal solution of the phosphate the deposition of silver metal is quite rapid and satisfactory. Two experiments gave, with a current liberating 0.20 c.c. oxyhydrogen gas per minute, in (a) 0.1065 grm. and in (b) 0.1061 grm. Ag, the required being 0.1062 grm. Ammonia just sufficient to dissolve the phosphate is all that should be used. As I have not observed this mode of depositing silver described in the literature of electrolysis I include it here, although it is only to the department of acid phosphate solutions that I wish to direct attention. The behaviour of lead phosphate in alkaline solution has

been recorded by me.* The results given are quite satisfactory. As already remarked, its phosphate being insoluble in phosphoric acid excludes experimentation in that direction.

One of the most interesting observations made in this study of acid phosphates and the electric current is that with manganese. It is well known that from nitric or sulphuric acid solution this metal is deposited as dioxide by the current. In the presence of phosphoric acid, where there is a decided excess of the latter, the deposition of dioxide upon the positive pole does not take place. This behaviour has enabled me to present the following separations of copper from manganese:—

1. 0.1770 grm. copper as sulphate, 0.1500 grm. manganese as sulphate, 30 c.c. Na_2HPO_4 (sp. gr. 1.0358), 10 c.c. H_3PO_4 (sp. gr. 1.347) with a total dilution of 120 c.c., were exposed to the action of a current giving 1 c.c. oxyhydrogen gas per minute. Copper found equalled 0.1765 grm.

2. The conditions the same as in (1), except that the current gave 1.4 c.c. oxyhydrogen gas per minute. Found copper weighed 0.1770 grm. The positive pole showed no dioxide deposition. When the current exceeded that given in (1) and (2) a pink colouration was observed about the anode. This non-precipitation of the manganese is very likely due to the formation of the phosphate of the sesquioxide, which is only decomposed, and then but partially, by much more powerful currents than were used in this separation.

The behaviour of other metallic phosphates in acid solution is receiving attention in this laboratory.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

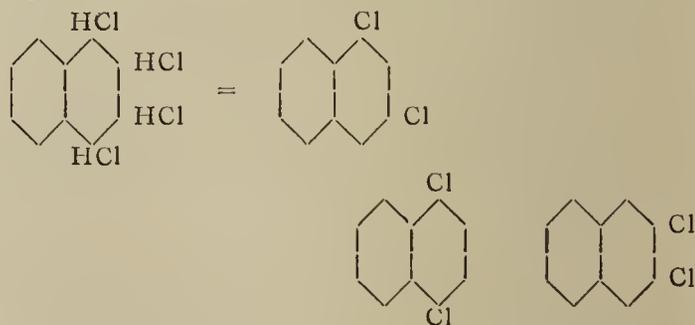
Ordinary Meeting, May 15th, 1890.

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

(Concluded from p. 275).

39. "The Chlorides of Naphthalene and its Derivatives, and the Manner in which they are Decomposed by Alkalies." By HENRY E. ARMSTRONG and W. P. WYNNE.

It being established that α -dichloronaphthalene is the homo- $\beta\beta$ -modification, it follows that naphthalene tetrachloride affords the three theoretically possible dichloronaphthalenes.



The 1:3 compound is produced in largest, the 2:3 in smallest, quantity.

Hitherto it has always been supposed that the dichloride which is the initial product of the interaction of naphthalene and chlorine decomposes only in one way, yielding α -chloronaphthalene; the authors find that β -chloronaphthalene is also produced. They have been led to this discovery by further study of the isomeric acid obtained in small quantity together with 1:4 chloronaphthalenesulphonic acid from α -chloronaphthalene by Armstrong

* *American Chemical Journal*, ii., 42.

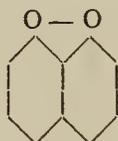
† *Ibid.*, xii., 110.

* *Proceedings Am. Phil. Soc.*, 1887.

The β -sulphonic acids are probably the most "degraded" products, and from this point of view the further study of the behaviour of the 1:4'- α chlorosulphonic acid and of the 1:1':4- $\alpha\alpha$ -dichlorosulphonic acids, as well as that of the 2:1' and 2:4'- $\alpha\beta$ - and 2:3 and 2:3'- $\beta\beta$ -dichlorosulphonic acids, will be of special interest, in order to ascertain whether or no the determining factor is the tendency of the molecule to acquire a configuration which most nearly approaches symmetry.

41. "A Third Naphthaquinone." By R. MELDOLA, F.R.S., and F. HUGHES.

In preparing monobromindone by the action of fuming nitric acid on dibrom- α -naphthol (*Proc. Chem. Soc.*, 1890, 57), a small quantity of a by-product is obtained which remains undissolved in alcohol on treating the crude indone with this solvent; a sufficient quantity of this substance has been obtained by the authors to enable them to identify it as a new naphthaquinone. The pure substance forms slender pale yellow needles, having no distinct melting-point, but blackening about 22c°. It is not reduced by sulphurous acid solution, but by treatment with zinc-dust and acetic acid it is converted into a dihydroxynaphthalene crystallising in whitish needles which become slate-coloured on exposure to the air and have no definite melting-point, but darken about 205°. The dihydroxynaphthalene has all the properties of a phenol, and is readily re-converted into the quinone by oxidation. Its diacetyl derivative fuses at 226—227°. On oxidation with alkaline permanganate it affords 1:2:3 hydroxyphthalic acid, $C_6H_4(CH)(COOH)_2$ (m. p. 194—197°), and hence the authors conclude that the quinone is the unknown peri-derivative:—

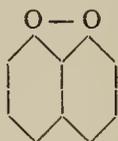


The formation of this quinone during the oxidation of dibrom- α -naphthol by nitric acid cannot at present be explained; but the authors suggest that in the bromination of α -naphthol a minute quantity of peri-monobrom α -naphthol is produced, and that this is converted into the quinone by the action of nitric acid.

Experiments to test this explanation are in progress.

DISCUSSION.

Dr. ARMSTRONG said it appeared to him that, regarding the quinones as diketones, four true quinones could not be derived from naphthalene; the new compound described by the authors either had the constitution indicated by the formula which they had suggested,—



or it was a keto-compound of higher molecular weight, viz.:—



Judging from its properties, this latter explanation appeared the more probable. It would, perhaps, be possible to decide this question by means of the Raoult method. The compound was of a novel type, and was one of great interest. The speaker also expressed the opinion that the formula assigned to the bromindone anilide which Professor Meldola had exhibited (*Chem. Soc. Trans.*, 1890, 399) did not satisfactorily account for its colour.

Dr. QUINCKE drew attention to Graebe and Veillon's experiments on the oxidation of acenaphthalene, and his own on nitroperinaphthaquinone; he thought that the

compound obtained by the former chemists was the quinone now described by Professor Meldola and Mr. Hughes.

Mr. GROVES, in reference to Dr. Armstrong's statement that the new substance was not a true quinone, remarked that the same had been said of β -naphthaquinone at the time of its discovery; it was a quinone notwithstanding. The new quinone, certainly, like dinaphthyl- β -diquinone, was very sparingly soluble in most solvents; but, on the other hand, it could easily be obtained in well-formed crystals, whilst the diquinone was a crystalline powder.

Professor MELDOLA stated that the limitation of the term quinone to such compounds as could be represented as diketones was quite arbitrary, and he thought it justifiable to apply the name to all four dioxy-derivatives of naphthalenes indicated by theory. It was for a long time undecided whether the quinones were peroxides or diketones, and even now the question could not, in his opinion, be regarded as definitely settled. He did not think the alternative formula suggested by Dr. Armstrong was more probable than their own, but the decision of the question by Raoult's method would be attempted, although he feared the extreme insolubility of the compound in most solvents would interpose great practical difficulties. The objection raised against the formula of bromindone anilide was of too general a nature to be met, especially in the absence of any alternative suggestion. He was not aware that any chemical formula could be written so as to account for the colour of an organic compound. It was well known that all the anilides of quinone were highly coloured bodies, and the formula proposed was the only one which satisfactorily represented the formation and properties of the compound in question. With respect to Dr. Quincke's observation, Professor Meldola expressed his acquaintance with the work referred to, and stated that reference had been made to it in their paper (*Chem. Soc. Trans.*, 1890, 398). The compound described by Graebe and Veillon had had the formula $C_{24}H_{14}O_2$ ascribed to it by those authors (*Ber.*, 1887, 659).

42. "The Relative Antiseptic Powers of Isomeric Organic Compounds." By THOMAS CARNELLEY, D.Sc., Aberdeen, and W. FREW, Dundee.

The authors have determined the relative antiseptic powers, in reference to ordinary aerial micro-organisms, of a number of isomeric organic compounds, more particularly di-derivatives of benzene, with the object of investigating the influence of atomic arrangement on this property.

A table of results is given which indicate that, so far as the compounds which have been tried are concerned (and with the exception of the hydroxybenzoic acids), para-compounds are more antiseptic than the corresponding ortho- and meta-compounds. On the whole, compounds containing the carboxyl-group are comparatively weak, while phenols and nitro-compounds are relatively strong antiseptics; paranitrophenol being, with the exception of α -naphthol, the most powerful of any of the compounds tried. These results entirely accord with those of Wolcott Gibbs and Hare, who have recently investigated the poisonous action of di-derivatives of benzene on dogs.

43. "Note on the Preparation of Pyrocatechol." By W. H. PERKIN, Jun., Ph.D.

The very high price of pyrocatechol renders it desirable to discover improved methods of preparing it; the author has, therefore, studied the action of iodhydric acid on guaiacol, which is easily procured at a moderate cost. He finds that an almost theoretical yield of pyrocatechol may be obtained by boiling guaiacol with a fuming solution of hydrogen iodide; details are given in the paper.

44. "Benedikt's Acetyl Values." (Second Notice). By J. LEWKOWITSCH, Ph.D.

The results quite recently brought forward by the author (*Proc. Chem. Soc.*, 1890) were so unexpected that it was determined to verify them by examining other fatty

acids; capric, lauric, and cerotic acids were therefore acetylated in the manner previously stated. The approximate purity of the acids used was ascertained by determining the quantity of caustic potash required for their saturation.

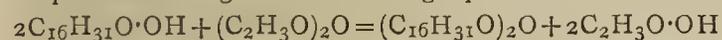
Capric Acid.—The acid value was found to be 318.65, while theory requires 326.2. The acetylated product gave an acid value of 176.4, and a saponification value of 350.4; consequently an acetyl value = 174.

Lauric Acid.—The acid value found was 273.02, the theoretical value being 280.5. The acetylated acid gave an acid value = 161.5, a saponification value = 293.99; its acetyl value therefore was 132.49.

Cerotic Acid.—The acid value found was 128.4; theory indicates for $C_{26}H_{52}O_2$ 141.6 (or for $C_{27}H_{54}O_2$ 136.8). The acetylated cerotic acid gave an acid value = 73.87, a saponification value = 142.1; so that the acetyl value was 68.23.

From the approximate coincidence of the acetyl value of capric acid (174) with the acid value of the acetylated acid (176.4), it might be inferred that the acetylated capric acid contains one acetyl-group, but an acid of the formula $C_{10}H_{19}O_2 \cdot C_2H_5O$ has a theoretical acid value of 262. Similarly, the value for a mono-acetyl derivative of lauric acid would be 231, and that for a mono-acetyl derivative of cerotic acid 128 (resp. 124). (The same formulæ would apply to mixed anhydrides of acetic acid and capric acid, &c.). It was easy to decide whether the action of acetic anhydride on fatty acids affected the COOH-group of the latter, for in that case an alcohol of the $C_nH_{n+2}O$ series ought not to become acetylated. The author experimented on cetyl alcohol, which was treated with acetic anhydride. The acid value of the resulting substance was—as is to be expected—*nil*; the saponification value found was 192.65. As a substance of the formula $C_{16}H_{33}O \cdot C_2H_5O$ has theoretically a saponification value = 198, it is evident that simply etherisation of the cetyl alcohol has taken place.

It was therefore to be supposed as the mixed anhydrides of the higher fatty acids and acetic acid could not have been formed, that by the interaction of acetic anhydride and the higher fatty acids the anhydrides of the latter had been produced—taking palmitic acid as an example—according to the following equation:—



In that case the quantities of caustic potash required by the equation $(C_{16}H_{31}O)_2O + 2KOH = 2C_{16}H_{31}O \cdot OK + H_2O$ ought to agree with the saponification values found. The following Table gives the quantities of caustic potash required by theory, in m.grms, compared with the quantities actually used in the above experiments:—

	Mol. wt.	Theory.	Exper.
Capric anhydride, $(C_{10}H_{19}O)_2O$..	326	344	350.4
Lauric anhydride, $(C_{12}H_{23}O)_2O$..	242	294	293.99
Palmitic anhydride, $(C_{16}H_{31}O)_2O$..	494	227	226.13
Stearic anhydride, $(C_{18}H_{35}O)_2O$..	550	204	221.18
Cerotic anhydride, $\left\{ \begin{array}{l} (C_{26}H_{51}O)_2O \\ (C_{27}H_{53}O)_2O \end{array} \right.$	774	145	142
	818	137	
Oleic anhydride, $(C_{18}H_{33}O)_2O$..	546	205.4	242

Considering the approximate purity of the acids used, the theoretical values agree very well with the experimental values; and it may be pointed out that with pure material it would be easy by this method to determine which is the formula of cerotic acid.

In the light of this explanation, the "acid values found for the products of the interaction of acetic anhydride and fatty acids lose every quantitative meaning; these values have only been found as the "acetylated" acids were dissolved in cold absolute alcohol for titration with potash, which hydrolysed at once the anhydrides; hydrolysis ceasing only when a limit is reached which depends on the quantity of alcohol present, and the nature and dilution of the standard solution, in some experiments half normal soda, in others decinormal potash. Had the

substances been shaken up with water (hot water does not decompose them), on the first drop of potash falling into the mixture the pink colour would have appeared at once, or very soon, when the limit for the system of substances was reached. It is hardly necessary to state that experiments carried out in this direction fully bear out the correctness of the author's conclusions. Thus the interaction of KOH or NaOH and the anhydrides in aqueous solution affords an elegant illustration of that class of actions which require a measurable time for their completion. The anhydrides of the higher fatty acids are now within easy reach, as they can be prepared in a very short time by means of acetic anhydride.

PHYSICAL SOCIETY.

June 16, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

MR. H. TOMLINSON, F.R.S., read a paper on "The Effect of Change of Temperature on the Villari Critical Points of Iron."

This, he said, was a continuation of the paper he read before the Society on March 21, and the method employed was the same as then described (see *Phil. Mag.*, vol. xxviii., p. 394). Since then, however, he has made experiments at various temperatures up to 285° C., the temperature being determined from the resistance of a platinum wire whose temperature coefficient was carefully determined. The following table shows some of the results obtained with a well annealed iron wire 1 m.m. in diameter, which had been repeatedly heated up to 300° C. and cooled to the temperature of the room until the temporary permeability with various loads attained constant values at both temperatures:—

Magnetising Force in C.G.S. Units.	Load in kilogrms. for which permeability is the same as for unloaded wire at temperature—					
	12° C.	76° C.	167° C.	244° C.	285° C.	
2.84	4.7	5.0	5.3 and 12	5.7 and 10	None.	
3.70	2.5	3.2	3.6	4.2	11.5	4.7 and 9.9
4.8	1.8	2.5	2.7	—	3.1	12.3
7.69	None.	None.	None.	None.	None.	
10.40	"	"	"	"	"	
15.32	"	"	"	"	"	

Curves from which these numbers were obtained are given in the paper, and in these load in kilogrms. and percentage change of temporary permeability are plotted. From the curves and Table it was seen that if the first points in which the curves cut the load line be considered, then at all temperatures the Villari values increase as the load decreases. If, however, the second points be taken, the critical values increase both with load and temperature. In both cases the Villari value is increased by rise of temperature. From the curves it follows that rise of temperature reduces the total variation of permeability produceable by loading. A table showing the temporary permeability of the unloaded wire at the various temperatures accompanies the paper.

A paper "On the Diurnal Variations of the Magnet at Kew," by W. G. ROBSON and S. W. J. SMITH was communicated by Prof. Rücker.

In some preliminary remarks the Professor pointed out the great advisability of having the results of magnetic observations at various observatories reduced and published in the same manner and for the same periods. In order that this may be effected the methods of reduction must be reliable but not very elaborate. The Greenwich plan is too laborious to be generally adopted, but the method suggested by Dr. Wild (*Rep. Brit. Ass.*, 1885, p. 78), in which the mean diurnal variation is obtained from measurements on five quiet days in each month, is feasible. With a view to further testing the reliability of this method the work described in the paper was under-

taken. Mr. Whipple had made a comparison of the two methods for the years 1870—71—72, with the result shown in the following table:—

$K_s - K_w = 0.7'$ (minutes of arc)	} Where K_s is the mean diurnal range at Kew as obtained by Sabine's method. K_w the mean diurnal range at Kew as obtained by Wild's method. And G the mean diurnal range at Greenwich by the Greenwich method.
$G - K_s = 1.2'$	
$G - K_w = 1.6'$	

He also found that the mean hourly differences followed some definite law.

The authors undertook the reduction of the Kew observations according to Wild's method for the years 1883, 1886—87; the first was chosen as being a year of maximum sun spots. The results give:—

1883.. ..	$G - K_w = 1.5'$
1886.. ..	" = 1.2'
1887.. ..	" = 1.9'

There is thus a difference of nearly two minutes in the variations at the two places, and this cannot all be accounted for by the method of reduction. Another peculiarity is that the range, as calculated by Wild's method, is greater by about 0.5' than that obtained by Greenwich method, although the latter includes days of moderate disturbance. The total range at both places has diminished by about 1.6' between 1883 and 1887. The paper is accompanied by tables and curves plotted from the differences in the mean hourly readings at Greenwich and Kew for each of the above six years, and a marked similarity exists between all of them. The mean of the six curves differs in no case by more than 0.4' from the curve for any year. It is thus possible to calculate the Greenwich values from the Kew numbers, and as these latter are published about two years sooner than the former, this fact may be very important.

Referring to the reduction of results, Prof. RÜCKER said that the Stonyhurst observers and Prof. Mascart were willing to adopt Wild's method; Falmouth, he hoped, would follow suit, and Greenwich had been asked to publish their results in both ways.

Mr. WHIPPLE said that before recording instruments were available, and the numbers were obtained from separate experiments, the labour involved was considerable, and a single large disturbance or magnetic storm might vitiate the result of a whole year's work. Methods were therefore adopted to eliminate these disturbances; of these, that used by Sabine may be particularly mentioned. Although declination records have now been obtained for a considerable number of years, the cause of the variations still remains unknown. They do not seem to be dependent on temperature or on astronomical facts. He considered it valuable to obtain magnetic data from different parts of the earth, but comparisons were only possible when all are published on the same plan. This, he hoped, would result from the efforts of Professors Rücker and Adams. When this is accomplished, the observations on magnetic force will need treatment; the work will be laborious, and the aid of volunteers like Messrs. Robson and Smith would be of great service.

Prof. W. G. ADAMS said he was glad to see the satisfactory nature of the work which had just been brought before the Society. Usually, the mass of figures to be dealt with was so large that the mere reduction was a great undertaking. If, however, the difference between results obtained by the Greenwich and Wild's method was not more than 0.4', it may be possible to make out the causes of the variations from observations reduced on Wild's plan. He himself would put more faith in

horizontal force observations, and wished they could be worked out by some ready method. He hoped the one adopted in America, of obtaining mean curves by photography, may prove satisfactory.

Prof. PERRY asked if a machine could not be made to do the work.

Mr. WHIPPLE said such machines had been used by the Meteorological Office, but they were so elaborate and expensive that clerical work was just as cheap. The method of photographing mean curves had been tried at Kew, but it was open to the objection that accidental disturbances such as those produced by the movement of iron in the vicinity and the approach of cabs, &c., were not eliminated.

Mr. BOYS referring to the use of integrators, said that for a harmonic analyser his disc-cylinder pattern was preferable to the ball disc-cylinder integrators of J. Thomson, for it is much cheaper and has less inertia.

The PRESIDENT said the movement initiated by Prof. RÜCKER would be of great service if it resulted in the numbers obtained at the various magnetic observatories being published in the same way. It was a great advantage to have such men, who were not permanently attached to an observatory, to take up the subjects and suggest improvements. The heads of such institutions were usually too much employed in making the necessary reductions to have time for devising improved methods. In his opinion greater freedom should be allowed to the chiefs of observatories, for it should be borne in mind that the object of observations is not to produce volumes of figures but to increase our knowledge.

Referring to the reduction of observations, he thought the voluntary services of senior physical students should be more generally accepted, and to this end he suggested that properly recommended persons should be allowed to spend some time in observatories as honorary assistants. This would be of great use to the students themselves and an advantage to the observatories, for the reduction of observations could then be expedited. As regards the accidental disturbances referred to by Mr. Whipple, he contended that regulations should be adopted to render them impossible.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, June 2, 1890.

SIR JAMES CRICHTON-BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—

C. J. Cullingworth, M.D., F.R.C.P.; Jonathan Hutchison, F.R.S., F.R.C.S.; Rudolph Messel, Ph.D., F.C.S.; Henry Charles Mylne; and Dan Rylands.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

OBITUARY.

L. SORET.

WE regret having to put on record the death of the illustrious chemist and physicist, Louis Soret, who died on May 13, at Geneva, where he held the chair of physics at the University.

The earliest researches of the deceased were in electricity. His study of the laws of electrolysis led him to define the conditions of the production of ozone, and to determine its density and its chemical constitution. He was the first *savant* who succeeded in installing his actinometric apparatus on the summit of Mont Blanc,

where he obtained a series of simultaneous measurements at three different altitudes. In optics, he devised the double prism showing anomalous dispersion, the circular grating giving focal images by diffraction, the improved fluorescent eye-piece, which renders it possible to observe the invisible ultra violet radiations up to their extreme limit almost as easily as the visible rays, finding that the extreme violet transparency is for some bodies one of the most delicate characters of the chemical purity.

In the body then known as erbia, Soret recognised in 1878 a new body which he designated as the earth X, and which he characterised by its absorption-spectrum. He accepted for it, in the sequel, the name "holmium," given by M. Clève.

His death, at the age of sixty-three, cannot but be regretted as premature.

CORRESPONDENCE.

SULPHATES IN NITRIC ACID.

To the Editor of the Chemical News.

SIR,—I have recently been a good deal perplexed by finding sulphuric acid in steel and pig iron, in which I knew it was not likely to be present, and on careful examination of the acids employed for solution I found that the nitric acid pur., 1.42 s. g., contained a considerable percentage of sulphuric acid. I have used this same make of acid for many years without having any reason to suspect its purity, though only occasionally, for sulphur estimations. The makers have been communicated with by the persons who supply me, and I understand their explanation is that the acid is quite pure as it leaves their factory, and that the sulphuric acid is derived from the bottles in which it is sent out. These are Winchesters of greenish colour, and new ones are always used. The acid of which I am speaking is part of a batch which has been in bottle since last November, and the makers are not surprised at its having picked up sulphuric acid from the bottles. No doubt there is sulphate of soda in the material of which the glass is made, but I find that I can obtain a pure re-distilled nitric acid in bluish-coloured Winchesters which is perfectly free from sulphuric acid, though it has been in bottle about the same length of time as the other. I don't know whether any of your readers have had similar trouble, but I think it may be of value to warn users of so-called pure nitric acid of the necessity of frequently testing it for sulphates, and I should be glad to have information as to the action of nitric acid upon glass bottles in which it is stored, as the present state of things seems to be rather anomalous; viz., that greenish glass Winchesters sometimes contain sulphates capable of being dissolved out by nitric acid, but that bluish glass Winchesters have not been known to contaminate nitric acid in this way; at least, so far as I can ascertain.—I am, &c.,

JAMES H. HUXLEY.

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CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 21, May 27, 1890.

Electro-conductivities of the Compounds of Ammonia and of Aniline with the Oxybenzoic Acids.—D. Bethelot.—The conductivity found experimentally,

contrary to what is observed in the case of the alkaline phenates is always in excess of the mean conductivity. Notwithstanding the difference of the conductivities of the three oxybenzoic acids the conductivity of the mixture is almost the same for the three isomers.

Researches on Dispersion in Organic Compounds (Alcohols of the Fatty Series).—Ph. Barbier and L. Roux.—For the alcohols of the fatty series, which the authors have examined, the dispersive powers are continuous functions of the molecular weights, and, contrary to what takes place for aromatic compounds, the dispersive powers increase at the same time as the molecular weights. The isomeric alcohols with a long chain, primary and secondary, have sensibly the same dispersive power and obey the same laws; only the abnormal primary alcohols studied possess smaller dispersive powers, though their values deviate very notably from that of the alcohols of long chains. The elimination of hydrogen occasions a considerable increase in the dispersive power.

On Homofluoresceine.—E. Grimaux.—The author considers that the trimethylfluoresceine or homofluoresceine of Schwartz is the aurine of orcine.

Justus Liebig's Annalen der Chemie.
Vol. ccliv., Part 2.

Communications from the Chemical Institute of the University of Bonn.—These communications contain memoirs by R. Anschütz and Ferdin. Reuter on the action of aniline upon citraconic acid and itaconic acid; on acetyltrichlorphenomalic acid, by R. Anschütz; contributions to a knowledge of the monosubstituted succinic acids, by R. Anschütz and Carl Bennert, and an account of the isomerism of fumaric acid and maleic acid by R. Anschütz.

Communications from the Chemical Institute of the University of Halle.—These communications comprise two papers by Hugo Erdmann on the derivatives and transformations of benzallevulic acid and on phenylangelialacton.

Communications of the University Laboratory of Freiburg.—Papers by W. Autenrieth on the thio-derivatives of the crotonic acids, and by O. Hinsberg and L. von Udransky on some benzoyl compounds.

Communications from the Chemical Institute of the University of Bonn.—Memoirs by R. Anschütz on a new formation of hydantoin and on the preparation of flavean-hydrogen.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xx., No. 11.

Precipitation of Albumenoids from Urine by Certain Bodies Considered Indifferent.—M. Boymond.—The author, having had considerable difficulty in filtering urine rendered turbid by the presence of bacteria, succeeded in obtaining a perfectly clear bright filtrate by shaking up the sample with talc which had been previously washed, first with hydrochloric acid, then with water, and then dried.

Trichloroacetic Acid for the Detection and Determination of Albumen.—M. Boymond.—The author uses this acid in preference to nitric or metaphosphoric acid. It has the advantage of not modifying the albumens. For the separation of globuline, serine, and Patein's variety he determines in one portion of the sample the globuline by means of magnesium sulphate; in another portion the sum total of globuline and serine by ebullition in presence of a few drops of acetic acid. In the filtrate from this precipitate Patein's variety is determined by means of trichloroacetic acid.

The Part of Ammonia in the Nourishment of the Higher Plants.—A. Müntz.

Examination of the Sugary Matters extracted from Dates.—L. Grimbert.—Dates contain glucose and levulose, but no saccharose.

Is Potassium Ferrocyanide Poisonous?—P. Carles.—The author points out the harmlessness of potassium ferrocyanide, the sale of which, in some parts of France, appears to be surrounded with red-tape precautions.

Monochloro-camphor obtained by Means of Hypochlorous Acid.—P. Cazeneuve.—These two papers have been already noticed.

MISCELLANEOUS

The Pharmaceutical Society.—At a meeting of the Council of the Pharmaceutical Society, held on the 5th instant, Mr. Michael Carteighe was re-elected President. The Society has just entered its Jubilee year, having been founded in 1841, with the late William Allen, F.R.S., as its first President.

MEETINGS FOR THE WEEK.

WEDNESDAY, 18th.—Geological, 8.

Meteorological, 7.

THURSDAY, 19th.—Royal, 4 30.

Chemical, 8. Ballot for the Election of Fellows.

"Invertase—a Contribution to the History of an Unorganised Ferment," by C. O'Sullivan, F.R.S., and F. W. Tompson. "The Action of Carbonic Oxide on Nickel," by Mr. Mond and Drs. Langer and Quincke. "The Interaction of Iodine, Water, and Potassium Chlorate," by Henry Bassett. "The Milk of the Gamoose," by A. Pappel and H. D. Richmond.

FRIDAY, 20th.—Physical, 8.

"The Stretching of Liquids," by Prof. A. W. Worthington. "The Measurement of Electro-Magnetic Radiation," by C. V. Boys, A. E. Briscoe, and W. Watson. "Notes on Secondary Batteries," by Dr. Gladstone and W. Hibbert.

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ON THURSDAY NEXT, at 7 p.m.

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THE CHEMICAL NEWS.

Vol. LXI. No. 1255



ON THE ANALYSIS OF CERTAIN SAMPLES OF TINNED MEAT.

By C. J. H. WARDEN, M.D., Chemical Examiner to Government; and Assistant Surgeon C. L. BOSE, M.B., Assistant Chemical Examiner to Government.

RECENTLY certain samples of tinned meat were examined in the Laboratory of the Chemical Examiner's Department, Calcutta, and the results are perhaps of sufficient interest to be placed on record. The samples were 6-lb. tins of the following brands:—

- 1.—Sydney Meat Preserving Co., New South Wales, Australia Mutton.
- 2.—New Zealand Packing Co., Peach Brand, Auckland Beef.
- 3.—New Zealand Packing Co., Peach Brand, Auckland Mutton.
- 4.—Fairbank Canning Co., Lion Brand, Chicago Beef.
- 5.—Armour Packing Co., Helmet Brand, Kansas City, U.S.A. Beef.
- 6.—Central Queensland Meat Export Co., Rockhampton Beef.
- 7.—Central Queensland Meat Export Co., Rockhampton Mutton.

Before opening the tins their dimensions were taken, and they were weighed with labels intact. The results are recorded in the following Table:—

Description of brand.	Weight (avoir.). lb. oz. gr.	Dimensions in inches and tenths.		
		Height.	Top.	Bottom.
Sydney Meat Preserving Co. Mutton	6 15 50	8.6	4.52 × 4.23	5.1 × 5
New Zealand Packing Co. Beef	6 9 70	8.94	4.9 × 3.7	5.4 × 4.15
New Zealand Packing Co. Mutton	6 14 107	8.94	4.9 × 3.7	5.4 × 4.15
Fairbank Canning Co. Beef	6 14 203	9.2	5.04 × 3.41	5.7 × 4.2
Armour Packing Co. Beef	7 14 202	8.79	5.39 × 4.19	5.41 × 3.7
Central Queensland Meat Export Co. Beef	7 14 105	9.25	4.9 × 3.67	4.14 × 5.37
Central Queensland Meat Export Co. Mutton	7 1 320	9.25	4.9 × 3.67	4.14 × 5.37

All the tins were in a sound condition and free from rust externally. The Fairbank Canning Co.'s tin was coated with transparent blue varnish, and had a small paper label. The New Zealand Packing Co.'s tins were only painted, the nature of the contents being printed in black ink. The remaining tins were painted and also covered with varnished paper labels, except at the top and bottom. We would suggest that in lieu of paper labels the preferable plan of painting and stamping cases of tinned provisions with the brand, nature, and weight of the contents, and year of manufacture. This last point is one which appears to us to be of very considerable moment.

Tinned provisions are, as a rule, chiefly employed when fresh ones are unavailable; and, though tinned meats will

keep for some time, they certainly do not improve by age. As at present put up, one can only roughly judge of their age by the external condition of the tin, a source of information which may obviously lead to very incorrect conclusions.

Out of the seven brands of tinned meat examined by us, only the Fairbank Canning Co.'s sample showed the date of manufacture.

All the tins were larger in area at the base than at the top; an expedient which admits of the contents being readily removed whole.

In the following Table the weights of the empty tins and their contents are recorded:—

Brand.	Weight of empty tin.		Weight of contents.		
	ozs.	grs.	lbs.	ozs.	grs.
Sydney Meat Preserving Co. Mutton	15	33	6	0	16
New Zealand Packing Co. Beef	12	35	5	13	35
New Zealand Packing Co. Mutton	12	393	6	1	151
Fairbank Canning Co. Beef	13	61	6	1	141
Armour Packing Co. Beef	14	35	6	2	167
Central Queensland Meat Export Co. Beef	15	22	6	1	82
Central Queensland Meat Export Co. Mutton	14	341	6	2	417

In the majority of cases the insides of the tins were bright and free from all traces of corrosion or rust.

In chemically examining the samples, the whole of the contents of a tin was in each instance thoroughly well pulped in a large marble mortar, and a portion of the pulped mass used for analysis. Great care was taken to thoroughly scrape the interior of the tins, so as to remove adherent fat and jelly. The tins were then warmed to melt the last traces of fat and jelly, which was also added to the contents of the mortar. The tins were subsequently washed with kerosene oil to dissolve traces of fat, and finally with soap and water, and after drying were weighed. The weight of the contents of a tin being taken as the difference between the weight of a full and empty one. In preparing a specimen of tinned meat for analysis, to merely take a slice and to examine that appears to us to be an erroneous procedure; the contents of a tin must be considered as a whole, and the method we have described of sampling appears to be the only accurate plan by which a knowledge of the general nature of the contents of a tin can be obtained.

In the analysis of an article so prone to decomposition as meat, especially in the tropics, the scheme of examination has to be somewhat carefully considered. We found that certain of the determinations could be made with the meat in the freshly pulped state, while others were preferably made with the desiccated pulp. The first pulp was used for the estimation of moisture, ash, phosphoric acid, chlorine, potash, and soda, and the dried meat for the determination of fat, nitrogen, and aqueous extractive.

For the estimation of moisture five to six grms. of pulp were teased with forceps on the bottom of a flat platinum dish, and exposed at first to a temperature of 100° C., and subsequently to 120° C. in a hot air-bath. The samples were moistened once with absolute alcohol after having been heated for some hours, and the heating continued. Desiccation occupied from eight to nine hours. In another large platinum capsule 30 or 40 grms. of pulp were similarly heated, and when crisp reduced to fine powder and again heated. The dried pulp was preserved in a well stoppered bottle, and used for the determinations already mentioned.

In determining ash,* the portion of the pulp used for

* The samples were examined for foreign metals—tin and lead—in the majority of cases with negative results.

the estimation of moisture was carbonised below redness, reduced to powder in the dish by a flat nail-headed glass rod, and the carbonaceous powder digested with hot water. The solution was then poured on a small filter, and the residue repeatedly washed with warm water. The filter containing the insoluble residue was then dried, and the particles brushed into the platinum dish, which was heated until the whole of the carbon had been consumed. The ash was again digested with warm water, and the solution passed through the same filter. The filter paper was again dried, and, finally, ignited in the dish. After deducting the filter ash, the residue represented the insoluble ash of the sample. The mixed filtrates, on evaporation and ignition just short of redness, affording the soluble mineral constituents. The filter-papers were of C. Schliecher and Schüll's manufacture, and had been extracted with HCl and HF. Control experiments were also made by which the total ash was obtained at one operation. In these determinations great difficulty was often experienced in burning off the last traces of carbon, and prolonged ignition was necessary. As will be seen from the following Table, the total mineral matter obtained by adding together the soluble and insoluble ash was, as a rule, a trifle higher than the "total ash" obtained by one operation, but the difference was not so large as might perhaps have been anticipated.

	Sum of soluble and insoluble ash.	Ash by one operation.
Sydney Meat Preserving Co.		
Mutton	1.530	1.31
New Zealand Packing Co.		
Beef	0.991	0.865
New Zealand Packing Co.		
Mutton	0.621	0.75
Fairbank Canning Co. Beef	1.944	1.628
Armour Packing Co. Beef	4.635	4.38
Central Queensland Meat Export Co. Beef .. .	1.716	1.7
Central Queensland Meat Export Co. Mutton ..	1.605	—

The soluble ash was used for the estimation of soda and potash, by being dissolved in water, and barium chloride, from chloride and ammonia, added successively, and heated for some time; the precipitate was then filtered off, washed, and the filtrate, after the addition of ammonium carbonate and oxalate, warmed for some time on the water-bath, and filtered. The filtrate and washings was then evaporated to dryness, and gently ignited to remove ammonium salts. On adding water to the residue, a trace of insoluble was filtered off, and the filtrate, after the addition of a few drops of HCl, evaporated to dryness with an excess of platinic chloride. This method of treating the ash of meat preparations is essentially the one described by Dr. A. Stutzer.*

In estimating the alkali metals we employed the following indirect method:—

The residue obtained, as described above, consisting of the double sodium-potassium and platinum chlorides, was treated with alcohol and ether in the usual manner, but instead of weighing the potassium-platinum chloride, it was ignited at a low temperature with the filter-paper on which it had been collected, the residue exhausted with warm water, and the solution of chloride of potassium titrated with standard silver nitrate. The alcoholic solution containing the sodium-platinum salt and an excess of platinum chloride was evaporated to dryness in a small beaker, and the residue washed into a platinum crucible. Ammonium chloride was then added in more than sufficient quantity to combine with the platinum, the mixture evaporated to dryness, and the crucible cautiously heated, first without its cover, and then covered. The residue was treated with warm water, and the chlorine estimated with standard silver nitrate. The

two chlorine titrations thus afforded data from which the amount of H₂O and Na₂O in the ash could be calculated. In carrying out this method of estimating the alkali metals, care must be taken not to under or over heat the residues. Intense ignition would entail loss of chlorides; while by under heating, the whole of the double alkali platinum salt would escape decomposition, and on adding water to the contents of the crucible the solution would have a yellowish colour; in which case, it would be requisite to evaporate the solution and again ignite. We did not find it necessary to separate the finely-divided platinum from the solution of the chloride before titration with silver.

(To be continued).

A SIMPLE FORM OF QUICK FILTER.

By JOSEPH TORREY.

THERE have been many good forms devised for a quick filter, and the principal objection to them collectively is that they are too expensive and cumbersome to be given out to every student. The writer has long felt the need of some form which would take little apparatus and cost as little as possible. The following form has recommended itself since its design by the writer about a year ago by its uniformly satisfactory performance under every test:—

A platinum disc, one inch diam., is cut from ordinarily stout foil. This is then perforated by a steel point with small holes, placed about the same as in Cooke's modification of Dr. Carmichael's reverse filtering button. A margin of about 1-16th inch ought to be left unpierced. The disc thus prepared is placed in a funnel, which can be cut off, if desired, so that the disc will be about 1/4 inch below the rim of the funnel. A small disc of filter-paper about 1-16th inch larger than the disc is now placed in the funnel just above the disc. Water is applied and pressure turned on. The paper at once settles down and makes an air-tight joint at the edge of the disc. The precipitate can now be brought on the paper and washed as usual.

The results are as good as to rapidity as in case of any form of quick filter, and the ease and convenience attending its use will, I hope, recommend it to some chemists.

Laboratory of Iowa College,
Grinnel, Iowa, May 18, 1890.

THE VIOLET FLAME PRODUCED BY COMMON SALT IN A COAL FIRE.

By A. PERCY SMITH, F.I.C., F.C.S.

THE *Journal of the Chemical Society* for June, 1890, contains an abstract from a paper by G. Salet (*Comp. Rend.*, cx., 282, 283), in which my conclusions as to the origin of the above are contradicted and cupric chloride asserted to be the cause. In the first place, M. Salet errs in describing the colour as blue. It may indeed be blue when copper chloride is heated, but all other chlorides produce a violet flame. I am confident that the violet flame is due to hydrochloric acid, and not to copper, for the following reasons (see also *Nature* and *CHEMICAL NEWS*, March—April, 1879):—

The chlorides of ammonium, potassium, sodium, strontium, barium, and mercury all produce the violet colouration when heated on wire gauze or in a porcelain crucible by coal-gas, a spirit lamp, or pure hydrogen. In these experiments no copper was present. The spectrum of the flame is identical with that produced by throwing common salt into a coal fire. In these experiments we have only two elements in common, viz., chlorine and hydrogen. I proved conclusively by other experiments

* *Analyst*, p. 57, 1885.

that neither sulphur nor carbon entered into the reaction, not that I thought they did, but to disprove the assertions of other people.

The violet flame may also be produced by introducing a drop of hydrochloric acid upon a loop of platinum wire into a Bunsen flame, or one of pure hydrogen; but my proof as to its origin rests upon the fact that when pure hydrochloric acid gas is slowly passed into either of the above flames the violet colour is abundantly formed.

The spectrum of this flame may be found mapped in *Nature*, March 27, 1879. Compared with that of a spark in HCl gas it is seen that the lines in the least refrangible portions are identical, but that the fluted bands of the chloride spectrum are absent in that of the gas, which is easily accounted for by the different conditions under which they are produced. The chloride spectrum is the same under all methods of production given above; that is to say, hydrochloric acid gas heated in a flame gives identically the same result as common salt thrown into a fire.

Dartford, Kent.

THE ELECTROMOTIVE FORCE OF METALLIC SALTS.*

By CLARENCE L. SPEYERS.

OWING to the close connection between chemical action and manifestation of electricity, the study of electrical action promises, if it does not solve, at least great assistance towards the solution of the problem, "What is chemical action?" How brilliantly Ostwald's investigations on electrical conductivity of solutions, aided by the dissociation hypothesis of Arrhenius and others, have illuminated chemical phenomena! The darkness surrounding solution,† diffusion, electromotive force between solutions of different concentration, thermo-neutrality, &c., has been dissipated. True, the light may be false and vanish, but it is the first ever shed on questions hitherto so obscure. If, then, the study of one phase of electrical conduction has taught so much, it is not unreasonable to expect something from an investigation of another side, namely the separation of electricity or production of an electromotive force.

Ordinary self-continued chemical changes are accompanied by a loss of energy (appearing in the form of heat), and it is natural to suppose that with proper arrangements all this heat can be converted into a corresponding quantity of electricity. In fact, Sir W. Thomson suggested this view. Experience, however, has shown that such a statement does not express the truth; a correction is required which, by some, is supposed to be caused by secondary reactions; by others, with Helmholtz at the head, to be due to the existence of two states of energy—the free and the bound. Applying thermo-dynamics to reversible cells, Helmholtz obtains an expression representing the difference between the chemical (as measured in heat) and the electrical energies consumed and developed respectively in the cell. Experience tells that now the case is correctly stated from a mathematical point of view; but the chemical explanation still remains to be discovered. How this will be achieved is, of course, at present uncertain, but will it not probably be through the study of the simplest cases in which an electromotive force is produced. At any rate, it was with this hope that the following investigation was commenced, the plan being to measure the electromotive force of solutions of metallic salts and its variation on systematic dilution. The present paper deals with hydrogen and zinc salts of Cl, NO₃, C₂H₃O₂, and SO₄.

Instead of zinc, an amalgam of this metal was chosen for two reasons: first, the surface presented to the liquid might be considered as homogeneous; secondly, a tarnishing of the brilliant surface would readily reveal any secondary reaction due to oxidation or hydration. With very few exceptions, whenever the electromotive force had an abnormal value, an examination of the amalgam showed an alteration of the surface, evidenced either by a dull film or loss of mobility. The apparent exceptions were probably due to such a thin film that an alteration of surface could not be perceived, but nevertheless existed. The anomalous values were sometimes too high, sometimes too low. Observations were suspended when tarnishing was unmistakably shown. Experiments by Lindeck* and others showed that less than 1 per cent of zinc imparted to mercury an electromotive force equal to that of zinc, justifying the substitution of an amalgam containing 1 per cent of zinc. Hydrogen amalgam not being available, a zinc amalgam was also used with the acids. The negative electrode was composed of pure mercury, so as to neutralise, as far as possible, any chance alteration of electromotive force due to a change of surface tension.

The mercury was purified by causing it to trickle through a solution of mercurous nitrate, comparative experiments showing that this method was as effective and far more convenient than heating with concentrated sulphuric acid.

All liquids contained one grm. equivalent in a litre of water, and, whenever possible, measurements were commenced with solutions of this strength. Zinc chloride and sulphate solutions were prepared by dissolving proper quantities in water, but to obtain solutions of zinc nitrate and acetate, other methods were necessary, owing to the formation of basic salts. The former was successfully made by carefully neutralising normal nitric acid with pure zinc oxide, using tropæolin as an indicator. The latter, by double decomposition, between barium acetate and zinc sulphate, titrating the resulting filtrate with potassium ferrocyanide and diluting with the proper quantity of water. In this way one-half equivalent‡ solution of zinc acetate was easily obtained free from any basic salt.

For measuring the electromotive force a capillary electrometer and compensation cells were used. The method has been so fully described by Ostwald‡ that anything more would be superfluous. To evaluate the electromotive force between the binding posts of the resistance box, as well as that of the compensation battery, two Clark cells were constructed according to Lord Rayleigh's directions.§ As no difference could be detected when the two cells were opposed, although the electrometer was sensitive to less than 0.0001 V, their electromotive force was considered equal to 1.435 [1—0.00077 (t—15)] V. At the close of the present series of experiments a slight inequality (0.001 V) was observable, which, however, could readily be accounted for by a large fluctuation in the temperature of the room during a few cold winter nights, and the Clark cells not having an equal temperature at the time of measurement. Every two weeks the electromotive of the compensation cells was determined, and every day that between the two binding-posts of the resistance box, the latter being measured by the aid of a compensation cell.

The cell containing the liquid to be experimented upon is outlined in the two figures. *b* is a portion of a thick test-tube drawn out and a platinum wire fused through the bottom *d*. This tube, with a capacity of about 15 c.c., contains the solution and amalgam *u*. Another piece of test-tube is drawn out, a platinum wire inserted, and the glass fused around it, at the same time bending the drawn-out portion upward so as to form a cup, *e*, in which a

* *American Chemical Journal*, Vol. xii., No. 4.

† The writer does not admit that any distinctions are to be made between physical and chemical action other than those of degree and convenience. Of course, mechanical action is excluded.

* *Wied. Ann.*, xxxv., 311.

† One grm. equivalent in two litres of water.

‡ *Zeitschrift f. Physikal. Chem.*, i, 403.

§ "Elementary Pract. Physics," Stewart and Gee, ii., 481.

globule of mercury can be placed. The platinum wire makes a metallic connection. The piece *c* must be drawn out in such a manner that when the cup is made its orifice is below the surface of the solution contained in *b*. By grinding *c* into *b* a glass stopper is formed, enabling the liquid to be thoroughly mixed after each dilution. Fig. 1 shows *b* and *c* in position; Fig. 2, *c* alone. Four such cells were constructed, enabling duplicate measurements to be made with two solutions at the same time.

The manner of operation was this:—Two pipettefuls of the solution were introduced, and then about 0.25 c.c. of the carefully cleansed amalgam, the stopper inserted, and the tube gently rocked to and fro, care being taken to fill the cup of the stopper with liquid. The cup was then filled with mercury, which displaced the liquid (the stopper being removed for this purpose), and proper connection made with the electrometer. When the electromotive force became constant, the value was recorded, the mercury in the cup tossed out, the liquid gently shaken, a fresh globule of mercury introduced, and another measurement made. If they did not coincide, the

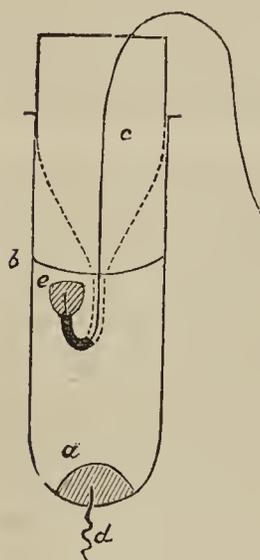


FIG. 1.

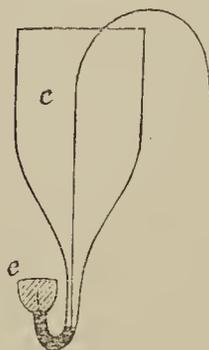


FIG. 2.

process was repeated until a satisfactory agreement was obtained.* Half the liquid being removed, an equal volume of distilled water was added and the above process repeated until the amalgam tarnished. Constant values were often reached in a few minutes with concentrated solutions, but as dilution proceeded a longer interval was required, which in one case (zinc nitrate and sulphuric acid) extended over sixty hours.† Usually, however, twenty-four, but sometimes twelve, hours were sufficient for a series. Now and then the electromotive force would rise and then fall continuously. Under such circumstances the highest value was recorded, justification being found in the fact that no constant value could be obtained by waiting, for the electromotive force decreased continuously throughout a long period of observation. This procedure, however, was only adopted when the highest value of the duplicate was sensibly the same. Such abnormal behaviour was observed only with dilute solutions and concentrated acids—caused in the former case, probably, by a slight alteration of the surface of the amalgam, in the latter by hydrogen evolved from the platinum wire when the latter was exposed to the strong acid while in contact with the amalgam.

The temperature at which the experiments were made was that of the room, about 20° C.

(To be continued).

A METHOD FOR THE DETERMINATION OF IODINE IN HALOID SALTS.*

By F. A. GOOCH and P. E. BROWNING.

(Concluded from p. 281).

In Series D it appears that the proportion of sulphuric acid increases from 8.3 per cent to 25 per cent of the whole volume before the liquid is found to be free from iodine as such, and even then there sometimes remain minute, though probably insignificant, traces of hydriodic acid.

In the experiment of Series E the liquid was diluted after concentration and the boiling repeated, and the volatilisation of the iodine was thus more nearly perfected than in the corresponding experiments of the previous series—a proportion amounting to 16.6 per cent apparently accomplishing the work done by 25 per cent of the same acid in a single concentration. The results of Series F, G, and H are closely comparable with those of the corresponding experiments of Series D. Throughout these experiments it is again made evident that it is the proportion, and not the absolute amount, of sulphuric acid which is the great factor in the liberation of the iodine. So far as concerns the purpose of good analysis these results indicate the elimination of iodine to a reasonable sufficiency when the reduction of bulk raises the percentage by volume of the strong sulphuric acid to twenty-five, and to perfection, as in the latter determinations of Series G, when the percentage reaches twenty-eight and a half. It remains to be seen whether the arsenious oxide reduced in the separation of the iodine will resist successfully, under the conditions of these experiments, the tendency to volatilise which the presence of chlorides and bromides, and the consequent liberation of hydrochloric and hydrobromic acids, might presumably induce.

The experiments of Series I were directed to the elucidation of this point.

Decinormal solutions of iodine and arsenious acid prepared, standardised, and tested against one another in the usual manner. Definite portions of the solution of arsenious acid were measured from a burette into Erlenmeyer beakers such as were used in the previous experiments, sulphuric acid [1:1] and sodium chloride were added, the volume of the liquid was adjusted to 100 c.m.³ or a little more, and the process of concentration by boiling was carried to the point desired and indicated by a mark upon the flask. After cooling, the acid was neutralised and the titration effected in the usual manner in the presence of an excess of acid potassium carbonate, and starch employed as the indicator. These experiments were arranged upon the presumption that the essential conditions determining the degree of volatility of the arsenic when the reduction is effected by hydriodic acid are imitated, though neither hydriodic acid, nor arsenic acid, nor free iodine is present.

It appears in these results that there is some loss of arsenic in nearly every case within the limits of our experimentation, the amount of volatilisation increasing with the ratio of sulphuric acid to the entire volume when the quantity of chloride present is constant, and likewise with the amount of chloride when the ratio of the acid to the total liquid is constant.

The effect of increasing the amount of chloride is naturally accounted for by the "mass action" of the hydrochloric acid thus liberated upon the arsenious oxide in solution; that it is the proportion, and not the absolute amount, of sulphuric acid which determines the degree of volatility of the arsenic is explicable upon the assumption that the smallest quantity of sulphuric acid employed is sufficient to liberate all the hydrochloric acid (or, at least, nearly all), and that this, by its action on the arsenious

* In a few cases, noted in the tables, satisfactory results could not be obtained.

† For the completed series.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xxxix., March, 1890.

oxide, forms the volatile chloride proportionately to the amount of water removed bodily by concentration or withheld from effective action by the attraction of the sulphuric acid.

In extending this line of experimentation to cases involving the action of hydrobromic acid upon arsenious oxide we found it sufficient for our purpose to employ only the highest degree of concentration recorded in the previous experiments, and to use 1 grm. of potassium bromide—an amount corresponding, molecule for molecule, to about 0.5 grm. of sodium chloride. The results, given in Series J, indicate that under these circumstances the loss of arsenic is inappreciable.

It appears, therefore from the results of Series I, that, when the amount of sodium chloride present is restricted to 0.5 grm., the liquid may be boiled until the sulphuric acid amounts to 33.3 per cent of it, with a loss, on the average, of 0.0008 grm. of arsenious oxide, and to 25 per cent with a loss of 0.0004 grm. With either of these proportions the results are sufficiently favourable to warrant quantitative testing of a method for separating chlorine and iodine based upon the volatility of iodine and the non-volatility of arsenious oxide under the conditions. The case is even more favourable for the similar separation of bromine from iodine—the loss of arsenic amounting on the average to 0.0001 grm., under similar conditions. The experiments of Series D to H indicated that the degree of concentration at which all iodine vanishes from the liquid corresponds to the presence of 28.6 per cent of the acid—a point midway between the points of concentration indicated above. We fixed this proportion, therefore, for the following experiments, as being rather more favourable as regards the fixity of the arsenic, and perfect as to the elimination of iodine. The smallest absolute amount of sulphuric acid which we have used—10 c.m.³ of the [1 : 1] mixture—demands evaporation of the liquid to a bulk too small to be easily determined with certainty in flasks of the shape and dimensions which we found convenient for this work. The larger amounts of acid are uncomfortably large in the subsequent neutralisation. We took, therefore, 20 c.m.³ of the [1 : 1] mixture of sulphuric acid and water as the amount best adapted to our purpose, and set the limit of concentration at 35 c.m.³.

The potassium iodide which we used was prepared with great care, by acting with re-sublimed iodine upon iron wire, three-fourths of the iodine being added to an excess of iron covered with distilled water, decanting the solution from the excess of iron when the colour of iodine had vanished, adding the remainder of the iodine, pouring the filtered solution slowly into boiling water, to which the exact amount of acid potassium carbonate necessary to combine with the iodine had been added, and filtering off the magnetic oxide of iron thus precipitated. The solution of potassium iodide thus made, very faintly alkaline and entirely free from chlorine and bromine, was made up to a suitable volume and standardised by precipitating the iodine of aliquot portions by weight as silver iodide, which was heated and weighed upon asbestos. Weighed portions of this solution, containing approximately 0.5 grm. of potassium iodide to 30 c.m.³, were taken for the tests in which the larger quantities of iodine were introduced; measured portions of a solution made by diluting the former were employed in the tests involving the smaller amounts.

The sodium chloride and potassium bromide used were shown to be free from iodine, and the hydrogen potassium arseniate contained no arsenious acid.

The mode of proceeding was, in general, like that of the previous experiments. The solution of potassium iodide was put in an Erlenmeyer beaker of 300 c.m.³ capacity, 2 grms. of hydrogen potassium arseniate were added in solution and followed by 20 c.m.³ of sulphuric acid [1 : 1], the liquid was diluted with water to a little more than 100 c.m.³, a platinum spiral was placed in the flask to secure quiet ebullition, a trap made by cutting off a two-bulb drying tube about an inch from

the inside bulb was hung, large end downward, in the mouth of the flask to prevent mechanical loss, and the liquid was boiled until the level reached the 35 c.m.³ mark put upon the flask. At this point the flask was cooled, the acid nearly neutralised with sodium hydrate in solution, the neutralisation completed by acid potassium carbonate, 20 c.m.³ of the last being added in excess, a definite portion of the starch indicator added, and the contents in arsenious acid determined by titration with a decinormal solution of iodine for the larger amounts, and a centinormal solution for the smaller. Due correction was made for the amount of iodine necessary to develop the test-colour in a solution prepared and treated similarly in all respects to the experimental solutions excepting the introduction of the iodide—the correction amounting to a single drop more of the decinormal solution than was required to produce the end reaction in the same volume of pure water containing only the starch indicator.

The decinormal solution of iodine was made by dissolving 12.65 grms. of carefully re-sublimed iodine in potassium iodide (proved free from iodate) and diluting to a litre. The centinormal solution was made by diluting the stronger solution. The standardising was effected by comparison with a solution of arsenious oxide containing 4.95 grms. to the litre. This mode of fixing the value of the solution should, and, as the sequel proved, did, indicate the correct standard, but for the sake of confirmation the value of the arsenic solution was re-determined by titration against iodine specially purified by subliming off potassium iodide, re-subliming between watch-glasses, and exposing during forty-eight hours over sulphuric acid. Portions of the iodine thus prepared were weighed in a glass-stoppered weighing-bottle, dissolved in the same without danger of volatilisation by introducing pure solid potassium iodide and a little water, and diluted and treated with the solution of arsenious acid measured from a burette until the colour of iodine vanished. The excess of arsenious oxide was determined by titrating against the standard solution of iodine, whose value in terms of measured portions of the solution of arsenious oxide was perfectly known.

In Series K are detailed experiments which follow the line marked out for the separation of iodine from chlorine and bromine in the haloid salts, excepting that the iodide was entirely omitted for the purpose of discovering whether hydrochloric and hydrobromic acids possess reducing action upon arsenic acid under the conditions. The evidence is plain that no arsenious oxide is formed by the action of 0.5 grm. of sodium chloride upon 2 grms. of the arseniate under the circumstances as given.

Hydrobromic acid, on the contrary, is slightly decomposed with the evolution of bromine enough to give visible colour to the concentrated liquid, but the amount of bromine lost, as indicated by the arsenious acid produced in its evolution, is only 0.0003 grm. for 0.5 grm. of potassium bromide, and 0.0001 grm. for 0.1 grm. of the bromide. Further experiments indicated, however, that concentration cannot go on to a volume less than 35 c.m.³ without causing serious loss when the maximum amount of bromide is present.

In Series L are given the results of twenty-six determinations of iodine by the method outlined.

Upon inspection of these results it appears that the method is good and reliable under all the conditions tested.

When neither chloride nor bromide is present, the iodine is determinable with a mean error of 0.0002 grm.

When sodium chloride accompanies the iodide, the results show a loss of arsenious oxide and a consequent apparent deficiency of iodine—as we should expect in accordance with the indications of Series I. This deficiency proves to be proportional to the amount of iodide broken up, or the arsenious oxide thus produced. For 0.56 grm., approximately, of potassium iodide and 0.5 grm. of sodium chloride, the deficiency measured in

Series D.

KI. Grm.	H ₂ SO ₄ [1 : 1]. C.m. ³ .	Per cent of strong H ₂ SO ₄ by volume.	H ₂ KAsO ₄ . Grms.	Final volume. C.m. ³ .	Free iodine.	Combined iodine.
0.5	10	8.3	1	60	Present	Abundant.
0.5	10	10	1	50	Present	Abundant.
0.5	10	12.5	2	40	Present	Distinct.
0.5	10	12.5	2	40	Trace	Distinct.
0.5	10	12.5	4	40	Trace	Distinct.
0.5	10	16.6	1	30	Trace	—
0.5	10	16.6	2	30	Trace	—
0.5	10	16.6	2	30	Trace	—
0.5	10	16.6	4	30	None	Distinct.
0.5	10	16.6	5	30	Trace	Distinct.
0.5	10	25	1	20	None	Faintest trace.
0.5	10	25	2	20	None	Faintest trace.
0.5	10	25	2	20	None	Faintest trace.
0.5	10	25	2	20	None	Faintest trace.
0.5	10	25	2	20	None	Faintest trace.

Series E.

0.5	10	16.6	1	{ 30 30 }	None	Faintest trace.
0.5	10	16.6	1	{ 30 30 }	None	Faintest trace.
0.5	10	16.6	1	{ 30 30 }	None	Faintest trace.
0.5	10	16.6	1	{ 30 30 }	None	Faintest trace.

Series F.

0.5	15	25	2	30	None	Faintest trace.
0.5	15	25	2	30	None	Faintest trace.
0.5	15	25	4	30	None	Faintest trace.

Series G.

0.5	20	25	2	40	None	Faintest trace.
0.5	20	25	2	40	None	Faintest trace.
0.5	20	25	2	40	None	None.
0.5	20	28.6	2	35	None	None.
0.5	20	28.6	2	35	None	None.
0.5	20	33.3	2	30	None	None.

Series H.

0.5	30	25	2	60	None	Faintest trace.
0.5	30	25	2	60	None	Faintest trace.

Series I.

H ₂ SO ₄ [1 : 1]. C.m. ³ .	NaCl Grm.	Final volume. C.m. ³ .	Per cent of strong H ₂ SO ₄ by volume.	As ₂ O ₃ taken. Grm.	As ₂ O ₃ found. Grm.	Loss. Grm.
{ 10	1	20	25	0.0495	0.0485	0.0010—
{ 10	1	20	25	0.0495	0.0493	0.0002—
{ 10	1	20	25	0.0495	0.0488	0.0007—
{ 10	0.8	20	25	0.0495	0.0488	0.0007—
{ 10	0.5	20	25	0.0495	0.0495	0.0000
{ 20	1	40	25	0.0495	0.0490	0.0005—
{ 20	1	40	25	0.0495	0.0490	0.0005—
{ 20	0.8	40	25	0.0495	0.0490	0.0005—
{ 20	0.5	40	25	0.0495	0.0490	0.0005—
{ 20	0.5	40	25	0.1385	0.1380	0.0005—
{ 20	1	30	33.3	0.0495	0.0476	0.0019—
{ 20	0.8	30	33.3	0.0495	0.0466	0.0029—
{ 20	0.5	30	33.3	0.0495	0.0481	0.0014—
{ 20	0.5	30	33.3	0.0495	0.0485	0.0010—
{ 20	0.5	30	33.3	0.0495	0.0490	0.0005—
{ 20	0.5	30	33.3	0.0495	0.0490	0.0005—
{ 30	1	60	25	0.0495	0.0485	0.0010—
{ 30	0.8	60	25	0.0495	0.0490	0.0005—
{ 30	0.8	60	25	0.0495	0.0490	0.0005—
{ 30	0.5	60	25	0.0495	0.0490	0.0005—

Summary of Series I.

H ₂ SO ₄ [1 : 1]. C.m. ³ .	Final volume. C.m. ³ .	Per cent of strong H ₂ SO ₄ by volume.	NaCl. Grm.	Mean loss of As ₂ O ₃ . Grm.	Number of determination.
10	20	25	1	0'0006-	3
20	40			0'0005-	2
30	60			0'0010-	1
10	20	25	{ 0'5 and 0'8 }	0'0003-	2
20	40			0'0005-	3
30	60			0'0005-	3
20	30	33'3	{ 0'5 0'8 1'0 }	{ 0'0008- 0'0019- 0'0029- }	{ 5 1 1

Series J.

H ₂ SO ₄ [1 : 1]. C.m. ³ .	KBr. Grm.	Final volume. C.m. ³ .	Per cent of strong H ₂ SO ₄ by volume.	As ₂ O ₃ taken. Grm.	As ₂ O ₃ found. Grm.	Loss. Grm.	Mean loss. Grm.
20	1	30	33'3	0'0495	0'0490	0'0005	} 0'0001-
20	1	30	33'3	0'0495	0'0493	0'0002	
20	1	30	33'3	0'0495	0'0495	0'0000	
20	1	30	33'3	0'0495	0'0495	0'0000	
20	1	30	33'3	0'0495	0'0495	0'0000	

Series K.

H ₂ SO ₄ [1 : 1]. C.m. ³ .	H ₂ KAsO ₄ . Grms.	NaCl. Grm.	KBr. Grm.	Final volume. C.m. ³ .	Iodine corres- ponding to As ₂ O ₃ reduced. Grm.	Chlorine corresponding (average). Grm.	Bromine corresponding (average). Grm.
20	2	0'5	—	35	0'0000	} 0'0000	—
20	2	0'5	—	35	0'0000		
20	2	0'5	—	35	0'0000		
20	2	—	0'1	35	0'0003	} —	0'0001
20	2	—	0'1	35	0'0001		
20	2	—	0'1	35	0'0001		
20	2	—	0'5	35	0'0005	} —	0'0003
20	2	—	0'5	35	0'0005		
20	2	—	0'5	35	0'0005		

Series L.

No.	H ₂ SO ₄ [1 : 1]. C.m. ³ .	H ₂ KAsO ₄ . Grm.	NaCl. Grm.	KBr. Grm.	Final vol. C.m. ³ .	KI taken. Grm.	Theory for Iodine. Grm.	Iodine found. Grm.	Error. Grm.	Average error. Grm.
1.	20	2	—	—	35	0'5616	0'4080	0'4079	0'0001-	} 0'0002-
2.	20	2	—	—	35	0'5630	0'4091	0'4086	0'0005-	
3.	20	2	—	—	35	0'5622	0'4083	0'4086	0'0003+	
4.	20	2	—	—	35	0'0506	0'0400	0'0396	0'0004-	
5.	20	2	—	—	35	0'0506	0'0400	0'0391	0'0009-	
6.	20	2	—	—	35	0'0506	0'0400	0'0400	0'0000	} 0'0002-
7.	20	2	—	—	35	0'0506	0'0400	0'0401	0'0001+	
8.	20	2	—	—	35	0'0051	0'0040	0'0037	0'0003-	
9.	20	2	—	—	35	0'0051	0'0040	0'0038	0'0002-	
10.	20	2	0'5	—	35	0'5611	0'4077	0'4066	0'0011-	
11.	20	2	0'5	—	35	0'5619	0'4082	0'4073	0'0009-	} 0'0011-
12.	20	2	0'5	—	35	0'5624	0'4086	0'4073	0'0013-	
13.	20	2	0'5	—	35	0'0506	0'0400	0'0402	0'0002+	
14.	20	2	0'5	—	35	0'0506	0'0400	0'0395	0'0005-	
15.	20	2	0'5	—	35	0'0051	0'0040	0'0037	0'0003-	
16.	20	2	0'5	—	35	0'0051	0'0040	0'0037	0'0003-	} 0'0002-
17.	20	2	—	0'5	35	0'5619	0'4082	0'4092	0'0010+	
18.	20	2	—	0'5	35	0'5697	0'4138	0'4136	0'0002-	
19.	20	2	—	0'5	35	0'5622	0'4083	0'4099	0'0016+	
20.	20	2	—	0'5	35	0'0506	0'0400	0'0410	0'0010+	
21.	20	2	—	0'5	35	0'0506	0'0400	0'0404	0'0004+	} 0'0008+
22.	20	2	—	0'5	35	0'0051	0'0040	0'0048	0'0008+	
23.	20	2	—	0'5	35	0'0051	0'0040	0'0049	0'0009+	
24.	20	2	0'5	0'5	35	0'5626	0'4087	0'4083	0'0004-	
25.	20	2	0'5	0'5	35	0'5660	0'4112	0'4111	0'0001-	
26.	20	2	0'5	0'5	35	0'5622	0'4083	0'4079	0'0004-	} 0'0003-

iodine amounted to 0.0011 gm. When the potassium iodide is decreased ten-fold (or more) the deficiency falls to 0.0002 gm. It should be recalled, too, in this connection that the results of Series I. pointed to increasing volatility of the arsenic with the increase of the sodium chloride present.

The presence of potassium bromide results in the liberation of minute amounts of bromine and a consequent increase in the arsenious oxide and apparent excess of iodine. The mean error due to this cause is 0.0008 gm. for 0.5 gm. of the bromide, and the variation in the quantity of iodide present is without effect upon it.

The simultaneous action of the chloride and bromide tends, of course, to neutralise the error due to each. Thus, in the mixture weighing about 1.5 grms. and consisting of sodium chloride, potassium bromide, and potassium iodide in equal parts, the mean error amounts to 0.0003 gm. —. The largest error in the series is 0.0016 gm. +, when the bromide was at its maximum and no chloride was present; and the next largest was 0.0013 gm. —, when the chloride was at its maximum and no bromide was present.

It is obvious that when the amounts of chloride and bromide present are known approximately it is possible to apply corrections which shall eliminate errors in the indicated amount of iodine due to the action of these substances. From the averages of Series L it is apparent that the amount to be added in each case may be obtained by multiplying the product of the weights in grms. of sodium chloride and potassium iodide by the constant 0.004; and the amount to be subtracted, by multiplying the weight in grms. of potassium bromide by 0.0016. Thus, for example, the correction in 24 will be 0.0011 gm. + (= 0.5 × 0.56 × 0.004) and 0.0008 gm. — (= 0.5 × 0.0016). The individual results of Series L thus corrected will stand as follows:—

No. of Expt.	Theory for Iodine.	Corrected amount of Iodine found.	Error.
	Grm.	Grm.	
1.	0.4080	0.4079	0.0001—
2.	0.4091	0.4086	0.0005—
3.	0.4083	0.4086	0.0003+
4.	0.0400	0.0396	0.0004—
5.	0.0400	0.0391	0.0009—
6.	0.0400	0.0400	0.0000
7.	0.0400	0.0401	0.0001+
8.	0.0040	0.0037	0.0003—
9.	0.0040	0.0038	0.0002—
10.	0.4077	0.4077	0.0000
11.	0.4082	0.4084	0.0002+
12.	0.4086	0.4084	0.0002—
13.	0.0400	0.0403	0.0003+
14.	0.0400	0.0396	0.0004—
15.	0.0040	0.0037	0.0003—
16.	0.0040	0.0037	0.0003—
17.	0.4082	0.4084	0.0002+
18.	0.4183	0.4128	0.0010—
19.	0.4083	0.4191	0.0008+
20.	0.0400	0.0402	0.0002+
21.	0.0400	0.0396	0.0004—
22.	0.0040	0.0040	0.0000
23.	0.0040	0.0041	0.0001+
24.	0.4087	0.4086	0.0001—
25.	0.4112	0.4114	0.0002+
26.	0.4083	0.4082	0.0001—

Mean error 0.0001 gm.—.

The mode of proceeding in the analysis of a mixture of alkaline chlorides, bromides, and iodides, according to this method, may be briefly summarised as follows:—

The substance (which should not contain of chloride more than an amount corresponding to 0.5 gm. of sodium chloride, nor of bromide more than corresponds to 0.5 gm. of potassium bromide, nor of iodide much more than the equivalent of 0.5 gm. of potassium iodide) is dissolved in water in an Erlenmeyer beaker of 300 c.m.³ capacity,

and to the solution are added 2 grms. of dihydrogen potassium arseniate dissolved in water, and 20 c.m.³ of a mixture of sulphuric acid and water in equal volumes, and enough water to increase the total volume to 100 c.m.³, or a little more. A platinum spiral is introduced, a trap made of a straight two-bulb drying-tube cut off short is hung with the larger end downward in the neck of the flask, and the liquid is boiled until the level reaches the mark put upon the flask to indicate a volume of 35 c.m.³. Great care should be taken not to press the concentration beyond this point on account of the double danger of losing arsenious chloride and setting up reduction of the arseniate by the bromide. On the other hand, though 35 c.m.³ is the ideal volume to be attained, failure to concentrate below 40 c.m.³ introduces no appreciable error. The liquid remaining is cooled and nearly neutralised by sodium hydrate (ammonia is not equally good), neutralisation is completed by hydrogen potassium carbonate, an excess of 20 c.m.³ of the saturated solution of the latter is added, and the arsenious oxide in solution is titrated by standard iodine in the presence of starch.

With ordinary care the method is rapid, reliable and easily executed, and the error is small. In analyses requiring extreme accuracy, all but accidental errors may be eliminated from the results by applying the corrections indicated.

THE SEPARATION AND DETECTION OF Al, Cr, Fe, Co, Ni, Zn, Mn, Ba, Sr, Ca, Mg, K, Na, NH₄.*

By J. S. C. WELLS, Ph.D.

In the following course of analysis I have adopted the plan used in "Fresenius," and as far as the methods are the same have used the text as given in that work.

The division into groups is the same as given by Fresenius, viz.:—1st Group—K, Na, NH₄. 2nd Group—Ba, Ca, Sr, Mg. 3rd Group—Al, Cr. 4th Group—Co, Ni, Fe, Zn, Mn.

1. Take a small portion of the solution to be tested, in a test-tube, observe whether it is coloured or not (Note 1), boil to expel H₂S if present (Note 2), if FeO be present (Note 13) add a few drops of HNO₃ and boil to oxidise it to Fe₂O₃ (Note 3), add a little NH₄Cl, then NH₄OH cautiously, just to alkaline reaction, heat gently, and observe if a precipitate is produced; then add some (NH₄)₂S, no matter whether NH₄OH has produced a precipitate or not.

2. a. Neither NH₄OH nor (NH₄)₂S produces a precipitate, pass on to 17, for Fe, Co, Ni, Zn, Mn, Cr, Al are not present (Note 4), nor are phosphates, borates (Note 5), silicates, oxalates (Note 6), or fluorides (Note 5) of the alkaline-earth metals, nor silicic acid originally in combination with other metals.

3. b. (NH₄)₂S produces a precipitate, NH₄OH having failed to do so: absence of phosphates, borates (Note 5), silicates, oxalates (Note 6), and fluorides (Note 5) of the alkali-earths, of silicic acid originally in combination with other metals, and also if no organic matter is present of Fe, Al, Cr. Pass on to 5, 6, 7, 12; omit 8, 9, 10, 11.

4. c. NH₄OH produces a precipitate before the addition of (NH₄)₂S. The course of proceeding now depends upon whether (a) the original solution is simply aqueous and has a neutral reaction, or (b) the original solution is alkaline or acid (Note 7). In the former case pass on to 5, since phosphates, borates, &c., cannot be present. In the latter case regard must be had to the possible presence of all the bodies enumerated in 2, and also in the presence of organic matter, of the combinations of alkali-earth metals with citric and tartaric acids.

The solution must be tested for these acids, and, if found, the analysis must be carried on according to

* School of Mines Quarterly, Vol. xi., No. 3.

scheme for phosphates, &c. See *School of Mines Quarterly*, Vol. x., No. 3).

5. DETECTION OF BASES OF GROUPS 3 AND 4 IF PHOSPHATES, &c., ARE NOT PRESENT.

Mix the solution mentioned at beginning of 1, a portion of which you have submitted to a preliminary examination, with some NH_4Cl (Note 8), then with NH_4OH just to alkaline reaction (Note 9), and then $(\text{NH}_4)_2\text{S}$, until the fluid, after being shaken, smells distinctly of that reagent, shake the mixture until the precipitate begins to separate in flakes, heat gently for some time, and filter.

Keep the filtrate (Note 10), which may contain bases of groups 1 and 2 for examination according to 17. Wash the precipitate with water to which a very little $(\text{NH}_4)_2\text{S}$ (Note 11) has been added, then proceed with it as follows:—Remove the washed precipitate (Note 12) from the filter with a spatula, or by rinsing it with the aid of a wash-bottle through a hole made in the bottom of the filter into a test-tube, and pour over it cold dilute HCl (one part HCl , sp. gr. 1.12, with about five parts of water) in moderate excess.

6. a. *The precipitate is not completely dissolved, a black residue being left.*

This indicates Co and Ni. This indication is not certain, especially in the presence of much FeS , particles of which may become enveloped in the separated S, and thus be protected from the action of the HCl . Filter and wash.

Examine the filtrate according to 8.

7. Test a small portion of the precipitate in the borax bead, first in the oxidising, then in the reducing flame. If the bead in the oxidising flame is violet whilst hot, and of a pale reddish brown when cold, and turns gray and turbid in the reducing flame, nickel is present; but if the colour of the bead is blue in both flames, and whether hot or cold, cobalt is present. As in the latter case, the presence of nickel cannot be distinctly recognised, examine the remainder of the residue as follows:—Dissolve in HCl and a little HNO_3 , evaporate nearly to dryness, dilute with water, and filter, if necessary, from any particles of S, neutralise carefully with KOH , and then add a solution of KCy , until the precipitate that first forms is completely dissolved; add a little more KCy , and then bromine water in considerable quantity, taking care, however, to keep the solution alkaline with KOH . The nickel is precipitated as the black hydroxide $(\text{Ni}_2(\text{OH})_6)$. As the cobalt has already been found by the borax bead, no further test for it is necessary.

8. b. *The precipitate dissolves completely* (except, perhaps, a little S); absence of Co and Ni, at least in notable quantity.

Boil until H_2S is completely expelled; if iron is present (Note 13), add a little HNO_3 and boil, so as to oxidise it to the ferric state (Note 14), filter if any particles of S remain suspended in the solution, and evaporate nearly to dryness. The course of proceeding now depends on whether the colour of the solution indicates chromium or not.

9. *Solution is coloured bluish green or violet, and indicates Cr.*

Add Na_2CO_3 to strong alkaline reaction, then bromine-water in excess, heat gently for some time, keeping solution alkaline with Na_2CO_3 , and finally heat to boiling, filter, and wash residue.

a. Filtrate contains Na_2CrO_4 , and possibly $\text{Na}_2\text{Mn}_2\text{O}_8$; the latter is indicated by pink or purple colour of the solution (Note 15). Acidify solution with $\text{HC}_2\text{H}_3\text{O}_2$, and test for Cr with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ —a yellow precipitate proves chromium.

b. Residue contains iron and aluminium as hydroxides, zinc and manganese as carbonates.

Dissolve in least possible quantity of HCl , and treat according to 10.

10. *Colour of solution does not indicate Cr.*

Neutralise carefully with Na_2CO_3 , dilute and add ex-

cess of $\text{NaC}_2\text{H}_3\text{O}_2$, boil and filter hot, wash precipitate with boiling water. Examine filtrate according to 12.

11. Precipitate consists of iron and alumina as basic acetates. Fuse on platinum with NaKCO_3 and a little KClO_3 (Note 16), dissolve in small quantity of boiling water, and filter.

a. Residue consists of Fe_2O_3 and possibly some alumina that has resisted the fusion.

Dissolve in a little HCl and test for iron with NH_4CyS .

b. Filtrate contains $\text{Na}_2\text{Al}_2\text{O}_4$; acidify with HCl , and then add $(\text{NH}_4)_2\text{CO}_3$ in slight excess—a white flocculent precipitate proves alumina.

12. Filtrate contains zinc and manganese, concentrate solution, add a little $\text{HC}_2\text{H}_3\text{O}_2$, heat to boiling and pass H_2S into it. Zinc is precipitated as ZnS (white) (Note 17), filter.

Filtrate contains manganese, add KOH in excess, a white precipitate turning brown on exposure to the air = Mn. Confirm result by testing in Na_2CO_3 bead in oxidising flame—green bead proves Mn.

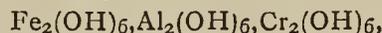
Method using BaCO_3 in place of $\text{NaC}_2\text{H}_3\text{O}_2$.

13. Proceed in the same way as given in 1, 2, 3, 4, 5, 6, 7, 8. In 8, after evaporating nearly to dryness, to expel excess of acid, dilute with water, and neutralise carefully with Na_2CO_3 .

To the neutral solution add BaCO_3 in excess, digest in the cold for some time, filter, and wash. Examine filtrate according to 12 (Note 18).

14. Precipitate contains iron, aluminium, and chromium as hydroxides, together with excess of BaCO_3 . Dissolve precipitate in HCl , add NH_4OH just to alkaline reaction and filter (Note 19).

Reject filtrate. Dry the precipitate—



and fuse in platinum with $\text{Na}_2\text{CO}_3 + \text{KClO}_3$. Dissolve in fusion small quantity of boiling water, and filter.

15. Filtrate contains chromium and aluminium as Na_2CrO_4 and $\text{Na}_2\text{Al}_2\text{O}_4$, divide solution in two parts, a and b.

a. Make acid with $\text{HC}_2\text{H}_3\text{O}_2$, then add a solution of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ —yellow precipitate = Cr.

b. Acidify with HCl , and then add a slight excess of $(\text{NH}_4)_2\text{CO}_3$ or NH_4OH and boil—white flocculent precipitate = alumina.

16. Residue left after treating fusion with water consists of Fe_2O_3 and possibly some Al_2O_3 . Test for iron by dissolving in HCl and adding NH_4CyS —red colour = iron (Note 13).

(To be continued).

NOTICES OF BOOKS.

Explosives Act, 1875. Fourteenth Annual Report of Her Majesty's Inspectors of Explosives, being their Annual Report for the Year 1889. London: Her Majesty's Stationery Office.

THIS report is in many respects gratifying. We find that the vigilance of the inspectors does not decrease, and that municipal authorities are slowly becoming alive to the importance of the Act and of its execution. The number of fatal accidents in the year was 7, one of them, it is worth noting, in an unlicensed factory. Although the average for the past eleven years was only 7.2, yet the present figure is a substantial improvement, since the number of factories, the average output in each, and the number of hands employed have increased. Hence, unless greater care and intelligence were brought to bear, we might naturally expect an increased death-rate. This is the more evident as some new explosives are being introduced where the conditions of safety or danger are not so thoroughly known.

We learn from the Report that a new Chemical Committee has been appointed by the War Office "for the purpose of investigating and dealing with chemical questions relating to explosives for use in the Imperial service." The functions of this Committee are consequently entirely distinct from those of the Inspectors, who have to deal only with the question of public safety in the manufacture, transport, and storage of explosives for civil purposes.

During the year ten new factories have come into existence, the total number under licence being 122, exclusive of "toy firework factories."

One of the accidents, resulting in the death of one man and injuries to three others, took place on October 3 during the unlawful and surreptitious manufacture of Quick-Firing Ammunition by Sir W. Armstrong, Mitchell, and Co. (Limited) on board a barge on the Tyne. This case will yet form the subject of criminal proceedings; hence no comments on the occurrence are made further than a notice of the gross negligence of the Commissioners of the River Tyne, who had allowed this unlicensed manufacture to continue for several months.

Two women—the only persons present at the time—were killed in the packing room of the detonator factory at Polmont, belonging to Nobel's Explosives Company. This accident took place on November 15, and is supposed to be due to the fall of a heavy plate containing detonators upon a similar plate. The two above-mentioned cases and one which took place at Pain's factory, June 4, were the only one which led to official inquiries.

A fatal accident happened in June at the Factory of the Roburite Explosives Company (Limited), near Wigan. The cause of death here was not explosion or fire, but the inhalation of poisonous gases. The victim was cleaning an air-flue into which the fumes of three roburite mixing-pans were discharged. Respirators and other precautions were certainly in use. It is stated that these flues have since been cleaned, when needful, without sending men into them.

One accident—not fatal—led to the detection of an unlicensed and therefore wholly illegal "firework factory," which, as the Report adds, "is not creditable to the local authority."

Some of the accidents in the storage of explosives show gross ignorance on the part of the persons concerned. Thus, at Grangemouth a workman lighted a match "in a store-room in which oil (doubtless mineral oil) and gunpowder were unlawfully kept together." The explosion killed a bystander and injured several persons.

It is remarked that the Act gives the inspectors no power concerning the use of explosives. In an accident due to an improper apparatus used for thawing dynamite the jury recommended the passing of an Act to regulate the use of "high" explosives.

Especial care should be taken by all parties concerned not to leave detonators about. They are sometimes picked up by children who are quite ignorant of their nature.

Cases of malicious attempts against life by means of explosives have not been wanting. On Lord Clanricarde's estate near Woodford, Galway, an infernal machine was arranged in an empty house which it was expected would be entered by the police. The arrangements adopted by the conspirators were essentially identical with those of the infernal machines discovered at Liverpool and Glasgow in 1883, the bombs found on Daly in April, 1884, and the attempted explosion at the *Times* office in 1883. It is noteworthy that at Woodford the peasantry, instead of crowding round, as at other evictions, had kept entirely aloof.

On September 7 an attempt was made to blow up a house in the outskirts of Tipperary, in which Mr. A. H. Smith-Barry collects his rents.

At Rochdale, on November 29, an attempt was made to blow up the School Board offices. The intended *modus operandi* was to bring sulphuric acid in contact

with potassium chlorate and sugar. The failure, says the Report, "may be referred to a cause which it is not desirable to specify."

As illustrations of modern "progress" in Japan we find that dynamite and dynamitards have penetrated thither also. A set of 500 candles, sent as a present to a famous temple, were all filled with dynamite. An attempt was also made to assassinate the Foreign Minister by throwing a bomb into his carriage as he was returning from a Cabinet meeting. Neither investigation nor punishment followed, as the intending assassin escaped by the hari-kari.

Several explosion outrages have occurred in Spain, Italy, Switzerland, Russia, and the United States. At Seattle, in the latter country, one Schaeffer killed four persons with dynamite and dangerously wounded a fifth. He was at once lynched.

There is a very full account of the Antwerp explosion and fire on September 6. The deaths are said to have been 95, whilst 130 persons were wounded more or less severely. The owner of the establishment, one Corvilain, seems by no means to have adhered to the conditions imposed in his license. He incurred only five-and-a-half years imprisonment and a penalty of £430 as damages!

Certain New Double Iodides of Bismuth and Potassium.—Ch. Astre.—The author has isolated the following compounds:— $(\text{BiI}_3)_2, 4\text{IK}$; $(\text{BiI}_3)_2, 3\text{IK} + 2\text{H}_2\text{O}$; $(\text{BiI}_3)_2, 6\text{IK}$. The number of the known double bismuth and potassium iodides is thus raised to five. They may be considered as resulting from the union of 2 mols. of bismuth iodide with a number of mols. of potassium iodide varying from 1 to 6.—*Comptes Rendus*, vol. cx., No. 22.

On Benzoyl-tannin.—Dr. Carl Böttinger.—This compound was obtained by mixing a cold dilute watery solution of 3 grms. tannin with 5 c.c. strong soda-lye and shaking it up with benzoyl chloride. The substance, after purification, is a crystalline granular powder, insoluble in water, alcohol, and ammonia, but soluble in hot aniline, dimethylaniline, and phenylhydrazine.—*Festus Liebig's Annalen der Chemie*, ccliv., Part 3.

Volumetric Determination of Tannin in Wines.—MM. Roos, Cusson, and Giraud.—The authors prepare a 10 per cent solution of tartaric acid, which is saturated with ammonia until slightly acid. A solution of neutral lead acetate is then added until the precipitate no longer re-dissolves in the liquid, and the whole is filtered. This liquor completely precipitates tannin from its solutions. It is standardised by means of a solution of pure tannin in ether, proceeding as follows:—25 c.c. of the solution of tannin at 5 grms. per litre, *i.e.*, 0.10 of tannin, are placed in a glass with the addition of 4–5 drops of ammonia. The solution of lead aceto-tartrate is dropped in from a burette, at first by 2 c.c. at a time. At the addition of each fresh quantity a drop is taken up with a glass rod and placed upon a double piece of Swedish filter-paper. The precipitate adhering to the rod remains upon the paper at the point touched, whilst the liquid spreads by capillarity and reaches the lower leaf. Near this spot he deposits a drop of a solution of sodium sulphide, taking care that the reagent mixes with the liquid of the first drop by capillarity without touching the precipitate. This precipitate (lead tannate) forms on the paper a spot with distinct outlines, which is darkened by the sodium sulphide, but which does not become surrounded with a brown halo until the moment when all the tannin is precipitated. The first rapid trial gives an approximation of about 2 c.c.; a second trial, made by adding 5 drops at a time, enables the standard to be fixed definitely. Samples of wine are then treated in the same manner.—*Journal de Pharmacie et de Chimie*, xxi., No. 2.

CORRESPONDENCE.

SULPHATES IN NITRIC ACID.

To the Editor of the Chemical News.

SIR,—I do not think there is much ground for Mr. Huxley's perplexity concerning the presence of sulphates in "pure" nitric acid. If he were accustomed to examine all the specimens supplied him he would be in no way surprised at any impurity. Out of five London firms with whom I have dealt for chemicals, one, and one only, has proved even moderately satisfactory in the quality of their "pure nitric acid," and then I caught tripping recently, and it was only after rejecting several samples that I got one reasonably clean, though even then it compared unfavourably with some re-distilled from the ordinary commercial acid in this laboratory without any special precaution whatever.

I believe the cause for this singular state of things lies in the fact that the manufacturer tries to produce a colourless acid at the sacrifice of purity. As to the contamination arising from sodium sulphate in the Winchester quarts, as alleged by the makers supplying Mr. Huxley, if it were not absurd on *à priori* grounds, would be disproved by Mr. Huxley's own experiment.

If every chemist instead of accepting whatever a manufacturer chooses to send him with the magic label "re-distilled puriss." were to regularly examine it, and resolutely and repeatedly send it back, some improvement might result. Moreover, manufacturers should be made aware that their liability for any loss in practice or reputation due to the use of impure chemicals labelled pure, by a chemist confiding enough to rely on that warranty, may be unpleasantly brought home to them through the medium of a court of law.—I am, &c.,

BERTRAM BLOUNT.

Laboratory,
Broadway, Westminster, S.W.
June 14, 1890.

MEDICAL OFFICERS OF HEALTH AND
PUBLIC ANALYSTS.

To the Editor of the Chemical News.

SIR,—The above subject, on which Mr. Rowland Williams writes (CHEM. NEWS, vol. lxi., p. 277), is one of much interest to Public Analysts and still more so to the public, whose interests are greatly in their hands.

I quite agree with the writer, that where the Medical Officer of Health is not well versed in practical chemistry he ought not to hold the double office, but this is no argument when he is competent and where the duties of Medical Officer of Health are insufficient to occupy his whole time. It could not, for example, be contended that the interests of the City of London suffered by the late Dr. Letheby performing the double function, or by Dr. Stevenson or Dr. Tidy holding similar dual offices.

The actual President of the Society of Public Analysts, who is a Medical Officer of Health as well as a Public Analyst, is a decisive proof that the two duties may be associated without disadvantage.

In Birmingham we have a well-known instance of the same kind, and another in the county of Warwick. In none of these instances has any question of incompetency or inefficiency arisen, although in the City of Birmingham alone about 1000 analyses of food, drink, and drugs are made every year.

But it is undeniable that where the Medical Officer of Health is required to perform analytical duties for which he is unqualified there is a great absurdity, and gross injustice is perpetrated, resulting either in little or nothing being done, or a breakdown painfully damaging to the "incompetent analyst." Besides this the work of the Public Analyst is brought into contempt, the place of the

trained analyst is usurped, and great hardship is inflicted on both traders and the public.

It is pointed out that membership of the Institute of Chemistry should be an "indispensable qualification" for a Public Analyst, and I quite agree with the suggestion, as it would be the best guarantee of efficiency.

Mr. Williams refers to a large town in Lancashire where the Town Council a short time since met for the purpose of selecting a Medical Officer of Health and Public Analyst. I do not know what town is indicated, but a friend of mine was quite recently a candidate for the double office also in a large town in the same county, and, although in addition to his holding as high medical and public health qualifications as it is possible to obtain, he is a sound practical chemist of unusually large experience in the special work required, a medallist in both practical and theoretical chemistry, and holds the "indispensable qualification" of membership of the Institute of Chemistry, his special fitness was ignored, and he was unsuccessful in his application for the appointment.

Can it be that the Town Council Committees are incompetent to make a proper choice of a candidate, or is it that "kissing goes by favour?"—I am, &c.,

JOHN WHITE, A.I.C.

Dudley Road, Birmingham,
June 10, 1890.

CHEMICAL NOTICES FROM FOREIGN
SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 22, June 2, 1890.

Reduction of Alkaline Sulphates by Hydrogen and Carbon.—M. Berthelot.—It is well known that at about a red heat hydrogen reduces the alkaline sulphates, forming a sulphide and water. This is not an accurate account of the reaction, as there is always formed, along with the water, hydrogen sulphide, and the final product contains caustic alkali. There is produced at the outset a hydrosulphate of the sulphide and an alkaline hydrate; the fixed product formed containing hydrogen, which is commonly supposed to be absent. This primitive reaction is exothermic, 2.6 cal. being set free in case of potassium and 9.3 in the case of sodium. Carbon does not seem to exert a direct action in the industrial reduction of the sulphates which seems to be effected by carbon monoxide. In the present conditions of the manufacture of alkali the reduction of sodium sulphate is a consequence of the two fundamental reactions of hydrogen and carbon monoxide, especially when it is effected in revolver furnaces under the influence of the flame from gases rich in hydrogen, hydrocarbons, and carbon monoxide.

The Determination of the Molecular Weight at the Critical Point.—Philippe A. Guye.—The author lays down the proposition that the critical coefficient of a mixture formed of several different mols. is very approximately equal to the mean critical coefficient of the molecular mixture.

Chloro-Salts of Iridium and its Atomic Weight.—A. Joly.—The physical properties of iridium, as prepared in a state of purity by Mr. Matthey upon the principles ascertained by Sainte Claire Deville and Debray differ from those formerly supposed. Its sp. gr. is found to be not 21.5, but 22.38. The atomic weight, calculated from the mean result of the author's experiments, is Ir = 192.75, which differs little from the mean found by M. Seubert, Ir = 192.744.

Manganese Oxides obtained in the Moist Way. Manganous Acid.—A. Gorgeu.—Not suitable for useful abstraction.

Soda Alum.—E. Augé.—The author shows that, contrary to the statements of the text-books, soda alum is very slightly efflorescent, and may be kept for months unchanged. Its solubility in water at 16° is only 51 per cent instead of 110 per cent. A solution of soda alum may be boiled indefinitely without ever losing the power of crystallising. In order to obtain soda alum it is merely necessary to concentrate the solution of the aluminium and sodium sulphates to 39°—43° Baumé, to place the paste obtained on plates of lead in an inclined position to collect the mother liquors which make up a fourth of the weight of the amorphous matter, and which carry off nearly all the impurities; crystallisation at the temperature of about 15°; drainage of the crystals.

The Bouquet of Fermented Beverages.—G. Jacquemin.—By adding the special ferments obtained from the wines of Ay, Beaune, Chablis, and Barsac, M. Jacquemin has obtained fermented liquors having the special bouquet of the wines in question from malt and from pure solutions. He has also, by a similar process, produced cider from barley.

MEETINGS FOR THE WEEK.

WEDNESDAY, 25th.—Society of Arts, 4. (Anniversary).

THURSDAY, 26th.—Royal Society Club, 6.30. (Anniversary).

FRIDAY, 27th.—Quekett Club, 8.

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Town Hall, Salford,
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THE CHEMICAL NEWS.

Vol. LXI. No. 596.

ON THE ANALYSIS OF CERTAIN SAMPLES OF TINNED MEAT.

By C. J. H. WARDEN, M.D., Chemical Examiner to Government; and Assistant Surgeon C. L. BOSE, M.B., Assistant Chemical Examiner to Government.

(Concluded from p. 292).

In order to test the accuracy of alkali determinations made in this indirect manner, the following control experiments were performed:—A solution of pure potassium nitrate and sodium chloride was prepared containing 1.1366 grms. KNO_3 and 0.5326 gm. NaCl in 100 c.c. of distilled water. Of this solution we took 10 c.c. for analysis, and duplicate determinations were made by each of us with the following results:—

Standard solution containing, per cent,			
KNO_3 .	K_2O .	NaCl .	Na_2O .
1.1366	0.529	0.5326	0.273
1.1366	0.529	0.5326	0.273
1.1366	0.529	0.5326	0.273
1.1366	0.529	0.5326	0.273

used for the estimation of chlorine. The greater part was concentrated and the phosphoric acid precipitated with molybdenum, but partially weighed as the phosphate of magnesium.

In the dried pulps, nitrogen was determined by Kjeldahl's method, and the results calculated back into the moist meat. The albumenoids were calculated from the nitrogen by using the factor 6.25.

The boiling water extractive was determined by boiling one gm. of the dry pulp with distilled water in a 100 c.c. flask, and, when cold, diluting up to 100 c.c. The liquid was then passed through a dry filter, and a portion of the very faintly opalescent filtrate evaporated to dryness in a platinum capsule for dissolved solids. The greater part of the filtrate was measured into an Erlenmeyer's flask, which was placed in boiling water until the water was evaporated off, and the extractive left as a varnish at the bottom of the flask. Sulphuric acid was then added to the dry residue in the flask for estimation of the nitrogen by Kjeldahl's method.

Fat was determined by very carefully weighing 0.5 to 0.6 of a gm. of the dry pulp into a small accurately stoppered weighing bottle, and adding a measured volume of light petroleum ether from a burette. The mixture was allowed to digest with agitation for about two days, then allowed to clear by subsidence, and a portion of the

Found by analysis, per cent,			
KNO_3	K_2O .	NaCl .	Na_2O .
1.237	0.577	0.4783	0.2557
—	—	0.4478	0.2373
1.260	0.590	0.430	0.228
1.250	0.586	0.427	0.225

The mean of these experiments shows the error of the process to be as follows:—

	Theory.	Found.	Error.
KNO_3	1.1366	1.2490	+0.1124 per cent,
K_2O	0.529	0.5843	+0.0553 "
NaCl	0.5326	0.4457	-0.0869 "
Na_2O	0.2730	0.2365	-0.0365 "

In the ordinary indirect estimation of the alkali metals, whether as chlorides or sulphates, or by Rose's method, in which the sodium-platinum chloride is decomposed and the sodium chloride extracted by water, gravimetric estimations are generally made, which is hardly necessary to indicate that when only very small amounts of salts have to be estimated, that greater accuracy is likely to result from volumetric than gravimetric methods of estimation. The method we have described appears to yield fairly accurate results, and is specially applicable to cases in which small amounts of sodium and potassium have to be estimated.

For the estimation of chlorine and phosphoric acid about 20 grms. of the fresh pulped meat were carefully weighed in a platinum dish and mixed with about 2 grms. of pure sodium carbonate,* dissolved in sufficient water to cover the pulp. The resulting magma was evaporated to dryness, carbonised below redness, and the residue first extracted with water and then with nitric acid, the solution being passed through a filter. The residue on the filter was dried and added to any particles remaining in the dish. The carbonaceous residue was then ignited until the whole of the carbon was consumed, the ash was again treated with dilute nitric acid, the solution being passed through the same filter; the filtrate and washings being collected in a 250 c.c. flask. The resulting solution was turbid from precipitation of phosphate of lime, the amount of nitric acid and ash being sufficient to neutralise the carbonate of soda. The alkaline solution was consequently rendered faintly acid by acetic acid, and diluted up to 250 c.c. A portion of this solution was

perfectly clean supernatant liquid withdrawn by a small burette, and a carefully measured volume discharged into a tared beaker. After evaporating off the ether, the residual fat was heated to 100° C. and weighed. No correction was applied for increase in volume of the petroleum spirit due to dissolved fat. This method is one suggested by Dragendorff,* for the estimation of oil, in his scheme for the systematic analysis of vegetable substances by the aid of various solvents. As a control experiment, one of us estimated the fat in a sample in the manner described, while the other determined it by thoroughly exhausting a portion with petroleum ether with the following results:—

- a. By Dragendorff's method, fat = 15.016 per cent.
- b. By thorough exhaustion, fat = 15.030 "

Working in the manner indicated the general results of the determination of the samples are shown in next page.

In order to compare the composition of tinned with fresh meat, the following analyses by König† of fresh meat are appended.

Nature of samples.	Water.	Albumenoids.	Fat.	Ash
Very fat ox flesh, mean of 7 analyses	55.42	17.19	26.38	1.08
Moderately fat ox flesh, mean of 21 analyses:				
Minimum	68.50	16.23	1.17	0.71
Maximum	78.00	25.35	9.50	1.95
Mean	73.25	20.78	5.33	1.33
Lean ox flesh, mean of 9 analyses	76.71	20.78	1.50	1.18
Fat cow flesh, mean of 9 analyses	70.96	19.86	7.70	1.07
Lean cow flesh, mean of 6 analyses	76.35	20.54	1.78	1.32
Very fat mutton, mean of 3 analyses	47.91	14.80	36.39	0.85
Moderately fat mutton, mean of 8 analyses ..	75.99	17.11	5.77	1.33

* The addition of sodium carbonate is recommended by Dr. Stutzer to prevent the formation of pyrophosphoric acid and the volatilisation of small quantities of chlorine during ignition.

* "Plant Analysis."

† *Zusammensetzung der menschlichen Nahrungs- und Genussmittel.*

It will be observed from a comparison of the tinned and fresh meat samples, that while the percentage of moisture in the former is in the majority of instances lower, the fat in the tinned meat, as a rule, exceeds the amount present in fresh meat. From a purely chemical point of view, and taking the albumenoids as representing the standard of nutritive value, the tinned meats are richer in that constituent, weight for weight, than fresh meat. But as the dietetic value of water need not be taken into consideration, and as the fat in the tinned meat samples is higher, as a rule, than in the fresh meat, it is worth while comparing anhydrous fat from tinned meat with fresh meat under similar conditions as regards the nitrogen content.

Description of samples.	Nitrogen on anhydrous meat.	Fat on anhydrous meat.	Nitrogen on anhydrous and fat-free meat.
New Zealand Packing Co. Beef	10.913	24.236	14.39
Fairbank Canning Co. Beef	8.932	36.137	13.98
Armour Packing Co. Beef	8.090	37.845	13.01
Central Queensland Meat Export Co. Beef ..	8.247	43.310	14.54
Sydney Meat Preserving Co. Mutton	9.700	32.960	14.31
New Zealand Packing Co. Mutton.. .. .	9.558	31.141	13.89
Central Queensland Meat Export Co. Mutton..	9.518	30.357	13.66
Fresh very fat ox flesh ..	6.170	59.010	15.07
Fresh moderately fat ox flesh:—Minimum ..	9.360	4.250	9.77
Maximum ..	14.620	34.240	22.23
Mean	12.090	18.630	14.84
Fresh lean ox flesh.. ..	14.290	6.390	15.26
Fresh fat cow flesh ..	11.300	25.530	15.03
Fresh lean cow flesh ..	13.930	7.250	15.01
Fresh very fat mutton ..	4.690	68.770	15.02
Fresh moderately fat mutton.. .. .	11.450	23.700	15.01

The results of analyses arranged in the manner shown in the last Table indicate that the anhydrous and fat-free flesh of the tinned meat samples is, when compared with fresh meat, distinctly lower in nitrogen, and consequently less rich in albumenoids. Taking the mean, and calculating the nitrogen into albumenoids by the factor 6.25 the following figures are obtained:—

Nature of samples.	Albumenoids in anhydrous and fat-free samples. Per cent.
Mean of all tinned beef	87.062
Mean of all tinned mutton	87.187
Mean of all fresh cow and ox flesh.	93.936
Mean of all fresh mutton	93.812
Mean of all tinned meat samples ..	87.124
Mean of all fresh meat samples ..	93.874

König in his work, to which we have already referred, quotes seven analyses by various chemists of tinned meats, the analyses having been made between the years 1878—80; the results are given in table (see next page).

The tinned meat samples compared with fresh roast meat also appear to show a slight diminution in albumenoids. An analysis by John Ranke, quoted by Pavy,* gives the composition of roast meat (nature not indicated) no dripping being lost, as follows:—

Albumenoids	27.60 per cent.
Fat	15.45 "
Salts	2.95 "
Water	54.00 "

* "Treatise on Food and Dietetics,"

Description of brand.	Moisture at 120° C.		Fat.	Nitrogen.	Albumenoids N × 6.25.	Total ash.	Ash soluble in water.	Ash insoluble in water.	Chlorine (Cl).	Phosphoric anhydride (P ₂ O ₅).	Oxide of potassium (K ₂ O).	Oxide of sodium (Na ₂ O).	Boiling water extractive per cent on meat.	Nitrogen in boiling water extractive, per cent on meat.	Meat bases and in boiling water extract = N × 6.25.
Sydney Meat Preserving Co. Mutton.. .. .	54.700	15.030	4.40	27.500	1.5302	1.3039	0.2263	0.544	0.345	0.364	0.417	7.249	0.906	5.660	
New Zealand Packing Co. Beef	57.350	10.338	4.65	29.062	0.991	0.665	0.326	0.146	0.359	0.220	0.117	6.953	1.000	6.250	
" Mutton	55.000	14.000	4.30	26.275	0.621	0.189	0.432	0.112	0.394	0.136	0.067	5.353	0.900	5.625	
Fairbank Canning Co. Beef	56.039	15.829	3.93	24.562	1.944	1.778	0.165	1.107	0.308	0.262	0.807	7.159	0.879	5.493	
Armour Packing Co. Beef	50.650	18.660	3.99	24.937	4.365	4.176	0.189	2.650	0.318	0.434	0.963	10.414	0.987	6.168	
Central Queensland Meat Export Co. Beef ..	49.050	22.080	4.20	26.25	1.716	1.474	0.242	0.999	0.402	0.230	0.609	7.951	1.010	6.312	
" Mutton.. .. .	52.600	14.390	4.51	28.187	1.605	1.244	0.361	0.847	0.329	0.237	0.458	9.464	1.100	6.875	

Description of samples.	Water.	Albumenoids	Fat.	Ash.	In anhydrous samples.		Albumenoids in anhydrous and fat-free sample.
					Nitrogen.	Fat.	
Wilson Export Co.	57.3	28.9	10.2	3.6	10.83	23.75	88.75
(?) Canning and Co. Export Co.	49.2	25.7	21.6	3.5	8.09	42.52	87.93
Brougham Export Co.	48.9	27.7	19.0	4.4	8.67	37.18	86.25
From Australia	54.03	29.31	12.11	4.55	10.20	26.34	86.50
Pressed corned beef, from Chicago	56.9	33.8	6.4	2.9	12.55	14.85	91.06
2-lb. tin containing 1020 grms.	57.7	31.5	7.3	3.5	11.91	17.62	92.81
4-lb. tin containing 1844 grms.	58.8	25.9	11.8	3.5	10.05	28.64	87.12
Mean	54.69	28.97	12.63	3.71	10.33	27.27	88.63

Calculating the albumenoids on the anhydrous and fat-free meat gives 90.34 as the percentage, figures which are also higher than the albumenoid content of the tinned meats. According to Playfair's experiments, it would appear that in roasting meat the loss is chiefly water, the proportion of carbon, hydrogen, nitrogen, and oxygen remaining the same.*

Summarising we may state that our results generally confirm those of other analysts, as indicating the lower nutritive value of tinned when compared with fresh meat. Our inferences are based on purely chemical data, but on physiological grounds there can also be no doubt that sodden tinned meat would be less easily assimilated than ordinarily cooked flesh, and that consequently its dietetic value would be even less than is indicated by its chemical composition.

THE SEPARATION AND DETECTION OF Al, Cr, Fe, Co, Ni, Zn, Mn, Ba, Sr, Ca, Mg, K, Na, NH₄.†

By J. S. C. WELLS, Ph.D.

(Concluded from p. 299).

Metals of First and Second Groups.

17. To a small portion of the solution in which ammonia and ammonium sulphide have failed to produce a precipitate, or of the fluid filtered from such precipitate, add NH₄Cl (if not already present), NH₄OH, and (NH₄)₂CO₃, and heat gently for a few minutes (Note 20).

18. *No precipitate forms.*

Absence of Ba, Sr, and Ca, at least in notable quantity (Note 21). Traces, however, may be present; to detect them, proceed as follows:—Add to a portion of the solution some (NH₄)₂SO₄; if the fluid becomes turbid it contains traces of barium.

To another portion add some (NH₄)₂C₂O₄, and allow to stand a few minutes; if a precipitate forms, traces of calcium are present.

Treat the remainder of the solution, a portion of which you have just tested, according to 24.

19. *A precipitate is formed.*

Presence of Ba, Sr, and Ca. Treat the whole filtrate with NH₄OH and (NH₄)₂CO₃; heat gently for some time and filter; take two portions of the filtrate and test one with (NH₄)₂SO₄ for traces of barium, the other with (NH₄)₂C₂O₄ for traces of calcium, which may possibly be present; if found, mix the two solutions and filter, and test the filtrate for magnesium according to 24. The remainder of the filtrate, to which neither (NH₄)₂SO₄ nor (NH₄)₂C₂O₄ has been added, is tested for potassium and sodium according to 25 or 28, the method used depending on whether magnesium is present or not.

20. Precipitate produced by (NH₄)₂CO₃ (contains BaCO₃, SrCO₃, CaCO₃).

Dissolve in least possible quantity of HC₂H₃O₂. Take a small portion of this solution and add to it some CaSO₄.

The course of proceeding now depends on whether the CaSO₄ gives an immediate precipitate or not.

21. *CaSO₄ causes an immediate precipitate*—proves Ba.

To the remainder of the acetic acid solution add a slight excess (Note 22) of K₂Cr₂O₇, and filter. Precipitate contains BaCrO₄ (yellow). To the filtrate add NH₄OH to alkaline reaction, and then (NH₄)₂CO₃; heat gently and filter. Reject filtrate. Dissolve the precipitate, consisting of SrCO₃ and CaCO₃, in acetic acid, divide solution into two parts, *a* and *b*.

22. *a.* Add an excess of CaSO₄, heat gently and shake well. A white precipitate proves Sr. (In dilute solutions the precipitate forms very slowly).

b. If strontium has been found in "*a*" (Note 23), add an excess of (NH₄)₂SO₄ to solution "*b*," boil, keeping solution alkaline with NH₄OH, and filter. Reject precipitate (Note 24).

To the filtrate add (NH₄)₄C₂O₄—a white precipitate shows presence of Ca.

If Sr is not present, the addition of the (NH₄)₂SO₄ is omitted, and the calcium tested for directly with NH₄OH and (NH₄)₂C₂O₄.

23. *CaSO₄ does not give an immediate precipitate.*

In this case add a little more of the acetic acid solution to it, and test for strontium according to 22, *a*. Then take balance of solution and treat it for calcium as directed in 22, *b*.

24. FILTRATE FROM (NH₄)₂CO₃ PRECIPITATE, OR SOLUTION IN WHICH THAT REAGENT HAS FAILED TO GIVE ONE.

Contains magnesium and the alkalies. Take the portion of the filtrate that has been freed from traces of Ba and Ca, by means of (NH₄)₂SO₄ and (NH₄)₂C₂O₄ (see 19), and add to it NH₄OH and Na₂HPO₄—a white crystalline precipitate proves the presence of Mg.

The method of testing for Na and K now depends on whether magnesium is present or not.

25. *Magnesium is present.*

As Mg interferes with the test for the alkalies, it must be removed before testing for them.

Evaporate the balance of the filtrate from the (NH₄)₂CO₃ precipitate (19) to dryness, and ignite until all ammonium salts are expelled. Dissolve the residue in a little water, add baryta-water as long as a precipitate forms, boil, filter; add to filtrate NH₄OH and (NH₄)₂CO₃, heat gently, filter and evaporate filtrate to dryness (add a little NH₄Cl during the evaporation, so that any alkaline hydroxide or carbonate will be converted into chloride) (Note 25); ignite gently until all ammonium salts are volatilised, then dissolve in a very little water, and test for Na and K, according to 26 and 27.

26. Test the concentrated solution in the flame on platinum wire. A strong yellow flame proves sodium. Confirm by adding to a portion of the solution some K₂H₂Sb₂O₇ (freshly prepared)—a white sandy precipitate indicates sodium. (In dilute solutions the precipitate forms very slowly; its formation is aided by rubbing watch-glass on which test is made with a glass rod).

27. To the remainder of the solution add a few drops of PtCl₄—a yellow crystalline precipitate proves K. If no precipitate forms on addition of PtCl₄, evaporate the solution nearly to dryness and add alcohol; this will show

* Parkes's "Hygiene."

† School of Mines Quarterly, Vol. xi., No. 3.

the presence even of traces of K, by leaving undissolved a yellow powder consisting of K_2PtCl_6 .

28. *Magnesium is not present.*

In this case it is only necessary to evaporate the solution to dryness, ignite carefully to drive off all ammonium salts, then dissolve residue, if any, in a very little water, filter if necessary, and test for Na and K according to 26 and 27.

29. Ammonia still remains to be tested for. Treat a portion of the original solution with KOH or $Ca(OH)_2$. Test the liberated gas, if any, with moistened red litmus paper; if it turns blue, ammonia is present (colour disappears on drying the test-paper).

Notes.

Note 1.—If the fluid is colourless, it contains no chromium. If coloured, the tint will to some extent act as a guide to the nature of the substance present; thus a green tint or violet tint turning green upon boiling, points to Cr; a light green to Ni; a reddish colour to Co; the turning yellow of the fluid upon boiling with HNO_3 to Fe.

It must be remembered, however, that these tints, except the last, are perceptible only if the metals are present in considerable quantity, and also that complementary colours, such as the green of Ni and the red of Co, will destroy each other, and that such a solution may be colourless.

Note 2.—The H_2S comes from the previous precipitation of the 5th Group metals, by that reagent. If not removed, it would cause a precipitation of sulphides on the addition of NH_4OH , and thus hide the reaction given by the latter.

Note 3.—The FeO should be oxidised to Fe_2O_3 , so that it will be precipitated on the addition of NH_4OH .

Note 4.—This only holds good for Al and Cr in the absence of non-volatile organic substances, especially acids such as citric and tartaric. Citric acid may also prevent the precipitation of Mn.

If organic matter is present, it should be removed by evaporating the whole of the solution used for the 3rd and 4th Groups to dryness and gently igniting.

It is a good plan to moisten the dry residue before igniting with a little HNO_3 (conc.). The ignited residue is then dissolved by boiling with a small quantity of strong HCl and filtering from any insoluble residue. The solution is now ready to be tested in the usual way.

Note 5.—The presence of much NH_4Cl has a great tendency to prevent the precipitation of borates and fluorides of the alkali-earth metals.

Note 6.—Magnesium oxalate is thrown down from HCl solution by NH_4OH only after some time, and never completely: dilute solutions are not precipitated by NH_4OH .

Note 7.—Phosphates, borates, &c., of the alkali-earth metals cannot exist in a neutral solution.

Note 8.— NH_4Cl is added to prevent the precipitation of magnesium and manganese; it also promotes the precipitation of the metals of the 4th Group as sulphides.

Note 9.—A large excess of NH_4OH should be avoided, as it increases the solubility of NiS in $(NH_4)_2S$, and dissolves some $Al_2(OH)_6$.

Note 10.—If the filtrate is dark brown, it indicates the presence of nickel, since NiS, under certain conditions, is slightly soluble in ammonium sulphide, especially if the latter contains any polysulphides (indicated by colour of the solution). Boil until $(NH_4)_2S$ is all decomposed and the free ammonia driven off, then add a few drops of dilute HCl, and filter from the precipitate of NiS and S. Make filtrate alkaline with NH_4OH , and proceed according to 17.

Note 11.—The addition of a little $(NH_4)_2S$ to the wash water prevents the oxidation of the sulphides to sulphates, a reaction likely to occur when they are exposed to the air.

Note 12.—Observe colour of precipitate—if pure white it indicates absence of iron, cobalt, and nickel.

Note 13.—Iron is tested for in the original solution with $K_6Fe_2Cy_{12}$, and NH_4CyS in order to determine which oxide is present, since after treatment with H_2S or $(NH_4)_2S$ it is always in the form of a ferrous salt, owing to the reducing action of these reagents. When making the test with NH_4CyS , if the colour does not appear on the addition of this reagent, add an excess of HCl to the test; this will counteract the influence of phosphates, borates, &c., which interfere when present.

Note 14.—Iron must always be in the ferric form for precipitation by $NaC_2H_3O_2$ or $BaCO_3$.

If the iron is not completely oxidised, there is likely to form a red modification of ferric oxide that runs through the filter paper and is very insoluble.

Note 15.—If the colour of the solution indicates manganese, heat it with a few drops of alcohol, and filter from the precipitated oxide of manganese.

Note 16.—The $KClO_3$ is added to the fusion mixture to oxidise any chromium that might possibly have been left unacted on by the bromine, and then precipitated with the basic acetates.

Note 17.—Be careful not to mistake a slight precipitate of sulphur, which is quite likely to form in the hot acid solution, for one of ZnS. In case of doubt, confirm by the blowpipe test with $Co(NO_3)_2$. A very delicate way of making this test is to dissolve the supposed ZnS in a few drops of HCl, then add a drop or two of $Co(NO_3)_2$; precipitate mixture with Na_2CO_3 , boil, filter and wash, and ignite precipitate on platinum foil. On triturating the residue the green colour will be distinctly seen.

Note 18.—Instead of the separation given in 12, the following method may be used:—

To the filtrate from the $BaCO_3$ precipitate add H_2SO_4 (dilute) in sufficient quantity to precipitate all of the barium in the solution, heat to boiling, and filter.

To the filtrate add KOH in excess; the manganese precipitates as $Mn(OH)_2$ (turning brown on exposure to the air), filter and pass H_2S into the filtrate—a white precipitate proves Zn. The precipitate is sometimes dark coloured, owing to impurities; in doubtful cases always test it by the blowpipe. (See Note 17).

Note 19.—The precipitate is dissolved in HCl, and then precipitated with NH_4OH , in order to get rid of the excess of $BaCO_3$. In cases where there is only a slight excess of $BaCO_3$, this operation may be omitted.

Note 20.— NH_4OH is added to prevent the possible formation of any bicarbonate, and also because the precipitate of the carbonates is more insoluble in ammonia water than in pure water. Heating causes the amorphous precipitate to contract and become crystalline, in which condition it is much more readily filtered; also decomposes any bicarbonate.

Note 21.—Owing to the slight solubility of $BaCO_3$ and $CaCO_3$ in NH_4Cl , traces of these metals are often held in solution by the NH_4Cl present in the solution.

Note 22.—A large excess of $K_2Cr_2O_7$ is to be avoided, especially in presence of much acetic acid, since $BaCrO_4$ is slightly soluble in chromic acid. The filtrate should only be coloured a pale yellow by the excess of $K_2Cr_2O_7$ contained in it.

Note 23.—It is not necessary to wait to see if Sr is found in "a" before testing for Ca. Proceed just in the same manner as if Sr was present, adding $(NH_4)_2SO_4$, boiling and filtering, and testing filtrate with the oxalate for calcium.

Note 24.— $(NH_4)_2SO_4$ precipitates calcium from strong solutions, so that the formation of a precipitate on the addition of this reagent does not prove the presence of Sr, unless the precipitate is repeatedly boiled with the $(NH_4)_2SO_4$ and NH_4OH , which will finally remove all of the $CaSO_4$, leaving only the $SrSO_4$.

Note 25.—In cases where the alkalis are present in the original solution as sulphates, the addition of $Ba(OH)_2$ to remove the magnesium converts them into hydroxides, and the latter, on the addition of $(NH_4)_2CO_3$ to precipitate the barium, are changed to carbonates.

THE SEPARATION AND DETERMINATION
OF ZINC IN PRESENCE OF IRON
AND MANGANESE.

By J. RIBAN.

THE methods hitherto proposed for the difficult determination of zinc in presence of iron generally require the previous separation of the iron in a form which renders it unfit for direct weighing, and besides the metal carries down with it valuable proportions of zinc. Hence it is necessary to re-dissolve and re-precipitate it before proceeding to the ultimate determination of the zinc. We are thus led to the successive washing of two gelatinous precipitates of iron, an operation always long and troublesome if this metal is in notable quantity. Further, in the analysis of a great number of ferruginous zinc ores it may be desirable to determine this latter metal first, or even exclusively; the iron, manganese, &c., having but a secondary importance or none at all. Some methods used for the initial determination of zinc do not allow of its determination in presence of lime, which occurs in the gangue of certain ores.

The author proposes a process which gets rid of all these difficulties and permits of the direct gravimetric determination of zinc. It is founded on the following facts established in a former memoir (*Comptes Rendus*, cvii., p. 341). (1) Zinc, in presence of alkaline or ammoniacal hyposulphates, gives with sulphuretted hydrogen a precipitate of sulphide, dense, granular, easy to wash, and insoluble in the cold by hyposulphuric acid set free; (2), iron is not thrown down by sulphuretted hydrogen in presence of the hyposulphates, and zinc, if present, carries down mere traces of iron.

For the direct determination of zinc in presence of iron (ferric or ferrous) and manganese the solution is first brought to such a degree of dilution that it contains at most 0.1 gm. zinc in 100 c.c.; it is then saturated with a solution of sodium carbonate until there appears a slight permanent precipitate, which is re-dissolved in a few drops of dilute hydrochloric acid. A current of sulphuretted hydrogen is then passed into the cold liquid, when the greater part of the zinc is precipitated with sulphur, derived from the reduction of the ferric salt; a large excess of a solution of sodium hyposulphate is then added, and the current of sulphuretted hydrogen is continued. The last remains of the zinc are precipitated, but the iron remains in solution. An excess of hyposulphate is not injurious. For these determinations it is convenient to prepare a solution of known strength and to pour in double the theoretical quantity as approximately calculated for the double decomposition with the zinc and iron. The use of an excess of hyposulphate supersedes the precautions.

If after the precipitation of the zinc it is proposed to determine the iron by means of ammonia, as ferric oxide always carries down some proportion of alkaline salts, it preferable to use ammonium hyposulphate, which is now also an article of commerce. The initial saturation of the free acid in the solutions is effected, not with sodium carbonate, but with ammonia or ammonium carbonate, until the yellow colouration of the solution containing iron passes to orange, the colour of the neutral or basic salts of this metal.

The precipitate of zinc sulphide, which is dense and collects readily, is white, sometimes greyish from the presence of traces of iron, which may be easily or quickly determined, as it will be seen. The precipitate is let stand for five or six hours at least, and is washed by decantation and filtration in hot water to which a solution of sulphuretted hydrogen has been added, when it very often takes a slightly violet tint; the washing is completed on the filter. The precipitate is ignited with sulphur in a current of hydrogen (H. Rose's apparatus) and weighed; it consists of zinc sulphide containing very small quantities of iron sulphide, which render it slightly

greyish. These traces are determined by dissolving the contents of the crucible in hydrochloric acid, peroxidising with a few drops of nitric acid, and then supersaturating with ammonia after the addition of a large excess of ammonium chloride to prevent the precipitation of the zinc. The quantity of iron carried down by the zinc is so slight that ammonia produces no precipitate in the cold, and it must be raised to a boil to cause a few light flocks of ferric hydroxide to appear. They are collected on a small filter and washed with solution of ammonium chloride. The weight of this peroxide is re-calculated into iron sulphide, which is deducted from the weight of the zinc sulphide as previously found, thus giving the nett weight of the latter.

If we wish to determine the iron in the liquids freed from zinc, it is sufficient to concentrate them and peroxidise with nitric acid, which throws its action immediately upon the iron, the hyposulphates being scarcely attacked. From the solution the iron is thrown down with ammonia in the ordinary manner.

The same method admits of the exact separation of zinc from manganese; zinc sulphide carries down merely inponderable quantities of manganese.

This method has been applied successfully to the analysis of ferruginous calamines; if they are at the same time plumbiferous it is necessary, first, to eliminate the lead, which would otherwise be precipitated along with the zinc by the sulphuretted hydrogen.—*Comptes Rendus* (cx., p. 1196).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY
SAMPLES OF THE WATER SUPPLIED TO LONDON
FOR THE MONTH ENDING MAY 31ST, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London
Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolitan Water Act, 1871.

London, June 7th, 1890.

SIR,—We submit herewith the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

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

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

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

Of the 182 samples examined, all were found to be clear, bright, and well filtered, excepting two, one of which was recorded as "slightly turbid," and one as "very slightly turbid."

The variations in mean composition of the water supplied to London, noticeable from month to month, continue to be, as is usually the case, confined within so limited a range as to afford very little occasion for remark or comparison. During the past month the maximum proportion of organic carbon present in any single sample of Thames-derived water examined was found to be 0.173

part in 100,000 parts of the water, corresponding to about only three-tenths of a grain of organic matter per gallon. The mean proportion of organic carbon present in the May supply was found to be 0.156 part in 100,000 parts of the water, as against a mean of 0.148 part in the April and of 0.154 part in the March supply.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 5th, 1890.

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

MESSRS. W. B. Shuttlewood and H. R. Kenwood were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Charles Edwin Day, 1, Merchiston Bank Terrace, Edinburgh; Robert Frost, St. James's Chambers, Duke Street, S.W.; George German, Huntingdon House, Ashby de la Zouch; Colin Gordon, Millwall Club, West Ferry Road, Millwall, E.; Frank Haydon, Ettrick, Putney Common, S.W.; Arthur E. Palmer, Ashley Mount, Tettenhall, Wolverhampton; Thomas Parkes, Grammar School, Stamford; Edward Cox Seaton, 35, George Street, Hanover Square, W.; James Mitchell Wilson, Hall Gate, Doncaster.

The following papers were read:—

45. "*The Production of Pure Metallic Copper in a Crystalline Condition.*" By C. C. DUNCAN, King's College, London.

The method of precipitating copper oxide from a boiling solution of copper sulphate with potassium hydroxide and then reducing in electrolytic hydrogen having been found unsatisfactory, as the last traces of sulphate could not be washed away, experiments were made on the reduction of the sulphate by zinc.

To a solution containing several grms. of purified sulphate made acid with chlorhydric acid, metallic zinc (containing only a trace of lead) was added in small fragments. Dark spongy-looking copper at once separated, and this soon protected the zinc from the action of the acid; consequently the copper was very slowly deposited: it was found to be in the form of feathery dendritic crystals.

A portion of the crystalline copper, well washed with dilute chlorhydric acid and distilled water, was dissolved in strong nitric acid free from sulphuric, the solution was diluted, and barium nitrate added; no precipitate of any kind formed, even after standing forty-eight hours, showing the absence of sulphur.

To discover whether the metallic copper contained zinc, two of the finest crystals (about 8 m.m. long) were again well washed and dried in hydrogen. These crystals were then fixed in an ordinary spark-stand, and the spark from a 2-inch Apps' coil, with a Leyden jar of one quart capacity in the circuit, was passed between them. The light from the copper terminals was analysed by one of Browning's two-prism spectroscopes, and the spectrum given by the copper was compared with that of zinc. None of the lines of zinc coincided with those given by the copper; it was therefore assumed that zinc was absent.

The bright lines given by the copper crystals agreed with those described by Thalèn ("*Mémoire sur la détermination des longueurs d'onde des raies métalliques.*" *Act. Nova Upsal.*, iii., vi., 1868, 29).

The spark and lines were extremely bright and no faint lines were to be seen (except the usual air-lines), showing the absence of any metallic impurity.

Microscopic examination proved the dendritic crystals to be built up of octahedrons. As the production of these crystals was quite accidental, experiments were made with different strengths of copper sulphate solutions, with and without free acid, in order to reproduce them.

In the literature relating to the reduction of metallic copper from its salts by means of metallic zinc, there is no mention whether the copper so reduced is in the crystalline state, except in a paper by Dr. Gladstone and Mr. Tribe (*Proc. Roy. Soc.*, xx., 1872, 219), who mention the deposition of metallic copper in a crystalline condition, but they make no remark on the purity or size of the crystals so formed.

In another paper, "On the Crystallisation of Silver, Gold, and other Metals" (*Proc. Roy. Institute*, vi., 1872, 428), Dr. Gladstone again refers to crystalline copper in the following terms:—

"Copper salts give round nodules which have no crystalline appearance when deposited from moderately weak solutions, but a very strong solution of the chloride—about 40 per cent—yields with zinc first a black thick

	CuSO ₄ .	Water.	Acid.	Results.
I.	10 grms.	400 c.c.	0	Copper was at once reduced in spongy state and then in minute dendritic crystals just visible to the unaided eye. The spongy copper proved to be composed of octahedrons under the microscope. The crystals did not increase in size on standing.
II.	20 grms.	400 c.c.	0	} Same as I.
III.	50 "	400 "	0	
IV.	10 "	400 "	10 c.c.	
V.	20 "	400 "	10 "	Same as IV.
VI.	10 "	400 "	100 "	Crystals of copper which were slightly larger than those produced in V.
VII.	20 "	400 "	200 "	Dendritic crystals of copper were produced, several of which were 10 m.m. in length. Sulphur was detected in these crystals, and in most other crystals which had been reduced in a solution which was very strongly acid. No zinc was detected by the spectroscope.
VIII.	40 "	400 "	200 "	The crystals produced were only very slightly larger than those in VII., but more numerous.

growth, then arborescent fringes of red metal terminating in crystals of very appreciable size."

In all the experiments made by the author with acid and neutral copper solutions, dendritic crystals of copper were found which could be seen with the unaided eye; they were small in the case of neutral, and large in the case of acid solutions.

The accompanying tables give the quantity of copper sulphate, water, and chlorhydric acid (relative density 1.152) used in the different experiments, and the results.

As sulphur had been detected in several of the crystals deposited from the copper sulphate solutions, a few experiments were made with copper chloride free from sulphate.

	CuCl ₂ .	Water.	Acid.	Results.
I.	10 grms.	400 c.c.	0	Small dendritic crystals of copper were quickly produced. On standing, the crystals increased slightly in size.
II.	20 "	400 "	0	Numerous small dendritic crystals with several about 7 m.m. long. No impurity detected.
III.	10 "	400 "	20 c.c.	Two or three crystals about 11 m.m. long with the usual mass of smaller crystals. No impurities were detected.
IV.	40 "	400 "	20 "	Four or five crystals 12 m.m. long with the usual mass of smaller crystals. No impurity detected.
V.	140 "	500 "	40 "	This solution gave the finest crop of dendritic crystals yet produced. One crystal measured 15 m.m., and its lateral branches were composed of clumps of crystals. The crystals were erect, and had a beautiful metallic appearance. Several of the crystals were from 5 to 8 m.m. in length, two or three 12 to 13 m.m., and only a little spongy copper was to be seen. No impurity could be detected.

The pure crystalline copper is insoluble in pure nitric acid (free from nitrous acid). See Velez (*Proc. Roy. Soc.*, 1890).

Crystalline copper is said to have been obtained by using iron and aluminium as reducing agents. Thus Gore, in his text-book of "Electro-Metallurgy," pp. 203—204, refers to the use of iron in recovering copper from large deposits of the Tharsis and Rio Tinto mines in Spain. The copper is dissolved by means of chlorhydric acid, and the liquid is run into large vats filled with scrap

iron. In a short time all the copper is reduced in the form of feathery crystals upon the iron. The process is described by P. Argall and G. A. Kinahan in the *Sci. Proc. Roy. Dublin Soc.*, N.S., iii., 1883, 302—328, and on p. 309 the production of crystalline copper is mentioned. No reference is made to the purity or size of the crystals.

The reduction of copper from its sulphate by the aid of aluminium is mentioned in "Watts' Dictionary of Chemistry," 2nd Sup., 1875, p. 383, in a passage which is extracted from Cossa (*Nuovo Cimento* [2], iii., 75. The crystals of copper are described as follows:—"Aluminium foil immersed in a solution of sulphate or nitrate of copper is not acted upon at once, but after two days the foil becomes covered with crystals consisting partly of dendrites, but for the most part of well-defined octahedrons." It was found that if the solution of the copper sulphate is neutral, only octahedrons are produced; but that if an acid is present, dendrites are produced. Sulphur was the only impurity detected.

"Copper is immediately reduced by aluminium from a solution of cupric chloride, and likewise, though more slowly, from the acetate." It is not mentioned whether the copper is deposited in the crystalline or amorphous state, but the author has found, on experimenting with these substances, that dendritic crystals of copper are produced in both cases. No impurity could be detected.

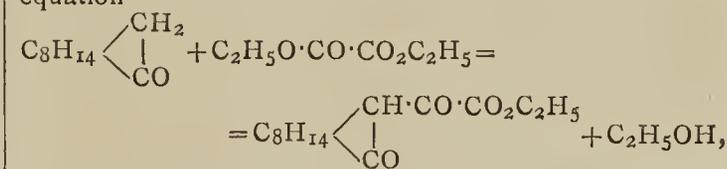
Magnesium was found to reduce copper from a solution of copper sulphate in very small quantities, the copper being formed in small patches composed of dendrites and octahedrons. Magnesium added to a solution of copper chloride caused an evolution of gas, throwing down a green precipitate, and at the same time reducing the copper in the spongy state. The well-washed copper contained magnesium.

In a note by M. A. Commaille "On the Action of Magnesium on Neutral Metallic Salts" in the *CHEMICAL NEWS*, xiv, 188, it is mentioned "that copper sulphate gives with magnesium the metal (copper), the hydrated peroxide and a green subsalt. With the chloride no metal (copper) is precipitated, but a deposit of Brunswick green."

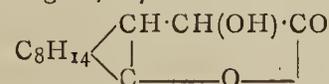
In experiments made by the author with the chloride, copper was reduced in appreciable quantity, but in an entirely amorphous state.

45. "The Action of Ethylic Oxalate on Camphor." By J. BISHOP TINGLE, Ph.D.

The author finds that camphor and ethylic oxalate in presence of metallic sodium interact according to the equation



forming ethylic camphoroxylate. This is an oily liquid, which decomposes on distillation; on hydrolysis it is converted into camphoroxylic acid, which crystallises in rhombic plates melting 88° C. On reducing this acid with sodium amalgam, a γ -lactone of the formula



is obtained, melting at 75—76°. Ethylic camphoroxylate and phenylhydrazine interact to form a monophenylhydrazone, which crystallises in white needles melting at 187—188° C. By the action of hydroxylamine a compound is formed which melts at 193° and will be further investigated. On ethylic camphoroxylate with aniline to 165°, oxanilide is produced.

46. "The Oxidation of Turpentine in Sunlight." By HENRY E. ARMSTRONG.

It was pointed out by Sobrero in 1851 (*C. R.*, xxxiii, 66) that when turpentine is exposed to light in presence of

moisture and oxygen a crystalline substance is formed which has the composition represented by the formula $C_{10}H_{18}O_2$; and that this substance is decomposed when boiled with dilute sulphuric acid, an oil being formed which has a powerful odour recalling both that of camphor and that of turpentine. The author's attention became directed to this substance about twelve years ago in the course of his studies of the terpenes and camphor, and in most years since, during the summer, he has carried on experiments on the oxidation of $C_{10}H_{16}$ hydrocarbons in sunlight, and has been able to confirm Sobrero's statements in every particular. As the crystalline product in question has not yet been named, it is proposed to term it—at all events, provisionally and until its constitution is determined—*sobrerol*.

Sobrerol is readily soluble in alcohol, and crystallises from this solvent usually in large, flexible, monosymmetric prisms having a peculiar hour-glass structure inside and showing hemihedrism. It is slightly soluble in water, benzene, chloroform, and petroleum spirit; the aqueous solution has a bitter taste. It melts at about 150° . The results obtained on analysis (carbon, 70.57 and 70.49 per cent; hydrogen, 10.71 and 10.74 per cent) show that, as Sobrero states, it has the formula—



and there can be very little doubt that it is a glycol; but, owing to its extreme sensitiveness, to the action of acids, it is difficult to prove this by the ordinary methods. Sobrerol is optically active in a high degree, the apparent specific rotatory power of the products from French turpentine in a 5 per cent. solution in alcohol (B.P.) being slightly above 150° . Sobrerol from American turpentine (from Savannah) was found to have about the same rotatory power, but in the opposite direction. The optical similarity of the two products is noteworthy, inasmuch as the American has less than half the rotatory power of French turpentine. It would seem that only the terpenes proper, and not the citrenes, &c. (*cf. Chem. Soc. Trans.*, 1879, 734; *J. Soc. Chem. Ind.*, 1882, 478) form sobrerol. To ascertain whether this be the case, and what are the crystallographic and optical relationship of the products obtained from terpenes from different sources, the author is engaged in conjunction with Mr. W. J. Pope—to whom he is indebted for assistance in this research—in studying the behaviour of pure $C_{10}H_{16}$ hydrocarbons of all kinds.

When boiled with dilute sulphuric acid, sobrerol is readily converted into the oil referred to by Sobrero; the product is undoubtedly identical with the isomeride of camphor which Wallach and Otto have obtained by treating turpentine with nitrous acid (*Annalen*, ccliii, 249), and which they have provisionally named *pinol*; as the compound is not an *ol*, *i.e.*, an alcohol, it may be suggested that it might appropriately be termed *sobrerone*. The product from sobrerol begins to boil at $150-160^\circ$, but passes over almost entirely at about 183° , leaving a small amount of a viscid oil; it readily combines with bromine, forming a dibromide (bromine found 50.78 per cent) which crystallises very beautifully in forms of the rhombic system, the lengths of the axes being in the ratio $a : b : c = 0.5696 : 1 : 1.5553$, dimensions which almost absolutely agree with those quoted by Wallach and Otto, *viz.*, $a : b : c = 0.5700 : 1 : 1.5553$. The dibromide was found to melt at 93.5° , 94° being the melting point given by Wallach and Otto.

The formation of sobrerone from sobrerol is of interest as serving to explain its formation by Wallach and Otto's method: very probably sobrerol is first produced, and is at once acted on by the acid. Sobrerol is probably always the initial product of oxidation of turpentine. It may be expected that sobrerone will be found among the oxygenated constituents of some essential oils, and it is proposed to search for it.

If, as appears probable, sobrerol be a glycol, the formation of sobrerone from it is analogous to that of pinacolin from pinacone; but in this latter case, an isomeric change

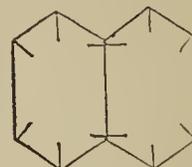
takes place, pinacolin being a ketone, $CM_3 \cdot CO \cdot CH_3$, and not the oxide corresponding to pinacone. Wallach and Otto's observations, however, show that sobrerone is not a keto-compound. It would, therefore, appear to follow that sobrerone is an oxide formed by withdrawal of the elements of a water molecule from two hydroxyls attached to contiguous carbon atoms.

47. "The Structure of Cycloid Hydrocarbons." By HENRY E. ARMSTRONG.

The appearance of Bamberger's remarkable papers (*Annalen*, cclvii, 1; *Ber.*, 1890, 1124), in which formulæ are proposed for naphthalene, anthracene, &c., apparently analogous to that suggested by v. Baeyer and the author for benzene, renders it desirable that the cases in which this formula is applicable should be carefully considered, especially as the somewhat novel conceptions which the author would associate with this symbol tend to limit the extension of the hypothesis.

Although superior to all other symbolic expressions in almost every respect, Kekulé's formula is, nevertheless, admittedly open to the objections (1) that it apparently involves the existence of two ortho- and two meta-derivatives; and (2) that it represents benzene as containing three pairs of carbon-atoms in the condition of those in ethylene. The *centric* formula was developed to meet these objections. It represents benzene as a symmetrical configuration, and is suggestive of only three derivatives. The six affinities which in Kekulé's symbol act in pairs, as in ethylene, are assumed actually to neutralise each other much as the affinities do in paraffins, but without constituting cross linkages within the ring as represented in the Claus formula, for example: the behaviour of the hydroterephthalic acids, of quinone and of anthracene, and among others, Kekulé's researches on the constitution of pyridine, of which he recently gave an account in Berlin, affording, in the author's opinion, abundant evidence of the non-existence of such cross linkages. The conception in his mind, to which, however, expression has not hitherto been given, has always been that the centric affinities act within a cycle rather than merely towards the centre in the manner pictured, and that there are peculiarities in the carbon-atom which render such a form of action possible: benzene, in fact, according to this view, may be represented by a double ring. It would appear that when an additive compound is formed the inner cycle of affinity suffers disruption, and, such a cycle being no longer possible, the contiguous carbon-atoms to which nothing has become attached of necessity acquire the ethylenic or unsaturated condition.

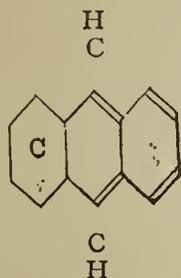
An extension of the hypothesis to naphthalene was suggested in September last year in a paper read at the British Association meeting at Newcastle (*B. A. Report*, 1889, 175). The following is the symbol there proposed:—



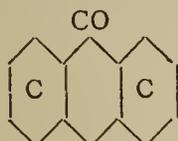
This symbol again involves the admission of the unusual conception that an affinity can act in two directions (*cf. Phil. Mag.*, June, 1888), the two carbon-atoms common to the two nuclei being represented as exerting an influence in both nuclei. In this case also the "centric" affinities are regarded as acting within a cycle composed, however, of 10 carbon-atoms; but no separation of the central carbon-atoms, such as Bamberger suggests, is supposed to have taken place. It becomes possible on this hypothesis, in a measure, to understand that a radicle in the one nucleus should, as is known to be the case, exercise an influence in a radicle in the other nucleus.

It appears to have hitherto been supposed that anthracene has a symmetrical structure: the author contends,

however, that this is not the case, and that it is to be represented by the formula

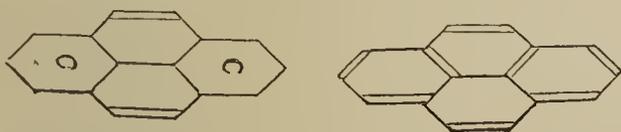


wherein C is the centric nucleus of benzene; but anthraquinone—which, strictly speaking, is derived from dihydroanthracene and not from anthracene—is symmetrical and contains two centric benzene nuclei, thus:—



The behaviour of anthracene and anthraquinone appears to be entirely in accordance with these conclusions. Phenanthrene may be regarded as composed of two lateral "centric" nuclei, to which is conjoined a median nucleus in which the only two "available" carbon-atoms are in the ethylenic condition.

The behaviour of anthracene is more nearly that which it may be supposed the hypothetical hydrocarbon having the structure indicated by Kekulé's benzene symbol would manifest. Pyrene, probably, is still more closely related to the ethylenic form of benzene, and has little, if any, resemblance to the centric form. Two formulæ may be assigned to this hydrocarbon.



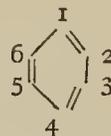
The first of these is the symbol of a phenanthrene derivative; but the behaviour of pyrene is so entirely unlike that of phenanthrene that it may be regarded as out of the question; the second would appear to be entirely in accordance with the results of Bamberger's researches.

It is contended that the formulæ now suggested serve to explain the exceptional physical properties of hydrocarbons such as anthracene and pyrene.

DISCUSSION.

Dr. JAPP desired to know what precise mechanical conception Dr. Armstrong wished to express by the broken bonds in his centric formula. They appeared to denote attractive forces which stopped half way—in other words, attractive forces which did not attract. In this way the centric formula would resolve itself into a benzene hexagon with triadic carbon.

Professor RAMSAY said that he did not see the necessity of substituting an unusual conception for the one in common use, which, in his opinion, gave a sufficient and clear mental picture of the relations between benzenoid compounds. In the case of crotonic and isocrotonic acids, an isomeric change is known whereby the position of the "double bond" is shifted. The difficulty in unreservedly accepting Kekulé's benzene formula, caused by the fact that two ortho-compounds are unknown, while they are required by his conception, was, to some extent, removed by Kekulé himself by his supposition that the double bonds were not stationary, but were sometimes between carbon-atoms 1 and 2, and sometimes between 2 and 3. In order to explain the fact that a change from the symbol—



to the symbol—



is possible, it may be conceived that so long as no external influence is exerted on the benzene ring, it has the constitution suggested by Kekulé. It is probable that two isomeric ortho-compounds are impossible, because, if formed by substitution of hydrogen-atoms 1 and 2, a change would take place whereby the double bond, connecting 1 with 2, would be dissolved and replaced by a single bond, while the double bonds would then exist between 1 and 6, 3 and 2, and 5 and 4. Or the contrary may be the case, and the single bond may be the more unstable form of union, in which case, if an ortho-compound were formed between 2 and 3, the position of the bonds would also be reversed. The case of a change of position of double bonds in the crotonic acids renders this hypothesis not untenable.

Mr. CROMPTON agreed with Professor Ramsay in his remarks, and thought that objections to the Kekulé symbol, based on the view that, because this symbol contained double bonds, benzene should behave as an olefinic compound, were unjustifiable. A double bond was nothing more than an incomplete representation, on paper, of an unsaturated condition or want of equilibrium in the molecule, a state of things that might be due to totally different and distinct causes in the two cases. The behaviour of benzene in this respect must, therefore, differ from that of ethylene. The difference would have to be looked for in the different configurations of the molecules; but it was just this point that received no representation, or only an inadequate one, in the plane formulæ at present in use. The problem would, no doubt, only be finally solved when satisfactory space formulæ for these compounds had been discovered.

In reply to Dr. Japp, Dr. ARMSTRONG said that the broken bonds were intended to figure as resultants, much as the conjoined effect of two forces acting from different directions was expressed by their resultant. Referring to Professor Ramsay's remarks, he expressed the opinion that the isomerism of the crotonic acids was not sufficiently understood to serve as an argument in such a case. However well the non-existence of isomeric ortho- and meta-derivatives might be accounted for by Kekulé's oscillation hypothesis, it was impossible in this way to explain the fact that benzene, on the whole, behaved as a saturated and not as an ethylenic compound; there was also no reason to suppose, as Mr. Crompton had suggested, that "double bonds" in a ring would behave differently from those in an open chain: the whole of v. Baeyer's recent work was in contradiction to any such assumption, and Thomsen's and other observations left little doubt that in the formation of benzene there is a considerable "outgoing of affinity" beyond that which takes place when ethylenic union is effected. He scarcely thought that the introduction of geometric considerations would materially advance the solution of the problem under discussion. Whatever the ultimate fate of his hypothesis, he was convinced that a settlement of many practical problems—those relating to laws of substitution and isomeric change, for example—required the knowledge of the inner structure of the cycloid hydrocarbons; and such speculations, even if proved to be entirely false, at least served to suggest fresh lines of experimental inquiry, and on this account were not only permissible, but also desirable.

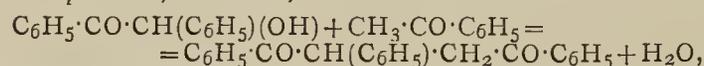
49. "Tertiary Butyl Mercaptan." By LEONARD DOBBIN, Ph.D., Chemical Laboratory of the University of Edinburgh.

The author finds that when tertiary butyl iodide is digested at a gentle heat with a sufficient quantity of zinc sulphide, an interaction takes place which results in the formation of tertiary butyl mercaptan. It is a colourless, extremely volatile liquid which boils at 65–66°, possessing an overpowering disagreeable smell, recalling that of other mercaptans; it solidifies in a freezing mixture of snow and salt to a white semi-translucent mass; it forms white insoluble compounds with mercuric chloride and with silver nitrate.

Products of higher boiling point are formed at the same time as the mercaptan; these are believed to be triisobutylene, and probably also tertiary butyl sulphide. This part of the subject is under investigation.

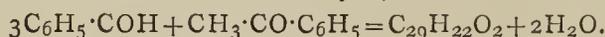
50. "Desylacetophenone." By ALEX. SMITH, B.Sc., Ph.D., Chemical Laboratory of the University of Edinburgh.

The author finds that a dilute solution of potassium cyanide in alcohol and water acts in many cases as a condensing agent. By boiling equimolecular proportions of benzoin and acetophenone in dilute alcohol with very little potassium cyanide, a condensation product, *desylacetophenone*, is formed,—



which is the saturated compound corresponding to Japp's anhydracetophenone-benzil. It may be got perfectly pure and white by re-crystallisation from acetic acid and alcohol. It melts at 126°. It is easily transformed into *triphenylfurfurane*, *triphenylpyrrole*, and *triphenylthiophen*, showing its constitution to be that given above. It forms a mono- and a di-hydroxime; by its interaction with one molecular proportion of phenylhydrazine, two molecular proportions of water being given off, an oiazone (pyridazine) is formed. This latter compound is converted by excess of phenylhydrazine into $\alpha\alpha'\beta$ -N-tetraphenylpyrrole.

A large quantity of another substance having the formula $\text{C}_{29}\text{H}_{22}\text{O}_2$ is formed at the same time as the desylacetophenone. It would seem that the benzoin, or a part of it, acts as a benzaldehyde,—



From acetone and benzoin the only substance isolable, if not, indeed, the only one formed, is that corresponding to the last-mentioned product from acetophenone. It has the formula $\text{C}_{24}\text{H}_{20}\text{O}_2$. The properties and constitutions of these two substances are still under investigation, as are also some other applications of the new interaction.

NOTICES OF BOOKS.

Alkali Works Regulation Act, 1881. Twenty-sixth Annual Report on Alkali, &c., Works by the Chief Inspector. Proceedings during the Year 1889, presented to the Local Government Board and to the Secretary for Scotland. London: Eyre and Spottiswoode.

THE Chief Inspector, in his introduction, refers to a difference between the inspection carried on under this Act and that conducted by sanitary inspectors under the Public Health Act. In this latter case "the senses of smell and sight are sufficient to determine whether a nuisance exists, though the toleration which ballast-burning in urban districts still enjoys is proof positive that men's notions on the definition of a nuisance are not uniform. The inspector under the Alkali Act has to determine the quality and quantity of any noxious gas found to be escaping, to ascertain if it exceeds the limits of tolerance, and the best practicable means of

minimising its emission. The Act, it must be observed, does not force the manufacturer to use any particular means for the suppression of the nuisance. The inspector, however, frequently finds it his duty to suggest and advise. "He cannot consistently complain of the imperfections in an operation unless he can show the possibility of attaining a better result. To this end he must possess a wide, a varied, and a profound chemical knowledge combined with abundant tact." As he, further, cannot well avoid becoming acquainted with the details of construction of the plant in the works inspected, and with the entire *modus operandi*, an inspector who sells or otherwise reveals trade secrets which have thus come under his cognisance certainly merits very severe punishment. German legislation, we must add, is pointing in this direction.

The number of works which come within the purview of the Act is declining. There are in England 116 alkali works, and in Scotland 16; other works scheduled in the Act, 787 in England and 113 in Scotland, making a total of 1032 registered works. This shows a decrease in the alkali works of 3, and in other scheduled works of 20, making, in England alone, a decrease of 23. The number of separate processes under inspection is increasing, as several distinct processes are often carried on in one establishment and by one and the same firm or company. It is interesting to find that the amount of hydrochloric acid vapour from the decomposition of salt is distinctly below one-half of the statutory limit. As regards the acid gases escaping from the lead chambers, they are below one-third of the legal limit, and are still diminishing yearly. The acids given off from chemical manure works is also decreasing. In 1883 the proportion was 0.5 grain SO_3 per cubic foot; it is now 0.349 grain, and in one district (East Lancashire and Yorkshire) reached 0.2 grain.

One firm only, manufacturers of ammonium sulphate, has been prosecuted under the Act.

The salt industry has decreased upon the whole by about 12 per cent, in consequence, doubtless, of the rise in price inaugurated by the "salt-ring." The production in Durham has, however, increased by 50 per cent.

The consumption of salt in the Leblanc soda process is slightly less than in 1888, viz., 584,203 tons as against 585,498 tons. Meantime, the proportion of salt consumed in the ammonia process is steadily increasing.

The production of ammonium sulphate is gradually increasing. Its value, taken at £12 per ton, has now risen to £1,500,000 yearly, and in the opinion of the Chief Inspector, this quantity might be increased ten-fold.

The recovery of sulphur from the vat-waste of the Leblanc process is now an established fact. The Chance process is in successful operation in twelve alkali works, although the plant required is very costly. There is little prospect of a permanent reduction of the sale price of sulphur. Were it to be lowered, many of the Sicilian mines would doubtless be closed. The amount of tank-waste deposited has now ceased to increase, but some time must elapse before the old heaps and their attending nuisance can disappear.

The influence of certain modern appliances in developing the intelligence of the workmen is fully acknowledged. As instances are mentioned the black-ash revolver, the gas-furnace, and the apparatus used in the recovery of sulphur by the Chance process.

Attempts are being made to suppress, or at least lessen, the injurious effects of salt works, the fumes from which, in the district of Winsford, have devastated the country for miles. Reference is here made to the value of the triple effect principle, by which, in many cases where evaporation is carried on, a vast saving of fuel and consequently of nuisance is effected. This system has been adapted to the salt manufacture by Dr. Pick, of Galicia, and is now being introduced at Shirleywich, in Staffordshire.

A Manual of Pharmaceutical Testing for the Man of Business and his Assistant; comprising Simple Instructions for the Testing of the Chemicals of the "British Pharmacopœia" with such Materials and Appliances as are in common use at the Dispensing Counter. By BARNARD S. PROCTOR, F.I.C. London: Offices of the *Chemist and Druggist*.

THE position of the pharmacist as regards his customers and the medical faculty is greatly changed. Time was when he could manufacture in his back shop or store-rooms the few and simple chemicals required in his business. Hence he might be supposed to know without special testing the quality of the articles in his jars and bottles and drawers. Now he is compelled to purchase from the manufacturer and the wholesale dealer. It is self-evident that he cannot afford to take for granted the skill, the care, and above all the honesty of those who supply him. Hence he is bound, in obedience to the reasonable requirements of the law, no less than in justice to the public, the medical profession, and to his own reputation, to examine all articles which come into his hands. It may possibly be thought that the ordinary manuals of analytical chemistry, qualitative and quantitative, will fully answer the requirements of the case. This, however, is a mistake. The Pharmacopœia lays down certain standards to which all chemicals sold by the chemist and druggists and used in medicine or in making up prescriptions must conform. Our author indicates the simplest, speediest, and most inexpensive manner of ascertaining if these requirements are obeyed. Whether a chemical is absolutely pure—in many cases a vain undertaking under the circumstances—he does not inquire. So long as no substance is present which would interfere with their efficacy, and so long as their strength or degree of concentration is practically correct, he is satisfied, and in so doing he is justified. "There are," he tells us, "sundry cases in which any deviation from the B. P. tests would not be legitimate, there is no alternative but to follow that process." In other cases simpler tests are given where those laid down in the B. P. are unsatisfactory, and certain errors, clerical or typographical, are pointed out. Thus, the instruction to add silver nitrate and barium chloride to an acidified solution of potassa is duly explained as an error.

All things being considered, we hold that there is not merely room, but actual need, for Mr. Proctor's treatise. It is of great importance for the pharmacist, especially in the outset of his professional career, to know when he has fulfilled all righteousness, and is consequently safe and can await the visits of any inspector with equanimity. We cordially echo the author's hope that this hand-book will encourage the habit of testing the chemicals used in medicine, and we believe that it will prove a safe and useful guide.

CORRESPONDENCE.

A RAPID METHOD FOR THE DETERMINATION OF ALUMINIUM IN IRON AND STEEL.

To the Editor of the Chemical News.

SIR,—Take 10 grms. of the iron or steel and dissolve the same in a mixture of 50 c.c. of strong HCl and 30 c.c. of water in a No. 8 beaker; when dissolved add 5 c.c. of a saturated solution of sodium phosphate, then 100 c.c. of water. To this solution add dilute ammonia until the free acid is neutralised; then take up the precipitate carefully with dilute HCl until the solution becomes clear, afterwards add 2 c.c. (not more) of strong HCl and boil; whilst boiling pour in 50 c.c. of a saturated solution of sodium hyposulphite; cover over and boil for one hour. Filter, wash well with hot water, afterwards wash the residue

from filter into the same beaker in which it was boiled, and dissolve in 100 c.c. of a 10 per cent solution of HCl, boil and filter off the sulphur. Evaporate filtrate to 5 c.c., then wash into a platinum dish, and neutralise with pure sodic hydrate (made from sodium). After neutralising add 2 grms. sodic hydrate in excess and boil for 30 minutes, dilute and filter from the iron, after washing the filtrate is made acid with HCl; then precipitate the aluminium down with ammonia; boil, filter off the aluminium phosphate, which is then dissolved in a small quantity of HCl and evaporated to dryness to separate the silica. Re-dissolve in HCl and filter, to the filtrate add 5 c.c. of ammonium phosphate, then ammonia with a few drops of ammonium acetate, and boil for 30 minutes; filter and wash residue well with hot water containing a little ammonium phosphate, ignite, and weigh the precipitate as $AlPO_4$, which contains 22.358 per cent aluminium.

This process, though appearing complicated, can be easily executed in six hours.—I am, &c.,

CHARLES PHILLIPS.

Phillips and Barker,
Chemical and Metallurgical Laboratories,
Fitzalan Square, Sheffield,
June 17, 1890.

UNAUTHORISED REPORTS.

To the Editor of the Chemical News.

SIR,—While reading the article on "Analytical Touts" (CHEM. NEWS, vol. xli., p. 195) the thought crossed me that it is not uncommon to find "pithy and concise reports, productive of excellent business results," manufactured from the simple returns of chemists who would not willingly mislead. Even the titles appended to one's name are at times subject to most curious enlargement. Having recently made a report to a company doing business some two thousand miles from here, I was favoured with a copy of the same in printed form. Judge of my surprise at seeing myself rated (in addition to my legitimate position in this institution) as "Chemist to the Board of Health of the State of New York" and "Consulting Chemist to the United States Government."—I am, &c.,

W. P. MASON.

Rensselaer Polytechnic Institute,
Department of Analytical Chemistry,
Troy, N.Y., June 10, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 23, June 9, 1890.

Action of Alkalies and Alkaline Earths, of Alkaline Silicates, and of Certain Saline Solutions upon Mica. Production of Nepheline, Sodalite, Amphigene, Orthose, and Anorthite.—Charles and Georges Friedel.—Only few experiments have been hitherto made upon the transformations which rocks and minerals have undergone under the influence of the various agents, physical or chemical, which must have been in action during geological periods. They have therefore thought it interesting to submit the minerals which form rocks to the action of water, with the addition of a certain quantity of alkalies, earths, silicates, and salts at high temperatures, reproducing thus the conditions which have been produced in Nature. They have used a thick tube of steel, lined with platinum, which, when two-thirds full of water, may be heated to about 500°. The subject of the experiments has been mica, and the result has been the production of the minerals mentioned above, *i.e.*, five of the minerals found in the eruptive blocks of Somma.

The Isomeric Conditions of Chromium Sesquibromide. The Blue Sesquibromide.—A. Recoura.—The solid blue bromide, if kept for some time at 100°, is transformed into its green isomer without a change of composition. It does not appear to be produced spontaneously at ordinary temperatures. If a solution of the blue bromide is left to crystallise there are formed, at first, long blue crystalline needles; then when the water has almost disappeared we see appear, among these needles, small green crystals which gradually pervade the entire mass. On the other hand, a saturated solution of the green bromide remains green, and in time deposits green crystals. If a solution of the green bromide, mixed with free hydrobromic acid, is let stand, it remains green for an indefinite time, and does not pass into the violet modifications.

Separation and Determination of Zinc in Presence of Iron and Manganese.—J. Riban.—(See p. 307).

Composition of Clays and Kaolins.—Georges Vogt.—The author's researches show that no process of levigation enables us to separate the hydrated aluminium silicate from the foreign bodies which accompany it. The alkalies contained in clays may have been introduced either by micas or by felspars.

Synthesis of the Carbon Fluorides.—C. Chabrié.—The author has obtained methylene fluoride, CH_2F_2 . He obtains this gas by heating to 180°, for half an hour, 1.7 grms. methylene chloride with 5.08 grms. silver fluoride prepared by Gore's process, and rendered anhydrous with the precautions described by Guntz.

Products of the Saccharification of Starchy Matter by Acids.—G. Flourens.—In opposition to Gruber, O'Sullivan, Brown, and Heron, the author concludes that there is produced in the action of acids upon starch only a single dextrine, as admitted by Payen, which is accurately determined by its high rotatory power, which approaches that of soluble fecula.

Decomposition of Organic Manures in the Soil.—A. Muntz.—In this paper the following conclusions are reached:—In the soils which are incapable of nitrification in consequence of their chemical constitution, the nitrogen of the organic matters is converted into ammonia. The same result happens in soils when nitrification is checked by compactness or where the nitric ferment has been killed. Even when the nitric fermentation is very energetic organic manures give rise to ammonia.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xxi., No. 2.

Two New Sugars extracted from Quebracho.—C. Tanret.—Both these papers have been already noticed.

Volumetric Determination of Tannin in Wines.—NM. Roos, Cusson, and Giraud.—(Already inserted).

A Falsification of Milk.—Dr. Perron.—In order to baffle the use of the lactobutyrometer, a novel fraud has been devised. Some oil of low sp. gr., and not possessing a bad taste, is emulsified with yolk of egg and added to the milk after the cream has been abstracted.

Justus Liebig's Annalen der Chemie.
Vol. ccliv., Part 3.

On the Euxanthon Group.—C. Graebe.—The author has produced euxanthon synthetically by heating 5 grms. resorcylic acid and 6 grms. hydroquinoncarbonic acid with 12 parts of acetic anhydride to a boil for four hours in a small retort with an ascending condenser. The product was then submitted to distillation. Acetic acid and anhydride passed over, and the last portions of the anhydride contained a little euxanthon. On heating more strongly the bulk of the euxanthon sublimed over, whilst much carbon remained in the retort. The syn-

thetic euxanthon has the same composition and properties as the natural kind obtained from Indian yellow.

Communications from the Agricultural-Chemical Laboratory of the University of Göttingen.—Papers by Dr. H. J. Wheeler and B. Tollens on xylose or wood-sugar, a second pentaglucose, and researches on wood-gum.

Communications from the Chemical Institute of Marburg.—Researches by W. Roser on narcotine.—Narcotine is a meconine hydrocarbon, and, like hydrastine, is closely connected with another opium alkaloid, papaverine. Both opium alkaloids are derivatives of a benzylisoquinoline. Narceine has no connection with narcotine.

On Benzoyl-tannin.—Dr. Carl Böttinger.—(Already inserted).

Action of Ammonia and Ethylendiamine upon Tetrachloridiacetyl.—S. Levy.—Not susceptible of useful abstraction.

ERRATUM.—P. 162, col. 1, for "Francis Walls" read "Francis Watts."

THE BANKHALL OIL AND CHEMICAL WORKS,
LIMITED (Formerly Thacker and Co.), LIVERPOOL

FOR SALE BY PRIVATE TREATY as a going concern the above old-established and well-known Oil and Chemical Works, including the whole of the Machinery and Plant and the Goodwill of the business. The Works stand on about 15,530 square yards of land, which is held on lease for seventy-five years from April 30, 1885, at a ground rent of £700 per annum. In addition there is a good private road on the East side of the Works which is occupied jointly with the Lancashire and Yorkshire Railway Co. The situation of the Works is everything that could be desired. They are bounded on the south and east by the Lancashire and Yorkshire Railway, on the west by the Leeds and Liverpool Canal, and on the north by Bankhall Street. There are sidings into the Works from the Lancashire and Yorkshire Railway, and there is also direct access to the Canal. The Works are also in close proximity to the Docks and to the London and North-Western, Midland, and Manchester, Sheffield, and Lincolnshire Railway Stations, and are only about 1½ miles from the Liverpool Exchange. An important feature in connection with these Works is that they are not liable to be restrained or prosecuted for emitting noxious odours, &c. The Buildings comprise extensive Oil and Cake Mills, with Elevator, Oil and Tallow Refineries, Oil Stores, Tar and Naphtha Distilleries, Soapery, large Warehouses, with very extensive Fireproof Vaults and Steam Hoist, Cooperage, Stables, and the usual Offices. The Machinery and Plant are comparatively new, in excellent condition, and capable of doing a very extensive manufacturing business. The business connection is a most valuable one. With a view to a speedy realisation a very moderate price will be accepted.

For orders to inspect the Works and to treat apply to the Liquidator, T. THEODORE ROGERS, 30, North John Street, Liverpool, or to Wm. F. MORECROFT and CO., Solicitors, 5, Castle Street, Liverpool.

COUNTY BOROUGH OF SALFORD.
(GAS DEPARTMENT).

TAR.

The Gas Committee invite Tenders for the purchase and removal of the surplus Tar to be produced at their Bloom Street, Regent Road, and Liverpool Street Works in twelve months from July 13th next.

The approximate quantity will be 4,500 tons.

Forms of tender and conditions of contract may be obtained on application to the Gas Engineer, Gas Offices, Bloom Street, Salford.

Sealed tenders, endorsed "Tender for Tar," addressed to the Chairman of the Gas Committee, must be delivered to me on or before Thursday, the 10th prox., at 5 o'clock in the evening.

By order,

SAMUEL BROWN, Town Clerk.

Town Hall, Salford,
June 12, 1890.

TAR.

The Directors of the Nuneaton Gas Company invite Tenders for the surplus TAR to be produced at their works for one year from the 1st of July next. Quantity about 150 tons. Tenders, sealed and endorsed, must reach me not later than the 10th July.

JOHN H. BLAND, Secretary.

Nuneaton, 19th June, 1890

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