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THE

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*A Journal of Practical Chemistry*

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

*WILLIAM CROOKES, F.R.S., &c.*

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No. 1754.—JULY 7, 1893.

## ESTIMATION OF SOLIDS AND FAT IN MILK. By JOHN BOYD KINNEAR.

THE observations of Messrs. Liebermann and Székely on the examination of milk, given in the CHEMICAL NEWS (vol. lxvii., p. 280), lead me to offer some remarks based on my own experience. Like these gentlemen (and many others) I have attempted to use the plan of direct solution of the fat in ether or petroleum spirit, and with very good success in samples tolerably rich in fat; but I have found that when the milk is very poor in fat, or is skimmed, the ether frequently assumes a gelatinous state. I do not know what may be the substance with which it unites in this combination, probably one of the albuminous compounds. It is not prevented by addition of salts of either mercury, copper, or lead; but I have found it in a great measure or entirely obviated by previous addition of carbolic acid. Unfortunately, however, the phenol itself is soluble in ether, and I have not ascertained whether it is wholly taken up by the ether, or whether part remains in the milk. This uncertainty prevents its use in quantitative analysis.

After many experiments I have come to adopt the following method for estimating accurately and rapidly the total solids and fat, and it has the advantage of being equally applicable to cream, or to rich or to skimmed milk:—On a piece of thin, flat crown-glass, previously tared, and 2 or 2½ inches diameter, pour a few drops of the milk, and weigh. About a gramme is a convenient quantity, but a little more or less is immaterial. It is then dried, either in a hot-air chamber or by being held at a considerable height over the flame of a lamp. The film being so thin, this process requires only from five to ten minutes. Before being perfectly dry (but after it has become solid) it is well to raise or scrape the film from the glass by a steel scraper, for which purpose a knife or a sharp carpenter's chisel answers very well, placing the glass on a sheet of black glazed paper, and putting a guard of the same material in front of the scraper, to prevent any loss of particles of the hard cheesy matter. After this it can be very quickly brought to a constant weight, and being very slightly hygroscopic, the percentage weight of the "dry solids" can be determined with great accuracy to the second decimal point.

If the specific gravity of the milk has been previously ascertained, Fleischman's formula will give the percentage of fat from these data within 0·1 or 0·2 per cent. But to obtain it gravimetrically I transfer the dry solids to a small tared stoppered bottle, about ½-ounce size and rather tall, and pour upon them 3 or 4 c.c. of ether. The stopper being tied down, the bottle may be placed in

warm water—from 100° to 120° F., according to the strength of the bottle—and left in it for a few minutes, then shaken up for another minute. The hot ether is a much more effective extractor of the fat than it is when below the boiling-point. After being cooled the bottle is weighed, and, deducting its own weight and that of the solids, we get the weight of the contained ether, which may be designated *E*. The stopper is now removed, and a portion (as much as possible) of the clear solution poured quickly into a small tared watch-glass, the stopper immediately replaced, and the bottle again weighed. The difference between this and the last weighing represents the ether plus fat in the watch-glass, which we will call *e+f*. On this being evaporated we obtain *f* only, which is accurately weighed on the watch-glass, and gives us the weight of *e* by difference. If we call the weight of the milk originally taken *M*, and the total fat it contained *F*, we get the proportion  $e : E :: f : F$ , from which

$$F = \frac{E \times f}{e},$$

and as the percentage of fat in the milk would be

$$\frac{100 F}{M},$$

we get, as the formula for calculating the percentage,

$$\frac{100 E \times f}{M \times e},$$

The advantage of taking an aliquot part of the ethereal solution, which is the method recommended by Dragendorff in plant analysis, is that it saves the very tedious process of filtering and washing the filter with ether. The whole of the fat is really in the solution, just as it is in Soxhlet's aræometric method, and the sole possibility of error arises from the evaporation of the ether during the moment of pouring from the bottle into the watch-glass. To the extent of this loss the quantity estimated by difference on the watch-glass will be over the truth, and the milk will appear poorer in fat. A small correction by deducting, say, 50 m.grms. from *e* in the divisor may be allowed for this. But an error of  $\pm 0\cdot050$  grm. in the ether taken, supposing that to be about three-fourths of the whole ether employed, will only amount to 0·06 per cent of fat in average milk, or to 0·01 per cent in skim milk, so that for practical purposes it is hardly worth attention. It would almost disappear if petroleum spirit were employed. The whole determination of solids and fat may by this method be completed in less than half an hour, and several samples may be examined simultaneously. An additional recommenda-

tion is the simplicity of the apparatus and the economy in the ether employed.

June 26, 1893.

## QUALITATIVE AND QUANTITATIVE ANALYSIS OF FORMALDEHYD.

By A. TRILLAT.

SINCE formaldehyd (the formol of commerce) is come into use as a material for the manufacture of certain dyes and as an antiseptic, it becomes important to know methods for detecting its presence and for determining its quantity in its solutions. The qualitative detection is effected as follows:—

On oxidising tetramethyldiamidodiphenylmethan by lead peroxide and acetic acid, there appears an intense blue colouration. I have utilised this reaction to detect the presence of formaldehyd in a solution in a free state, or, in certain cases, in combination. We pour half a c.c. of dimethylaniline into the solution in question, and stir briskly after having acidulated with a few drops of sulphuric acid. The combination between dimethylaniline and formaldehyd is easily effected by heating the mixture for half an hour on the water-bath. After having rendered it alkaline with soda, it is heated to ebullition until the odour of dimethylaniline has completely disappeared, when it is passed through a small paper filter. After washing, the filter is spread out at the bottom of a small porcelain capsule, moistened with acetic acid, and there is thrown upon it a small quantity of lead peroxide in fine powder. The blue colouration shows the presence of formic aldehyd.

### Second Method.

I have found that the formation of anhydroformaldehyd-aniline,  $C_6H_5N : CH_2$ , is very easily effected by causing formaldehyd to act upon aniline; not in presence of acids, but simply in a dilute aqueous solution. This aqueous solution of aniline is obtained by dissolving 3 grms. of aniline in 1 litre of distilled water. I mix 20 c.c. of this solution in a test-tube with 20 c.c. of the liquid in question, and neutralise. In presence of formic aldehyd there appears, after some hours, a very slight white cloud. This reaction is very sensitive, enabling formaldehyd to be detected in a solution at  $\frac{2}{100000}$ . In this case the turbidity appeared only after some days. The reaction is common to acetic aldehyd.

### Detection of Formaldehyd in Alimentary Substances.

The liquid products, after being decolourised and filtered, are submitted to one of the foregoing methods.

Solid products are treated with hot water, in order to dissolve trioxymethylene, which may be derived from the polymerisation of formaldehyd. A microscopic examination of the substance may give useful indications.

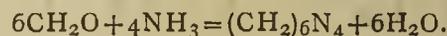
The detection of formaldehyd in alimentary substances is often impossible, because it forms with certain organic principles compounds from which it cannot be separated.

### Determination of Formaldehyd.

*First Method.*—A method has been proposed for determining formaldehyd which consists in estimating the quantity of ammonia necessary to transform it into hexamethylene. In this method we add to a solution of formaldehyd a known quantity of ammonia, and titrate the excess with sulphuric acid. This process is faulty, because the solutions of commercial formol have always a certain degree of acidity, and because hexamethylene-amine has an alkaline reaction, which the method overlooks. To avoid these causes of error I proceed as follows:—

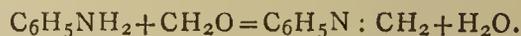
I determine previously the acidity of a known quantity of the solution by means of normal soda, using phenolphthalein as indicator.

I measure 10 c.c. of the solution in question into a flask, dilute with water, and add a known quantity of a standard solution of ammonia until the odour is distinctly ammoniacal. The contents of the flask are then treated with a current of steam so as to expel the excess of ammonia, which is collected in water, and determined by means of a standard solution of sulphuric acid. We find the quantity of combined ammonia by deducting from the total quantity added that which is found in excess in the distillate, and taking account of the original acidity of the solution. The following equation enables us to calculate the proportion in which the combination takes place:—



In this process a small portion of the hexamethylene-amine is carried away in distillation.

*Second Method.*—To a solution of 3 grms. aniline in 1 litre of water we add, drop by drop, with constant agitation, from 1 to 4 c.c. of the solution in question, according to its suspected strength. There is formed a white cloud, which after repeated agitation is entirely deposited. After forty-eight hours the liquid is passed through a tared filter, and we ascertain that the filtrate contains an excess of aniline. We dry at  $40^\circ$ , and weigh. The corresponding quantity of formaldehyd is given by the equation—



By operating under these conditions, we obtain results strictly comparable; but the analysis of the anhydroformaldehyd-aniline does not give figures which exactly agree with the formula. Still, they approach it so closely as to be in most cases approximately satisfactory.—*Comptes Rendus*, cxvi., p. 891.

## GENERAL METHOD FOR THE ANALYSIS OF BUTTERS.

By RAOUL BRULLÉ.

THE falsification of fatty substances has become extremely common, and the injury which it occasions to the dairy industry is so great that the public authorities and the agricultural societies and syndicates have been endeavouring to find means for the repression of the fraud.

Unfortunately, the substances used for sophistication are themselves so varied that it has been hitherto impossible to find a procedure sufficiently general to be applicable in all cases.

The foreign fatty matters added to butters are sometimes of animal origin (oleomargarine, grease, &c.), sometimes of vegetable origin (seed oils, olive oil, &c.).

All these different cases of falsification may be detected by a combination of reactions which I have learned in the course of a prolonged practice.

1. The presence of seed oils in butters is detected by the use of silver nitrate in an alcoholic solution, which gives very characteristic changes of colouration when there is a mixture. We heat 12 c.c. of butter in a test-tube with 5 c.c. of solution of silver nitrate at 25 per 1000. The microscopic examination of the crystals obtained on cooling enables us to detect adulteration with olive oil—the only one which would escape this test.

2. The detection of animal fats is more difficult. For this purpose we heat 5 c.c. of butter, previously melted and filtered, to  $148^\circ$  on the oil-bath. The butter is placed in a flat-bottomed capsule, 7 c.m. in diameter. When the substance has reached the temperature of  $130^\circ$  we add a pinch of powdered pumice and eight drops of fuming nitric acid. We mix, and heat for about twelve minutes; it is then set to cool in a place at  $21^\circ$ . After an hour, we proceed to the assay with the *oleogrammeter*. This instrument consists of a vertical rod surmounted by

a broad plate, and gliding in a ring fixed to a stand. The end of the rod is applied on the hardened surface of the refrigerated fatty matter. Weights are placed upon the plate until the point of the rod sinks abruptly into the substance. The weights represent the resistance of the butter under examination to the oleogrammeter. The results obtained are very surprising. In fact, if the sample is a pure butter, the penetration of the butter is effected with a mean load of 250 grms. The same experiment made with pure margarine requires 5000 grms. The intermediate figures enable us to estimate with sufficient accuracy the proportions of a mixture of margarine and butter. A weight of 900 to 1000 grms., e.g., corresponds to a butter containing 10 per cent of margarine.

When the margarines contain considerable proportions of seed oils, the indications of the oleogrammeter present great deviations, but the use of silver nitrate enables us to overcome this difficulty, as the two methods are complementary to each other. — *Comptes Rendus*, cxvi., p. 1255.

## A NEW METHOD FOR REDUCING METALLIC OXIDES.\*

By WM. H. GREENE and WM. H. WAHL.

In a previous paper by ourselves, presented at the January meeting of the Section, we gave an account of the various methods that have been proposed for the production of metallic manganese, and described a method which we had devised for the production of this metal, and which we believe to be adapted for commercial use, based on the reduction of one of the lower oxides of manganese by means of aluminium.

In the search for commercially available reducing agents applicable to the solution of the manganese problem we gave consideration to all the elements of which the known thermo-chemical data gave us reason to hope for an exothermic reaction with the oxides of manganese.

Among these silicon did not escape our observation, inasmuch as the heat of formation of its oxide  $\text{SiO}_2$ , according to the most reliable estimates, is sufficiently greater than that of  $2\text{MnO}$  to permit us to expect that the desired reaction should take place.

The references in the literature of chemistry to the reducing action of silicon are not numerous. The only investigations that appear to have a direct bearing thereon are those of Gore,† who makes the observation that "crystals of silicon thrown upon melted argentic fluoride become red hot, undergo rapid combustion, forming fluoride of silicon and depositing silver." By adding crystals of silicon to melted black oxide of copper, the same author‡ observed a sudden incandescence which raised the temperature to full white heat; copper was also deposited and melted to a red metallic bead and could be hammered to a thin sheet. He noted also that crystals of silicon immersed in a solution of fluoride of copper, containing free hydrofluoric acid, instantly coat themselves with bright copper, and that when silicon is thrown into melted fluoride of sodium, bubbles of vapour are evolved which explode and burn with a yellow flame at the surface of the liquid. The silicon was found subsequently to have lost in weight.

More recently Warren (CHEMICAL NEWS, vol. xlv., 75) has published an account of a number of instructive experiments, which strikingly illustrate the energetic reducing properties of silicon. He notes the fact that metallic silicon, though a very stable and inert substance, yet when in admixture with a large number of metallic oxides, becomes at once oxidised, the oxide in admixture with the same becoming itself reduced. Litharge, for

example, when mixed in excess with silicon and heated to dull redness, becomes reduced to metallic lead. With copper and all other readily reducible oxides, either a silicide, or, when the oxide is in excess, the pure metal, is obtained. He observes that even the oxides of chromium, tungsten, and molybdenum are reduced to the metallic state when heated with silicon.

The fact that silicon in the elementary form can only be obtained by indirect and costly methods rendered any serious consideration of its availability for our purpose out of the question. The thought presented itself, however, that compounds of silicon might possibly be found to answer our purpose, and a very slight consideration of the subject encouraged us to believe that in the metallic silicides we had at hand a ready means of utilising the chemical energy of one of the most powerful reducing agents.

It appeared reasonable to conclude, also, that the reducing power of such silicides might be found serviceable not only in the reduction of the oxides of manganese, but also in the reduction of many other metallic oxides.

Certain facts in connection with the metallurgy of steel and copper when given their proper interpretation appeared to strengthen this view. Thus, in one of the modifications of the open-hearth process of steel making, in which pig iron and scrap are melted on the hearth in contact with oxides of iron, not only the greater part of the carbon but also practically all of the silicon which is invariably present in small proportion is eliminated from the resulting steel, by the reaction with the oxides of iron, and finds its way into the slag as silicate.

Also, in the commercial operations of reduction, re-melting and casting of certain metals and alloys, serious practical difficulties arise from the formation or retention therein of small quantities of oxide which have an unfavourable influence upon the strength, ductility, and other desirable properties of the metals and alloys, and often render it troublesome to roll them or to obtain sound castings from them.

To counteract such difficulties, compounds in which silicon is present have come into use, either for the purpose of prevention or correction. We may refer as illustrations to the use of ferro-silicon in foundry practice and in the open-hearth process, and to the suggested use of copper, tin, and zinc silicides to copper, tin, and zinc and their alloys, all for the same general purpose of insuring the production of homogeneous metal and sound castings. In these cases the utility of the silicon appeared to us to be due manifestly to its energetic reducing action on the minute quantities of oxides retained in the molten metal, and to be strictly comparable to the action of phosphorus, magnesium, manganese, aluminium, and other energetic reducing agents employed in the purification or refining of metals from small quantities of retained oxides.

Having satisfied ourselves from preliminary considerations of this nature that the use of silicon in the form of the metallic silicides might hopefully be applied as the basis of a commercial method for the reduction of oxidised ores of the metals, we proceeded at the first opportunity to make a number of experiments to test the correctness of our reasoning.

The requirements of iron founders and steel makers, we found, had caused a considerable demand for pig irons containing relatively high proportions of silicon. These are known to the trade as ferro-silicon, silico-spiegel, and silico-ferro-manganese, the last two being so designated from their manganese content. These products may be described as silicides of iron, or of iron and manganese, containing from 5 to 30 per cent. of silicon, and a relatively low percentage of carbon. These silicides seemed adapted to our purpose.

We will confine ourselves here, for convenience, to the description of our method as applied to the production of ferro-alloys. It is obvious that in the production of such alloys, which, if useful at all, will find their principal

\* Read at the Chemical Section of the Franklin Institute, March 21, 1893.

† CHEMICAL NEWS, vol. xxix, 291.

‡ Gore, "The Art of Electro-metallurgy" (1877), p. 220.

application in the manufacture of special steels, the presence of carbon in notable proportion will be highly detrimental.

For this reason we require for our purpose a silicide containing as high a proportion of silicon and as low a proportion of carbon as possible. Silicon irons and spiegels containing as high as 15 per cent. or 20 per cent. of silicon, and with carbon not exceeding 1 per cent., can readily be obtained, and, as we are assured, by special selection of ores and fluxes, can be supplied on demand even higher in silicon than the figures just named. It is interesting also to note the fact that, as a rule, the quantity of carbon, in such silicides varies with the silicon in an inverse ratio, the carbon decreasing as the silicon increases, and *vice versa*.

We may fully illustrate our method by describing its application to the production of a ferro-manganese; the object in view being substantially the manufacture directly from the oxide of a ferro-alloy sufficiently high in manganese and at the same time sufficiently low in carbon that it may be employed with economic advantage in the production of manganese steel, the deoxidation of the charge in the Bessemer converter, or on the open hearth.

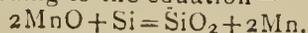
The possible utility of the method may most strikingly be illustrated with reference to the ultimate production of manganese steel, an alloy that is known to possess certain unique and highly desirable qualities, but which presents certain practical difficulties in its manufacture in large quantities which thus far have proved to be troublesome.

By the way of explanation it should be stated that by the present method of manufacturing this alloy, which consists substantially in the addition of ordinary ferro-manganese to fluid iron, the proportion of manganese that can usefully be introduced into the steel is rigorously limited by the carbon, which to the amount of 5 to 6 per cent. is present in the ferro-manganese and which cannot be eliminated therefrom because of its affinity for manganese.

With this explanatory comment we proceed to describe the production of a ferro-manganese by the method which we propose. The chemistry of the operation is extremely simple. When a ferro-silicon (or other silicide) is heated in any suitable furnace chamber (which for our purpose is preferably lined with basic material, such as lime or magnesia) in contact with a metallic oxide (or a mixture of such oxides) and in the presence of a suitable base, such as lime, magnesia, or alumina, the oxygen of the oxides combines with the silicon, forming silica, which at once unites with the base to form a more or less fusible silicate that separates as slag, while the metals set free combine to form an alloy.

The mode of our procedure is, precisely stated, as follows:—We select a ferro-silicon or silico-spiegel adapted for our purpose, and melt the same on the hearth of a furnace or in a crucible. Then the manganese monoxide (or the protosquioxide) with which a fluxing material has been incorporated is added in proper quantity. The reaction takes place promptly, the silicon of the ferro-silicon seizes upon the oxygen of the manganese ore, and is thereby converted into silicic oxide which forms with the flux a liquid slag, while the manganese set free by the reduction of the ore combines with the molten iron set free from the silicide. The whole charge of manganese and flux may be added to the ferro-silicon at once, or the addition may be made by portions until a sufficient quantity of the oxide has been employed to utilise the reducing power of all of the silicon that was present in the ferro-silicon, thus reducing a chemically equivalent quantity of manganese oxide to the metallic state.

Assuming that we operate with a silicide containing iron 88 per cent, silicon 10 per cent, carbon 1 per cent, the reaction for simplicity's sake may be supposed to take place according to the equation—



We would then employ silicide and manganese oxide in quantities that satisfy the above proportions, *i.e.*, for every 28 parts of silicon in the silicide 142 parts of manganese monoxide and a quantity of lime, manganese, or alumina, or a mixture of these that will completely combine with the silicate to form a fusible silicate.

It is necessary, of course, to use a larger quantity of manganese ore than that required by theory, for the reason that a certain quantity of the manganous oxide is always seized upon by the silica and passes into the slag in the form of manganous silicate.

A charge of ferro-silicon (containing 10 per cent silicon, 1 per cent carbon) 100 pounds, manganese monoxide 70 pounds, lime 50 pounds, we have found to yield about 128 pounds of a metallic alloy having the composition—Iron 70 per cent, manganese 29 per cent, carbon 0.7 per cent, silicon trace.

Assuming that the permissible percentage of carbon in a certain manganese steel is 0.5 per cent, then 100 pounds of a manganiferous alloy of the above composition will produce by mixture with 40 pounds of decarburised iron, 140 pounds of manganese steel of the composition—Iron 78.8, manganese 20.7, carbon 0.5, silicon trace.

In the preparation of a manganese steel containing the same percentage of carbon by melting decarburised iron with ordinary ferro-manganese containing 80 per cent manganese and 5.5 per cent carbon, the resulting metal would contain 92.23 per cent iron and only 7.27 per cent manganese. Or, making the comparison on the basis of equivalent quantities of manganese, the manganese steel made from the ordinary ferro-manganese would contain for 20.7 per cent manganese, 1.4 per cent carbon; that made by our process would contain for 7.27 per cent manganese only 0.18 per cent carbon.

In many cases it is obvious that a metal of the desired composition may be obtained directly by one operation on the furnace hearth. It is probable, for example, that for the production of a manganese steel of a given composition, the required proportions of scrap wrought iron and ferro-silicon of suitable composition could be melted on the hearth, in contact with the manganous oxide.

By procedures substantially like that described, but substituting for the manganous oxide, oxides of nickel, chromium, and tungsten, we have succeeded in forming ferro-alloys of nickel (containing as high as 50 per cent of this metal), chromium (with nearly 20 per cent of chromium), and tungsten (with more than 50 per cent of tungsten). With titanium we have thus far obtained only doubtful results. In all these cases the resulting ferro-alloy is relatively low in carbon, and, as the method we propose does not involve the introduction of carbon either as the reducing agent or from external sources, the carbon in the product being derived wholly from that which is contained in the ferro-silicon employed in the operation, we have reason to believe that we will be able to produce, on the commercial scale, ferro-alloys with any desired metals so low in carbon as to meet all the requirements of the metallurgical arts.

Thus far our experiments have been confined to the ferro-alloys and have been on the laboratory scale. It will be obvious, however, that the chemical reactions involved will hold good for other classes of alloys, and that alloys of copper, for example, with difficultly-reducible metals, may be obtained quite as readily by fusing the appropriate oxides with copper silicide.

In conclusion, the method which we propose, we believe, will enable the metallurgist advantageously to effect the reduction of numerous metallic oxides without the employment of carbon, and the production of numerous useful and important alloys.

On the Scission of Carbonic Acid in consequence of Solar Radiation. — A. Bach. — Very diffuse solar radiation, and even the light of a gas-flame, occasions the splitting up of carbonic acid in presence of dimethylaniline. — *Comptes Rendus*, cxvi., No. 24.

## THE DETECTION OF LEAD IN URINE.

By LEE K. FRANKEL, Ph.D.

DURING the winter of 1891-92 the author, while investigating some cases of supposed lead-poisoning, had occasion to require a method whereby lead could be accurately and, what was of equal importance, rapidly detected in the urine. As far as accuracy was concerned, the methods recommended by Victor Lehmann (*Zeitschrift für Physiologische Chemie*, vi., 1) were found to be thoroughly satisfactory, but it was hoped that a modification of his electrolytic method could be devised which would shorten the time limit of the process. Unfortunately, the desired end was not attained, since the results are altogether of a negative order. These, however, show a sufficiency of new and interesting data to warrant their publication.

In the article above referred to, Lehmann states that lead may be detected electrolytically in urine, either with or without previous destruction of the organic matter present there. The best results are given when the organic matter is first destroyed. He uses in his investigations the apparatus devised by Bloxam (*Chemical Society Quarterly Journal*, xiii., 12) for the electrolytic detection of arsenic. The apparatus consists essentially of a jar, which is closed below with parchment, and in which the solution to be examined is placed. The jar stands in an outer vessel which contains sulphuric acid. In Lehmann's apparatus, the platinum electrode which is attached to the negative pole of the battery dips in the outer vessel, while that attached to the positive pole enters the jar. He states that with such an arrangement the lead present in the urine deposits as peroxide on the positive pole.

To ascertain how minute the quantity of lead in a solution might be, and still show as peroxide when the solution was electrolysed, the author made the following determinations: In a platinum dish, connected with the negative pole of a battery, 100 cubic centimetres of water and 1 cubic centimetre of lead-nitrate solution were placed. To these 3 cubic centimetres of concentrated nitric acid were added. The positive electrode was now introduced directly into the solution, and the latter electrolysed with a current generating 1.4 cubic centimetres of oxyhydrogen gas per minute. At the end of 30 minutes the deposit of peroxide of lead on the platinum foil was already very distinct, and at the end of several hours had the usual dark brown appearance of the lead-peroxide deposit. The lead-nitrate solution used was of such a strength that in the solution finally electrolysed 1 part of lead was present in every 100,000 parts of water.

Two more experiments were made with solutions containing 1 part of lead to 500,000 and 1,000,000 parts of water respectively, the amounts of nitric acid and the strength of current being the same as in the preceding experiment. The deposits of lead peroxide on the platinum foil, while very faint, were still distinctly recognisable. The delicacy of this electrolytic test led the author to hope that the presence of urine would not materially interfere with the deposition of the peroxide of lead. The following experiments will, however, show that the results obtained were radically different from those which were anticipated from the above action of the lead solution.

To 100 cubic centimetres of urine 1 cubic centimetre of a lead-nitrate solution (containing about 1 m. grm. of lead) and 10 cubic centimetres of concentrated nitric acid were added. The solution was put into a platinum dish and electrolysed for 24 hours with a current generating 1.4 cubic centimetres of oxyhydrogen gas per minute. At the expiration of that time, to the author's surprise, no peroxide of lead had deposited on the positive electrode. The current was then allowed to act 48 hours longer; even then no disposition was noticeable on the positive pole, but on the platinum dish (the negative electrode) a

metallic deposit resembling lead had formed. The quantity of the deposit, however, was so small that it did not respond to the ordinary tests for lead.

130 cubic centimetres of urine and 2 cubic centimetres of the lead-nitrate solution, the free nitric acid in this case being omitted, were similarly electrolysed, with the difference that in this determination the platinum dish was made the positive electrode and the platinum foil the negative electrode. After electrolysing for 24 hours with the same strength of current as before, a greyish-brown spongy deposit was found on the platinum foil. This was carefully washed with water, dissolved in nitric acid, and the solution evaporated to dryness. On dissolving the residue in hydrochloric acid, and passing hydrogen sulphide gas through the solution, the characteristic reaction for lead was given. No deposit was found on the positive pole. The experiment was repeated, using varying amounts of the lead-nitrate solution, and in every case was a similar deposit found on the negative electrode, which gave the confirmatory reactions for lead. At no time was a deposit found on the platinum dish—the positive electrode.

While these results were satisfactory for the detection of lead in urine to which a lead solution was directly added, results entirely different were obtained with urine in which the lead that was present had been previously assimilated by the system. Fortunately, for this purpose it was not necessary to inject animals with a lead solution, as the urine from several cases of acute lead-poisoning (both before and after treatment with potassium iodide) was placed at the author's disposal by the officers of the University Hospital. In all the samples of urine (some 25 in all) that were examined for lead by the electrolytic method just given, both with and without the presence of nitric acid, in no case was a deposit found on either the positive or negative pole sufficiently large to give a confirmatory reaction for lead on dissolving the deposit in nitric acid, evaporating the solution to dryness with hydrochloric acid, and then adding hydrogen sulphide. In one or two cases the current was allowed to run for five days, and increased to 3 cubic centimetres of oxyhydrogen gas per minute. The oxidising action of the current was so strong that at the end of this time the scum and mucus which separated on the surface of the solution during the earlier passage of the current had entirely disappeared. Even then no deposit was found either on the dish or on the foil that would react for lead. That lead was present in these samples of urine was proved by taking the solutions on which the current had no effect, and rapidly oxidising the organic matter present with potassium chlorate and hydrochloric acid. When the solution had become colourless, the excess of hydrochloric acid was evaporated, and hydrogen sulphide gas passed into the solution. The precipitates that were thus obtained were re-dissolved in nitric acid, and further tested for lead with sulphuric acid and potassium chromate. Every sample of urine examined in this manner showed the presence of lead.

These results are of interest, since they show that lead salts passed through the system are, by the time they become components of the urine, of such a composition that they cannot be decomposed by any but the strongest reagents. In the cases cited the lead is probably in combination with the organic acids present in the urine, and in such a stable form that a current of the strength used is not sufficient to break up this combination into its constituents.

For detecting lead in urine, the author has invariably obtained good results by first oxidising the organic matter with potassium chlorate and hydrochloric acid. If desirable, the lead can then be determined electrolytically, as advised by Lehmann. This method, however, is time-consuming. The test for lead with hydrogen sulphide is not alone rapid, but so delicate that preference would be given to it, particularly where the amounts of lead present are small.—*Therapeutic Gazette*.

## ACTION OF THE HALOID ACIDS, IN GAS FORM, UPON MOLYBDIC ACID.\*

By EDGAR F. SMITH and VICKERS OBERHOLTZER.

DEBRAY (*Comp. Rend.*, xlvii., 1098, and *Ann. der Chem. und Pharm.*, cviii., 250) first called attention to the fact that a very volatile crystalline compound of the formula  $\text{MoO}_3 \cdot 2\text{HCl}$  resulted upon exposing molybdic acid, heated from 150—200° C., to the action of hydrochloric acid gas. It is true that the constitution of this volatile product may also be represented by the formula—



which would make it a molybdenum hydroxychloride. Dismissing the question of constitution for the present, and considering the point of ready volatility, it seemed to us that this behaviour might be utilised for the separation of molybdic acid from tungstic acid, as the latter apparently does not enter into volatile combination with hydrochloric acid gas. We therefore exposed weighed amounts of sublimed molybdic acid to the action of the acid gas, and succeeded in expelling the molybdic acid completely from the porcelain boats containing it. Applying the same treatment to what we considered pure tungstic acid, we were greatly surprised to discover that very appreciable quantities of a sublimate, similar in every respect to that of molybdenum hydroxychloride, were expelled from the boat. An examination of this product proved it to be the molybdic acid compound. In short, our tungstic acid was not pure. We, however, continued to heat portions of it in hydrochloric acid gas until a sublimate was no longer formed, when, on mixing molybdic acid in known amount with the residual tungstic acid, we discovered that we could completely expel the former acid from the latter. Our next step was to observe the effect of heating anhydrous sodium molybdate in hydrochloric acid gas. The appended results show a quantitative conversion into sodium chloride, consequently a complete volatilisation of the molybdic acid.

$\text{Na}_2\text{MoO}_4$ in Grms.		NaCl.	NaCl required.
0·1302 gave at 150—200°	.. ..	0·0738	0·0739
0·1832	.. ..	0·1038	0·1040
0·2046	.. ..	0·1159	0·1162
0·3845	.. ..	0·2186	0·2183

As we were about to apply this method to the quantitative separation of molybdic and tungstic acids, both present as sodium salts, a closer scrutiny of the existing literature relating to this subject revealed that E. Péchard (*Compt. Rend.*, cxiv., 173, and *Zeit. f. Anorg. Chem.*, i., 162) had already carried out the determination of molybdic acid and its separation from tungstic acid in this way with very evident success. Our own experiments confirm those of Péchard in every particular.

As previously observed, the tungstic acid that we thought pure contained molybdic acid. Traube (*Neues Jahrbuch für Mineralogie, Geologie, und Paläontologie, Beilageband*, vii., 232) has demonstrated that natural calcium tungstate, scheelite, and commercial tungstic acid obtained from the mineral wolframite, contain molybdic acid. E. Corleis (*Liebig's Annalen*, ccxxxii., 265) has shown that the latter acid is even present in the "Wolframsäure puriss" of trade, while Friedheim (*Zeit. f. Anorg. Chem.*, i., p. 76) asserts that commercial sodium tungstate is strongly contaminated with sodium molybdate, and that, even when exercising the greatest care in the process of purification, the tungstate continued to show traces of molybdenum.

We found molybdic acid present in the purest sodium tungstate that we could get, and in the minerals scheelite and wolframite, when these were exposed to the action of

hydrochloric acid gas at a temperature not exceeding 400° C. Hence we are disposed to regard this method as excellently adapted for the detection of molybdic acid, as well as for the purification of tungstic acid and tungstates containing molybdenum.

Our original purpose having been the study of the behaviour of molybdic acid in atmospheres of all the gaseous haloid acids, we may now briefly recount our experiences in those directions.

*Action of Hydrobromic Acid, in Gas Form, upon Molybdic Acid.*—The molybdic acid used by us was purified by converting the commercial acid into the ammonium salt, which was re-crystallised a number of times, and then ignited with air access. The product was sublimed very carefully from a platinum crucible. The hydrobromic acid was prepared by dropping bromine from a separatory funnel upon crude anthracene contained in a half-litre flask. It passed through a hard glass tube, 6 inches in length, filled with anthracene, then through two U-tubes containing a paste of amorphous phosphorus, and two U-tubes provided with fused calcium chloride, while the sixth and last tube contained phosphoric anhydride. Having completed this circuit it was admitted to a perfectly dry combustion-tube, into which had been introduced a porcelain boat filled with molybdic acid. The anterior portion of the combustion-tube was closed with a calcium chloride tube to exclude all moisture. The heat used in the experiment was supplied from a combustion-furnace. An ordinary thermometer was placed above the combustion-tube; its bulb rested directly over the boat. In this manner we recorded the approximate temperature at which the reaction took place. As soon as the entire apparatus was filled with the gas, three burners of the furnace, directly under the boat, were lighted, and the heat gradually raised until it reached 200° C. A change took place almost instantly. Just beyond the boat appeared a heavy sublimate, with a colour resembling that of potassium permanganate. Beyond this solid a brownish-yellow coloured liquid separated; on cooling it changed to long, beautiful yellow needles; these proved to be unstable, melting almost immediately when brought in contact with the air. At the expiration of an hour the passage of the hydrobromic acid gas was interrupted. The permanganate-coloured sublimate was removed from the sides of the tube as completely as possible, introduced into a porcelain boat, and then carefully re-sublimed in a current of dry carbon dioxide. The compound sublimed in fern-like aggregates, consisting of dark red or purple-red, shining, overlapping plates, extending from one side of the combustion-tube to the other. They dissolved in water with liberation of heat. Their aqueous solution was colourless, but upon standing became blue in colour. The crystals themselves changed in appearance on prolonged exposure to the air. By preserving them in an atmosphere of carbon dioxide they suffered no decomposition. Examined under a polarisation microscope they showed their ability to polarise light, and that they consisted of aggregations of perfectly square plates. After the re-sublimation portions of the substance were weighed off in weighing tubes, and analysed. For the bromine determination the material was dissolved in as little cold water as possible, dilute nitric acid added, and this followed immediately with silver nitrate. The resulting silver bromide was treated in the usual manner. In estimating the molybdenum, the substance was brought into a weighed porcelain crucible, and dilute nitric acid added. The solution was evaporated almost to dryness at a very gentle heat, when the crucible contents were treated with concentrated nitric acid, after which followed evaporation to perfect dryness. This operation was repeated, and a gentle but direct heat applied to the crucible for periods varying from one-half to one hour. This was done to fully oxidise the molybdenum to trioxide. Portions of the new compound were mixed with freshly-ignited litharge, and heated in a current of dry air, using a perfectly dry combustion-tube, provided with a weighed

\* Read before the Chemical Section of the Franklin Institute, April 18th, 1893.

calcium chloride tube. The weight of the latter showed no increase, so that we were safe in considering our substance free from hydrogen.

ANALYSES.

Bromine Determination.

	AgBr. Grms.	Bromine Percentage.
0·1334 grms. substance gave..	0·1793	= 57·19
0·3353 ..	0·4499	= 57·09
0·0680 ..	0·0908	= 56·82

The mean of these bromine percentages is 57·037 per cent.

Molybdenum Determination.

	MoO <sub>3</sub> . Grms.	Molybdenum Percentage.
0·2545 grms. substance gave..	0·12865	= 33·69
0·2916 ..	0·1466	= 33·52
0·1115 ..	0·0559	= 33·42

The mean of the molybdenum percentages is 33·54 per cent.

We experienced difficulty in wholly eliminating the traces of blue oxide in all of the molybdenum determinations; hence we look upon the results given above as low.

Regarding our compound as consisting of molybdenum, bromine, and oxygen, with the above percentages, and taking the oxygen by difference, we deduce, as the most probable formula, MoO<sub>2</sub>Br<sub>2</sub>, MoOBr<sub>2</sub>, or Mo<sub>2</sub>O<sub>3</sub>Br<sub>4</sub>,—molybdenum sesquioxide tetrabromide. The theoretical requirements of this formula are:—34·28 per cent Mo, 57·19 per cent Br, and 8·57 per cent O.

The only existing molybdenum oxybromide until the present has been MoO<sub>2</sub>Br<sub>2</sub>,—molybdenyl bromide, discovered by Blomstrand on passing bromine vapour over the heated dioxide of molybdenum, or by heating a mixture of molybdic acid and boron trioxide with potassium bromide. It is mentioned as forming yellow deliquescent tablets. For the sake of comparison, we made Blomstrand's compound by the second method. We found that when it was sublimed upon a previously heated portion of the tube it separated in "mehr ausgebildeten Krystalltafeln auf; bei rascher Sublimierung in undeutlich krystallinischen Schuppen. Farbe schön gelbroth." (Blomstrand, *Four. Prakt. Chem.*, lxxxii., 439). Our compound, however, is formed simultaneously with that of Blomstrand when vapours of bromine are conducted over heated molybdic acid; the tube in which this reaction was made was freed from air by conducting bromine vapours through it, and heat was not applied until we were satisfied that bromine alone was present.

The brownish-yellow liquid formed at the same time with the purple-red coloured solid was crystallised in the tube in which it had been produced; the tube was then severed at a point between the yellow and red-coloured compounds. The yellow immediately liquefied on exposure to the air. The liquid was collected in a small and previously weighed beaker; this was then placed in a sulphuric acid desiccator and the air exhausted. At the expiration of from two to three days the yellow needles had re-formed. The beaker and its contents were then rapidly weighed. Water was poured on the needles; their solution was colourless or slightly yellow tinged. On standing, the liquid slowly acquired a deeper yellow or reddish yellow hue, and after twenty-four hours a blue oxide of molybdenum had separated.

The bromine and molybdenum of this product were determined in the same manner as in the purple-coloured solid. We, however, had no difficulty in obtaining perfectly white molybdic acid in all the determinations that follow:—(See Table, next column).

The mean of these percentages is 24·03 per cent. The formula we deduce from these results is MoO<sub>3</sub>·3HBr; it perhaps might be better represented as a trihydroxy-

ANALYSES.

Bromine Determination.

	Silver Bromide. Grms.	Bromine Percentage.
0·0250 grms. substance gave..	0·1403	= 62·83
0·2523 ..	0·3700	= 62·50
0·2709 ..	0·3967	= 62·37
0·0250 ..	0·0365	= 62·12

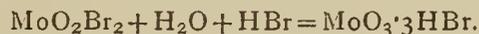
The mean percentage equals 62·45 per cent.

Molybdenum Determination.

	MoO <sub>3</sub> . Grms.	Percentage of Mo.
0·0946 grms. substance gave..	0·0346	= 24·39
0·0946 ..	0·0337	= 23·75
0·1892 ..	0·0686	= 24·06

bromide, MoO(OH)<sub>3</sub>Br<sub>3</sub>. The theoretical requirements are 62·02 per cent Br, and 24·80 per cent Mo.

It is interesting to note that the long yellow-coloured needles of this compound were also obtained upon passing hydrobromic acid gas over the oxybromide of Blomstrand at a gentle heat. This change may easily be conceived as occurring if we grant the presence or production of water through the formation of secondary products.



As we were not in a position to ascertain the true composition of the individual substance or substances from scarcity of material, we offer the above suggestion as a possible explanation for the appearance of the hydroxybromide in the manner just indicated.

*Action of Hydriodic Acid, in Gas Form, upon Molybdic Acid.*—A violent reaction occurred, in the cold upon passing the dry acid gas over molybdic acid; much heat was evolved, and iodine was liberated. The non-volatile product that remained in the boat possessed a bright violet colour. It was exposed for a period of two hours to a temperature ranging from 45° to 50° C., during which time a continuous stream of dry and pure gas was conducted over it. Carbon dioxide was next introduced and passed for an equal period, while the temperature was maintained at 50° C. The results obtained from many analyses of this product pointed to the probable composition MoO<sub>3</sub>HI; but as the quantity of iodine varied according to the length of time during which the hydriodic acid gas acted and with the temperature, we feel unable to assign any definite composition to the compound. It has seemed to us, from a careful study of the experimental results, that several derivatives were formed, but we were unable to separate them; and indeed, by continuing the action of the gas for periods varying from six to eight hours, at the same time elevating the temperature from 105° to 120° C., iodine continued to separate. At last a violet-blue coloured product remained; this appeared to be homogeneous. Prolonged action of the gas was without further reduction, therefore carbon dioxide was introduced to expel it. The blue-coloured product suffered no change on exposure to the air. We obtained what appeared to be the same substance by exposing the iodine-containing compound mentioned above to a temperature of 200° C., in an atmosphere of carbon dioxide. Indeed, mere exposure of the iodine compound to the air for some time gave the blue-coloured derivative.

The same form of apparatus was used here that we have described with the oxybromides. The hydriodic acid gas was made from moist phosphorus and iodine. It was carefully dried.

*Analyses.*—An analysis of the blue-coloured residue resulted as follows: the molybdenum was determined as under the bromine derivatives:—

	Mo <sub>3</sub> O <sub>5</sub> Grms.	Mo Per cent.
0.1099 grms. substance gave..	0.1053	= 64.19
0.1017	0.0972	= 63.72
0.0807	0.0775	= 64.02
0.0959	0.0937	= 64.92
0.1386	0.1350	= 64.93

The mean molybdenum percentage is therefore 64.35 per cent.

#### Water Determination.

	H <sub>2</sub> O. Grms.	Per cent.
0.1533 grms. substance gave..	0.0138	= 9.00
0.1673	0.0142	= 8.49

The mean of these percentages would therefore be 8.74 per cent. An intense red heat was required to fully expel this water content. The figures obtained would lead to an oxide of the formula Mo<sub>3</sub>O<sub>10</sub>.3H<sub>2</sub>O; this would require 64.21 per cent Mo and 9.03 per cent H<sub>2</sub>O. Iodine was not found in the compound. The dehydrated residue was brown in colour. Three determinations of its molybdenum content indicated it to be Mo<sub>2</sub>O<sub>5</sub>. As a result, then, of the action of hydriodic acid gas upon molybdc acid, we can point to no definitely iodated product, but to a blue oxide, a product of reduction. In this connection we may direct attention to the observation of Schulze (*Fourn. Prakt. Chem.* (N. F.), xxix., 440), that molybdc acid sustains reduction when heated with potassium iodide, air being excluded. The resulting products possess variable composition, but by the use of four parts of molybdc acid and one part of potassium iodide a definite product was prepared. It proved to be a new oxide of molybdenum, steel-blue in colour, crystalline, and possessing metallic lustre. Its analysis gave results agreeing with the formula Mo<sub>4</sub>O<sub>11</sub>. Our reduction product is quite analogous to this, except that it is hydrous.

*Action of Hydrofluoric Acid, in Gas Form, upon Molybdc Acid.*—The hydrofluoric acid gas was evolved from fluorspar and sulphuric acid. It passed directly over the molybdc acid contained in a platinum boat, and the latter in a platinum combustion-tube from which a delivery-tube led into a platinum flask, cooled by ice-water. At a temperature ranging from 300° to 400° C, all the molybdc acid was converted into a volatile product that collected upon the anterior portions of the platinum combustion-tube in crystals, having a peculiar red colour. On holding the tube in which these crystals had been sublimed toward the light, it appeared to be filled with violet vapours of iodine; this was, however, due to reflection of light from the sides of the flat needle-like crystals. It is scarcely necessary to remark that before disconnecting the apparatus, carbon dioxide was conducted through it to expel the hydrofluoric acid. The platinum flask also contained the volatile molybdenum product. Much hydrofluoric acid was with it. This was expelled by the introduction of the carbon dioxide.

The new product when removed from the vessels containing it was found to be deliquescent, and it gradually decomposed into a blue oxide of molybdenum. It attacked glass, was insoluble or nearly insoluble in water, but dissolved to a colourless liquid in hydrofluoric acid. Portions of it were weighed off as rapidly as possible in platinum crucibles, and the molybdenum determined as trioxide by evaporation with nitric acid, followed by gentle ignition.

#### Molybdenum Determination.

	MoO <sub>3</sub> Grms.	Mo. Per cent.
0.0526 grms. substance gave..	0.0479	= 60.70
0.1066	0.0967	= 60.66
0.1166	0.1051	= 60.94
0.1265	0.1164	= 61.35

The mean of these determinations is 60.91 per cent Mo. Formed in the same manner as molybdenum sesquioxide

tetrabromide, we find that these results agree very closely with an oxyfluoride of analogous formula, Mo<sub>2</sub>O<sub>3</sub>Fl<sub>4</sub>, which would require 60.76 per cent Mo. In experimenting with the above oxyfluoride we several times observed a slight quantity of a colourless liquid, which upon careful evaporation with nitric acid left a very appreciable quantity of molybdc acid. It may, perhaps, be an analogue of the very volatile MoO<sub>3</sub>.2HCl, and the unstable liquid MoO<sub>3</sub>.3HBr. We endeavoured to fix its composition, but experienced so great difficulty in getting material that we could safely consider sufficiently pure that we abandoned it entirely. The work attending its preparation is anything but pleasant, and the yield exceedingly uncertain.

But one other oxyfluoride of molybdenum is known; namely, that prepared by Schulze (*Fourn. Prakt. Chem.* (N. F.), xxi., 442), by fusing metallic fluorides together with molybdc acid with the exclusion of air. It has the constitution represented by the formula MoO<sub>9</sub>Fl<sub>2</sub>.

Reviewing the action of the gaseous haloid acids upon molybdc acid we observe:—

(1.) That hydrochloric acid gas converts the acid into a solid, very volatile product, MoO<sub>3</sub>.2HCl.

(2.) That hydrobromic acid changes molybdc acid to a volatile brownish-yellow liquid, MoO<sub>3</sub>.3HBr, forming long yellow needles at low temperatures and under diminished pressure, as well as a beautifully crystallised solid of the formula Mo<sub>2</sub>O<sub>3</sub>Br<sub>4</sub>.

(3.) That hydriodic acid reduces molybdc acid to a new oxide, Mo<sub>4</sub>O<sub>10</sub>.3H<sub>2</sub>O.

(4.) That hydrofluoric acid converts the molybdc acid into at least one well-formed but volatile product, having the constitution represented by the formula Mo<sub>2</sub>O<sub>3</sub>Fl<sub>4</sub>.

Püttbach (*Annalen*, cci., 137) divides the known molybdenum oxychlorides into two classes:—

Saturated.	Unsaturated.
MoOCl <sub>4</sub>	Mo <sub>3</sub> O <sub>3</sub> Cl <sub>7</sub>
Mo <sub>2</sub> O <sub>3</sub> Cl <sub>6</sub>	
Mo <sub>3</sub> O <sub>5</sub> Cl <sub>8</sub>	Mo <sub>2</sub> O <sub>3</sub> Cl <sub>4</sub>
MoO <sub>2</sub> Cl <sub>2</sub>	

But one oxybromide is known. Its formula is MoO<sub>2</sub>Br<sub>2</sub>. Our experiments add to this the compound Mo<sub>2</sub>O<sub>3</sub>Br<sub>4</sub>, which would correspond to Mo<sub>2</sub>O<sub>3</sub>Cl<sub>4</sub>. The latter is light brown in colour, while the former possesses a deep purple colour. Schulze's oxyfluoride would correspond to MoO<sub>2</sub>Cl<sub>2</sub> and Mo<sub>2</sub>O<sub>3</sub>Br<sub>2</sub>, while that obtained by us corresponds to Mo<sub>2</sub>O<sub>3</sub>Cl<sub>4</sub> and Mo<sub>2</sub>O<sub>3</sub>Br<sub>4</sub>. Püttbach's division presupposes the presence of a sexivalent molybdenum atom in the saturated members, while the unsaturated are regarded as derived from two molecules of MoCl<sub>5</sub> by the substitution of oxygen for equivalent amounts of chlorine. Our oxybromide, Mo<sub>2</sub>O<sub>3</sub>Br<sub>4</sub>, and oxyfluoride, Mo<sub>2</sub>O<sub>3</sub>Fl<sub>4</sub>, may be looked upon as possessing similar origin, although their corresponding pentabromide and pentafluoride are unknown. The compound MoO<sub>3</sub>.3HBr, like MoO<sub>3</sub>.2HCl, presupposes the presence of a sexivalent molybdenum atom, and may be properly considered a hydroxybromide, represented by the formula Mo(OH)<sub>3</sub>Br<sub>3</sub>, a derivative of the unknown hexabromide MoBr<sub>6</sub>.

## REACTION FOR CERIUM OXIDE.

By H. C. PLUGGE.

THE author recommends a solution of strychnine in concentrated sulphuric acid as a characteristic and sensitive reagent.

If to a trace of cerium hydroxide precipitated by alkalis, almost dried on the filter, and then placed in a porcelain capsule, we add a few drops of the above-mentioned solution of strychnine, there appears at once a splendid blue colour, which soon disappears, and is succeeded by a more permanent cherry-red or faint red according to the

quantity of the cerium oxide contained in the precipitate. This reaction is an inversion of Sonnenschein's well-known reaction for strychnine. Plügge used a solution of 1 part of strychnine (or its nitrate or sulphate) in 1000 parts of concentrated sulphuric acid, as also a solution of cerium oxide in a slight excess of dilute sulphuric acid, the latter diluted with so much water that 1 c.c. of the solution contains 1 m.grm. cerium oxide.

Of this solution of cerium quantities accurately measured were each time evaporated down, and two, three, or more drops of the reagent were added to the dry residue when cold. The residues from 10 and from 5 c.c. solution of cerium sulphate were strongly coloured, but those from 1 and even from  $2\frac{1}{2}$  c.c. of this liquid showed no perceptible colouration. With the salts of cerium (sulphate, oxalate, &c.) the reaction is not remarkably sensitive. But with the following modification it becomes so delicate that the limit of sensitiveness can be taken as 0.00001 grm. cerium oxide. A little of the solution of the cerium salt with the addition of so much dilute soda-lye as may serve to render the liquid distinctly alkaline is evaporated in a capsule, and the dry residue is covered with a few drops of the strychnine solution. For very dilute solutions containing little free acid a single drop of very dilute soda-lye is sufficient, so that the excess of alkali in the evaporated residue will neutralise but very little of the sulphuric acid of the reagent.

With this modification the evaporated residue of 1 c.c. solution containing 1 part of cerium oxide in 100,000 c.c. (i.e., 0.01 m.grm. cerium) gave a distinct violet colour, which, however, soon disappeared. The residue from the evaporation of 10 c.c. of this solution (0.1 m.grm.) gave under the same conditions a very strong reaction, at first blue and then a permanent red.

Whilst very small quantities of cerium oxalate do not become coloured if covered with the above reagent, similar quantities of this salt, after previous heating or moistening with a little dilute soda-lye, and drying on the water-bath, are very strongly coloured.

The precipitate thrown down by alkalies from solutions of the cerium salts may, after desiccation, be used at once for Plugge's reaction. If this reagent is applied to the white precipitate produced by ammonium chloride and ammonia in a mixed solution of zinc, aluminium, and cerium it easily shows the presence of cerium along with aluminium. This does not, however, directly succeed in the white precipitate given by ammonium chloride, ammonia, and ammonium sulphide, as then, on adding the above reagent,  $H_2S$  is liberated from the zinc sulphide, which destroys the colour or prevents its formation.—*Archiv der Pharmacie* and *Zeitschrift für Analytische Chemie*.

## ON AMIDOPHOSPHORIC ACID.\*

By H. N. STOKES.

By replacing the hydroxyls of orthophosphoric acid successively by amido groups, three amides may be derived, namely, amidophosphoric acid,  $PO.NH_2.(OH)_2$ , diamidophosphoric acid,  $PO.(NH_2)_2.OH$ , and phosphoryl triamide,  $PO(NH_2)_3$ , and from these, by abstraction of water or ammonia, an imido acid,  $PO.NH.OH$ , an imidoamide,  $PO.NH.NH_2$ , and a nitrile,  $PO.N$ . Of these, amido- and diamidophosphoric acids have not yet been described. In the dictionaries of Fehling (*Neues Handwörterbuch der Chemie*, v., 423), and of Ladenburg (*Handwörterbuch der Chemie*, ix., 100) the formula  $PO.NH_2.(OH)_2$  is given to a body described by Schiff (*Ann. Chem. (Liebig)*, ciii., 168), and called by him *phosphaminsäure*. This rests on an error of the compilers, as Schiff gives to his acid the formula  $PO.NH.OH$ , with which his analyses agree, while they differ widely from that of amidophos-

phoric acid. Moreover, as will be shown, amidophosphoric acid is a body of entirely different properties.

Schiff (*Ann. Chem. (Liebig)*, ci., 300) also describes the triamide,  $PO(NH_2)_3$ . Although his analyses agree quite well with this formula, the existence of the body is called in question by Gladstone (*Four. Chem. Soc.*, [2], vii., 18), who, in repeating Schiff's method of preparation, treating phosphorus oxychloride with dry ammonia, was unable to replace the third chlorine atom at any temperature below that at which further decomposition occurs (above  $300^\circ$ ). The correctness of the formula  $PO.NH.OH$  assigned by Schiff to his phosphamic acid is also questioned by Gladstone and Holmes (*Four. Chem. Soc.*, [2], ii., 229, 235), who point out the general resemblance of its properties, as described, to those of pyrophosphodiamic acid obtained by them. They regard it as a mixture of the latter with metaphosphoric acid. The identity of Schiff's acid with pyrophosphodiamic acid (diamidopyrophosphoric acid) has also found acceptance in some handbooks (Gmelin-Kraut, *Handbuch der Anorg. Chemie*, i, 2 Abth., 529; Graham-Otto, *Anorg. Chem. (Michaelis)*, ii., 401).

The imidoamide,  $PO.(NH).NH_2$ , was described by Gerhardt (*Ann. Chim. Phys.*, [3], xviii., 188) under the name phosphamide, and was obtained by treating phosphorus pentachloride with dry ammonia and then with water. Its nature has not been questioned.

The body  $PO.N$ , described by Gerhardt (*Ann. Chim. Phys.*, [3], xviii., 188) as biphosphamide, by Schiff (*Ann. Chem. (Liebig)*, ci., 304) as monophosphamide, and by Gladstone (*Four. Chem. Soc.*, [2], vii., 18) as phosphonitryle, is the final product of heating the triamide, the imidoamide or the amido chlorides. Its constitution is not known, but is probably much more complex than is represented by the formula given.

In addition to the above, Gladstone and Holmes (*Quar. Journ. Chem. Soc.*, iii., 353; *Journ. Chem. Soc.*, [2], ii., 225; [2], iv., 1290; [2], vi., 64, 261; [2], vii., 15) have obtained a series of complex amides, derivable from pyro- and tetraphosphoric acids.

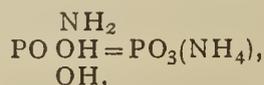
The difficulty in preparing amido orthophosphoric acids lies in part in the impossibility of regulating the decomposition by water or acids of the products of the action of ammonia on phosphorus pentachloride and oxychloride. Gerhardt's imidoamide and Schiff's triamide seem to be capable of giving ammonia and phosphoric acid only; at least no mention is made of intermediate products. The bodies derived from phosphorus oxychloride by partial replacement of chlorine by amido groups are so decomposed by water as to give the amidopyrophosphoric acids of Gladstone, and further action results in the separation of ammonia before the pyrophosphoryl group is broken up. The reason for this, as will be seen below, lies in the great ease with which amidophosphoric acid passes over into ammonium phosphate. As phosphorus pentoxide is a derivative of pyrophosphoric acid, it is not to be expected that it would give orthophosphoric amides with ammonia.

I have overcome these difficulties in part, by acting with ammonia on phosphoric ethers, and in this way have obtained the primary amide,  $PO.NH_2.(OH)_2$ . Attempts to obtain other amides by the same method are in progress.

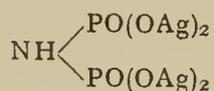
By dissolving the chloride of diphenylphosphoric acid,  $PO.Cl.(OC_6H_5)_2$ , in alcohol, and adding alcoholic ammonia, diphenylamidophosphate,  $PO.NH_2.(OC_6H_5)_2$ , a beautifully crystalline substance is at once formed. This, on saponifying with ammonia or baryta, gives phenylamidophosphoric acid,  $PO.NH_2.(OC_6H_5).(OH)$ , and with caustic potash or soda amidophosphoric acid. The free acid obtained by decomposing the lead salt by sulphuretted hydrogen and precipitating with alcohol is a well characterised body, forming fine microscopic crystals. It forms two series of salts, acid and neutral, of which the acid salts are invariably, the neutral often, crystalline, and in many cases the forms are characteristic. Boiled in aqueous solution, either alone or with an acid,

\* *American Chemical Journal*, vol. xv., No. 3.

it decomposes almost instantly into ammonia and orthophosphoric acid. Its cold aqueous solution may be kept a short time without much decomposition, but quickly passes into primary ammonium orthophosphate. Dilute mineral acids in the cold effect the change much more rapidly, but in either case the first product is not orthophosphoric acid, but an acid or mixture of acids giving white amorphous precipitates with silver nitrate. At 100° the dry acid passes without loss of weight into an ammonium salt, giving a white silver salt. This is possibly metaphosphate, or a mixture of the different metaphosphates,—



but the nature of the product has not yet been established. The acid salts on heating give off ammonia and leave metaphosphates. Such of the neutral salts as contain crystal water pass first into ammonium salts, and on further heating into pyrophosphates. The neutral silver salt, which is anhydrous, is an exception. At 180° it gives off one-half its nitrogen as ammonia, apparently forming a very stable *pyrimidophosphate*.



which stands a red heat without further change, or at least without loss of weight. Other salts which are especially characteristic are the acid sodium salt, almost insoluble in water, and the neutral magnesium salt, isomeric with crystallised ammonium magnesium phosphate. In the absence of any experimental proof of the contrary, the constitution of the acid is regarded as—



in accordance with the usually assumed structure of acid amides, rather than as  $\text{P}(\text{NH})(\text{OH})_3$ , in harmony with the most recent views on the nature of organic amides.

#### DESCRIPTIVE PART.

*Diphenylamidophosphate*.  $\text{PO} \begin{array}{c} \text{NH}_2 \\ (\text{OC}_6\text{H}_5)_2. \end{array}$ —One mol. wt. phosphorus oxychloride and 2 mol. wts. phenol are boiled in a flask fitted with return condenser until no further evolution of hydrochloric acid occurs. The product is a mixture of—



and unchanged oxychloride. It is not necessary to isolate the diphenylphosphoric chloride. The liquid is diluted with absolute alcohol, and alcoholic ammonia is added slowly, with cooling, to alkaline reaction. The product is mixed with several volumes of water, whereby ammonium chloride dissolves and crystalline amidophosphate separates, mixed with oily phenylphosphates. This is sucked out in a funnel as far as possible, washed with water, dried on porous plates to remove the oil, again washed, dried, and re-crystallised two or three times from alcohol, or better, chloroform. The yield is about 35 per cent of the theoretical.

	Calculated or $\text{PO}.\text{NH}_2(\text{OC}_6\text{H}_5)_2.$		Found.	
P	12.46	—	12.37	—
N	5.67	5.70	5.64	5.67

Phosphorus was determined as magnesium pyrophosphate after evaporating first with alkali, then with acid; nitrogen as ammonia after evaporating with hydrochloric acid; both as ammonium chloroplatinate and by titration, after distilling.

The ether fuses at 148°, and on cooling solidifies to a crystalline mass with a surface of brilliant facets. At 180° there is a very slow evolution of ammonia and

phenol, which becomes quite rapid at 230°, when it is accompanied by sublimation of unchanged substance. The non-volatile product of decomposition is first an oil, later a solid substance containing phosphorus.

*Phenylamidophosphoric acid*,  $\text{PO} \begin{array}{c} \text{NH}_2 \\ \text{OH} \end{array} \text{OC}_6\text{H}_5.$ —The free

acid could not be obtained in the solid state. On decomposing the lead salt in the cold with sulphuretted hydrogen a solution is obtained which is not precipitated by alcohol. On evaporating *in vacuo* over sulphuric acid, the acid takes up water, and is converted into the ammonium salt of phenylphosphoric acid, which contains only traces of amido acid, which were isolated as the silver salt described below.

*Acid ammonium phenylphosphate* is easily soluble in water, and crystallises in long prisms. It also crystallises from alcohol, in which it is difficultly soluble, as pearly rhombic plates or flat needles, fusing at 140—145° with decomposition. Silver nitrate gives a precipitate of radiating flat prisms consisting of the *neutral silver salt* (a) which is anhydrous. By neutralising the filtrate with ammonia a further precipitate of the same salt (b) is obtained.

	Calculated for $\text{PO} \begin{array}{c} (\text{OAg})_2 \\ \text{OC}_6\text{H}_6 \end{array}$	Found.
		(a) (b)
Ag	55.64	54.88 55.44

Phenylphosphoric acid therefore resembles phosphoric acid in that its acid salts give directly the neutral silver salt, and differs from amidophosphoric acid, which gives either acid or neutral silver salt according as acid or neutral salt be used as precipitant.

*Ammonium phenylamidophosphate*,  $\text{PO} \begin{array}{c} \text{NH}_2 \\ \text{ONH}_4 \end{array} \text{OC}_6\text{H}_5,$  obtained

by saponifying the diphenyl ether with aqueous ammonia, is easily soluble in water, and the solution may be evaporated without decomposition.

*Silver phenylamidophosphate*,  $\text{PO} \begin{array}{c} \text{NH}_2 \\ \text{OAg} \end{array} \text{OC}_6\text{H}_5,$  from the

ammonium salt, after recrystallising from water, forms scales, or long, narrow, pointed plates of pearly lustre. It is difficultly soluble in cold, moderately in boiling water, and has a strong tendency to separate as a crystalline scum on the surface. It is unaffected by light.

	Calculated for $\text{PO}(\text{NH}_2)(\text{OC}_6\text{H}_5)(\text{OAg}).$		Found.	
P	11.09	—	11.11	—
N	5.02	—	5.08	—
Ag	38.53	38.31	—	38.19

*Barium phenylamidophosphate* is formed by boiling the ether with baryta water until nothing crystallises out on cooling, and removing the excess of baryta by carbon dioxide. It forms scales, is quite soluble in water, and resembles the silver salt in forming a crystalline scum on the surface.

*Lead phenylamidophosphate*, from the barium salt by lead acetate, forms brilliant scales, nearly insoluble in water.

*Amidophosphoric acid*,  $\text{PO} \begin{array}{c} \text{NH}_2 \\ (\text{OH})_2. \end{array}$ —The alkali salts of this acid are readily obtained by saponifying the ether with a strong solution of caustic potash or soda. The chief difficulty in obtaining them pure is in separating them from the small quantity of phosphate formed at the same time. In the case of some of the salts this may be effected by methods mentioned below. The conversion into phosphate by boiling alkali is very slow. A weighed amount of ether was boiled with concentrated caustic potash, and the ammonia determined in the distillate by titration. An hour's boiling showed a decomposition of only 3 per cent.

$\text{NH}_2$   
Acid potassium amidophosphate,  $\text{PO OK}$ .—If a lump of  
 $\text{OH}$

caustic potash be placed on some diphenyl ether, and a few drops of water be added, a somewhat violent reaction occurs. On boiling with an excess of concentrated caustic potash, the saponification is complete in ten minutes. The oily solution is acidified with strong acetic acid, care being taken to keep it cool with ice-water. On adding several volumes of alcohol, the acid salt is at once precipitated. It is purified by washing with alcohol, dissolving in a little water, and re-precipitating by alcohol. It cannot be re-crystallised from hot water, as its solution is rapidly converted by heating into acid potassium ammonium phosphate. A weighed amount of acid potassium salt was dissolved in water and boiled ten minutes;  $\frac{1}{10}$  n. caustic soda was added in excess, and the solution again boiled to remove ammonia. The loss of alkalinity due to the escape of ammonia indicated that, by ten minutes' boiling, 98 per cent of the amide was converted into ammonium salt. The same change occurs in a few days in the cold aqueous solution. The salt forms six-pointed stars, or sometimes rhombohedra, readily soluble in cold water, insoluble in alcohol. Its solution is neutral towards litmus, methyl orange, and phenolphthalein. On ignition it gives off ammonia, and leaves potassium metaphosphate.

The analysis of two air-dried preparations (*a* and *b*) gave—

	Calculated for $\text{PO.NH}_2.\text{OK.OH}$ ,		Found.	
			<i>a.</i>	<i>b.</i>
P	22.96		22.76	—
N	10.39		10.26	10.35

The loss on ignition gave—

	Calculated for $\text{PO.NH}_2.\text{OK.OH}$ .	Found.
$\text{NH}_3$	12.61	13.83

The excess found is due in part to a small amount of water which the salt retains, in part to a little acid potassium ammonium phosphate which cannot be removed by precipitating with alcohol. The amount of ammonium salt may be determined by distilling off the ammonia with alkali solution, and determining it in the distillate, making a slight correction for the decomposition of the amide itself as above determined (3 per cent per hour). In this way the amount of ammonium salt in preparation (*a*) was found to be 4.75 and 5.10 per cent, in (*b*) 4.15 per cent. As the acid potassium salt is used for preparing other salts, this small amount of phosphate has to be taken into consideration, as the latter would otherwise be contaminated with phosphate. Its presence may be obviated by methods below mentioned.

Neutral potassium amidophosphate is extremely soluble in water, and not appreciably decomposed by boiling.

(To be continued).

Valuation of Ipecacuanha.—G. Kottmayer (*Pharm. Post*) mixes 15 grms. of powdered ipecacuanha with 148 c.c. of alcohol at 90 per cent, and 2 c.c. hydrochloric acid of sp. gr. 1.12, and digests for four days at 40° in a stoppered flask, with frequent shaking. 100 c.c. of the perfectly clear liquid, cooled down to 15°, are drawn off with a pipette and mixed in a capsule with 20 c.c. of an alcoholic solution of lead acetate (1 part sugar of lead, 9 parts of alcohol at 50 per cent); 1.5 grms. hydrate of lime are added, and the whole is evaporated down on the water-bath to the consistence of a paste. To this paste he adds 5 grms. of moderately fine glass evaporated to dryness with constant stirring, and the readily friable residue is extracted with chloroform for ten hours. The chloroform solution is evaporated, the dried residue weighed, treated with .2 c.c. normal hydrochloric acid, and the undissolved matter (after careful washing and drying) is weighed again. The difference between the two weights shows the emetine present.

## PROCEEDINGS OF SOCIETIES.

### PHYSICAL SOCIETY.

Ordinary Meeting, June 23rd, 1893.

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

Prof. J. COX, M.A., was elected a Member of the Society.

Mr. F. H. NALDER exhibited a Bridge and Commutator for comparing Resistances by Prof. Carey Foster's Method, the chief features of which are simplicity, compactness, long range, and great accuracy. The commutation of the coils to be compared is effected by mercury cups, the eight holes necessary for this purpose being arranged in a circle. An ebonite disc carrying the four connectors is mounted on a spindle in the middle of the circle, and the positions of the coils are interchanged by rotating the disk through 180°. A large range is secured by providing a number of interchangeable bridge wires, and a fine adjustment for the galvanometer key enables great accuracy to be attained.

Mr. W. R. PIDGEON and Mr. J. WIMSHURST each read a paper on "An Influence Machine," and exhibited their machines in action. In designing his machine Mr. Pidgeon has endeavoured, 1st, to make the capacity of each sector large when being charged and small when being discharged; 2nd, to prevent leakage from sector to sector as they enter or leave the different fields of induction; and 3rd, to increase the capacity of the machine by making the sectors large and numerous. The first object is attained by arranging fixed inductors of opposite sign to the sectors near the charging-points, and of the same sign near the places of discharge. Objects 2 and 3 are secured by imbedding the sectors in wax, run in channels in the ebonite discs which form the plates of the machine, and carrying wires from each sector through the ebonite, each wire terminating in a knob. In this way the sectors can be placed much nearer together than otherwise, without sparking back. By setting the sectors skew with the radius, they are caused to enter the electric fields more gradually,—consequently the potential difference between adjacent sectors is kept comparatively small. Experiment showed that the use of the stationary inductors at the charging-points increased the output threefold, and as compared with an ordinary Wimshurst the output for a given area of plate passing the conductors was as 5.6 : 1. The recovery of the machine after a spark had occurred was particularly rapid.

Mr. Wimshurst's new machine consists of two glass discs, 3 feet 5 inches diameter, mounted about  $\frac{3}{4}$ " apart on the same spindle. Both plates turn in the same direction. Between the discs are fixed four vertical glass slips, over 4 feet long, two on each side, and each covering about  $\frac{3}{4}$ ths of a disc. Each slip carries a tin-foil inductor, which has a brush, touching lightly on the inside of the adjacent disc, on its leading edge. Collecting and neutralising brushes touch the outsides of the discs and the few metallic sectors attached thereto. An account of some experiments made to determine the efficiency of the machine was given. The author also showed that when all the circuits of the machine were broken, it still continued to excite itself freely, and sparked from the discs to the hands when brought near.

In a written communication Prof. O. LODGE said his assistant, Mr. E. E. Robinson, constructed a machine on lines similar to Mr. Pidgeon's, a few months ago, and had now a large one nearly completed. Mr. Robinson's fixed inductors are carried on a third plate fixed between the

two movable ones. The sectors are quite small, and neither they nor the inductors are embedded. On close circuit the machine gives a large current (1000 ampère) and on open circuit exceedingly high potentials. In Dr. Lodge's opinion Mr. Pidgeon attaches too much importance to his sectors and their shape.

Mr. J. GRAY wrote to say that stationary inductors enclosed in insulating material would probably give trouble at high voltages, because of the surface of the insulator becoming charged with electricity of opposite sign to that on the inductor. He suggested that this might explain why Mr. Pidgeon could not obtain very long sparks.

Prof. C. V. BOYS enquired as to how far the wax made insulating union with the ebonite, for, if good, glass might possibly be used instead of ebonite. He greatly appreciated the design of Mr. Pidgeon's machine.

After some remarks by the PRESIDENT, on the great advances which had been made, Mr. Pidgeon replied, and Mr. Wimshurst tried some further experiments with a small experimental machine.

A paper on "A New Volumometer," by Mr. J. E. MYERS, B.Sc., describing the developed form of Prof. Stroud's instrument, was, in the absence of the author, taken as read.

Mr. R. W. PAUL exhibited a compact form of sulphuric acid voltameter of small resistance. The voltameter is a modification of a pattern designed at the Central Institution, in which the rate of decomposition is determined from the time required to fill a bulb made in the stem of a thistle-funnel. He also showed a handy form of Daniell cell, devised by Prof. Barrett. When not in use, the porous pot containing the zinc is removed from the copper sulphate solution, and placed in a vessel containing zinc sulphate or sulphuric acid.

A paper on "Long-Distance Telephony," by Prof. J. PERRY, F.R.S., assisted by H. A. BEESTON, was read by Prof. Perry. The case of a line of infinite length, having resistance capacity, self-induction, and leakage, is taken up, and the state of a signal as it gets further and further away from the origin is considered. Taking the shrillest and gravest notes of the human voice to have frequencies of about 950 and 95 respectively, the distance from the origin at which the ratio of the amplitudes of these high and low frequency currents is lessened by  $1/m$ th of itself, has been determined when  $m=4$  for different values of leakage and self-induction; and under similar conditions the distances at which the relative phase of the two currents become altered by  $1/n$ th of the periodic time of the most rapid one, have been worked out for  $n=6$ . The results are given in the form of Tables, from which it appears that, if there was no self-induction, increasing the leakage increases the distance to which we can telephone, whilst if there was no leakage increasing the self-induction increases the distance. When self-induction and leakage are not so great, increasing either increases the distance, and for particular values the distances become very large. At the end of the paper Tables of general application are given, from which the limiting distances for any line can be readily found by multiplying the numbers by simple functions of the constants of the line.

Mr. BLAKESLEY said that some ten years ago he discussed the subject when capacity and resistance were alone considered, and now pointed out that when self-induction and leakage were introduced, the equations were still of the same form. He also suggested how terminal conditions on lines of finite length might be easily taken into consideration.

Prof. PERRY, in reply, said the introduction of self-induction and leakage rendered the calculations much more laborious, and that the terminal conditions were much more complicated than Mr. Blakesley supposed.

## NOTICES OF BOOKS.

*Rules for the Estimation of Alcohol in Imported Spirits.* With Tables giving the Specific Gravity of Alcohol from 984 to 936, computed to the third place of decimals. By C. J. H. WARDEN, M.D., Medical Examiner to the Government of Bengal. Issued by order of the Board of Revenue, Bengal. Calcutta: Bengal Secretariat Press, 1892.

THE manipulation of highly volatile liquids such as commercial spirits in localities where the temperature is high presents considerable difficulties. In the author's laboratory the usual temperature during a great part of the year ranges from 80° to 95° F., and the atmosphere is at the same time heavily charged with moisture. When a specific gravity bottle is filled with a liquid at 15.5 centigrade, and the stopper with a capillary bore is inserted, the bottle cannot be at once weighed, on account of the extent to which water has been condensed upon the surface of the bottle. By the time the temperatures of the balance case and of the liquid have become equalised, the latter will have expanded, and a not inconsiderable proportion of it will have escaped.

The author has devised a method of avoiding this source of error. His rules for testing spirits will be found well adapted for use in tropical climates. The accompanying tables have been specially re-calculated by Babu Gündra Nath Bose.

Dr. Warden points out the advantage of having in a set of decimal weights pieces for 3, 0.3, and 0.03 grm.

*The Mineral Industry, its Statistics, Technology, and Trade, in the United States and other countries from the Earliest Times to the end of 1892.* Vol. i. Edited by R. P. ROTHWELL. New York: The Scientific Publishing Company.

THIS most useful work is designated as the "Statistical Supplement of the *Engineering and Mining Journal*." The compilation has been chiefly made with a view to American conditions and exigencies. Nevertheless, the mining industries of the whole world are fairly and, in general, very fully described.

The editor, in his preface, apologises for the retention of the English system—or unsystem?—of weights and measures. But in his denunciation he forgets the two causes which have, so far, delayed the introduction of the metric system into Britain. The first of these is the polysyllabic nomenclature which the French innovators sought to impose upon the world in their rage for everything classical. Had the various denominations of the metric system received monosyllabic names, it would have met with much more general acceptance in our midst. The second obstacle is the reluctance of the English people to be dictated to. The general use of the new weights and measures could only be enforced by a system of espionage and interference which might easily overthrow a ministry. But we submit that nations which persist in the use of Bauné's hydrometer scale have little room to take up their parable against us.

It will be seen that, in addition to mining and metallurgy, this work embraces in its scope some of the most important chemical manufactures, such as cements, alkali, bleaching powders, manures, salts of chromium, &c.

The author very justly denounces the Cornish copper assay. But he admits that there is no small difficulty in changing a system which for more than a century has been at the foundation of all business in this department. The difficulty is likely to diminish from the circumstance that the yield of the copper mines in the United Kingdom has greatly fallen off.

Mica-mining is said to have greatly fallen off owing to

THE CHEMICAL NEWS.

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THE ASSAY OF MANGANESE OXIDES WITH HYDROGEN PEROXIDE.

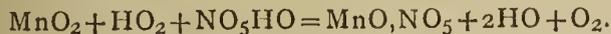
By ADOLPHE CARNOI.

It is known that oxygenated water is decomposed with effervescence in contact with manganese peroxide, and that a small quantity of this oxide suffices to destroy an indefinite quantity of oxygenated water.

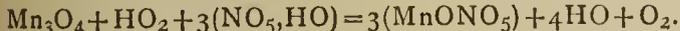
It is not the same when the peroxide and the oxygenated water are in presence of an acid, even if very dilute or weak, but capable of combining with manganous oxide. There occurs then a simultaneous decomposition of the two peroxides, and the quantity of oxygen liberated is exactly double that which exists in the manganese peroxide over and above MnO.

This reaction occurs readily, even in the cold, whether with nitric or sulphuric acid (very dilute), or with acetic acid as long as none of these acids attacks MnO<sub>2</sub>. It is explained in the same manner as many other simultaneous and correlative decompositions, the mechanism of which has been explained by M. Berthelot.

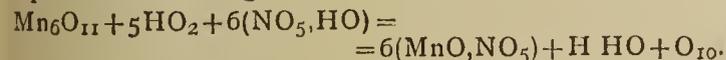
The final transformation is expressed for manganese peroxide by the following formula:—



It occurs similarly for the red ignited oxide, Mn<sub>3</sub>O<sub>4</sub>:—



It is also verified exactly for the oxide precipitated by oxygenated water and ammonia in excess containing, as I have shown, 5 equivalents of available oxygen to 6 equivalents of manganese, Mn<sub>6</sub>O<sub>11</sub>:—



After having satisfied myself of the perfect exactitude of the relations indicated, I sought to deduce from them a practical process for the determination of the *available oxygen* in the higher oxides of the manganese; or what is often called the commercial assay of the ores of manganese, collecting and measuring over water the gas evolved.

The arrangement adopted is very simple.

We fix on a support with clamps a small flask of the capacity of about 150 c.c., having a caoutchouc stopper with two perforations. Through one of these passes a straight tube fitted with a funnel, or a phial with a glass cock, the point of which must descend to the bottom of the flask. The other aperture has a gas delivery-tube bent four times, ending in a graduated gas jar, filled with water and arranged on the trough. We introduce into the flask 1 grm. of the manganese oxide reduced to a fine powder, then about 30 c.c. of water, and 20 c.c. of nitric acid, which decomposes any carbonates present in the sample. We allow the carbonic acid to escape entirely; then we insert the stopper, leaving the cock open. We can then observe that not only the graduated jar, but also the delivery-tube is filled with water up to the point where it emerges from the water-trough.

We close the cock, pour into the funnel a measured volume of 20 c.c. oxygenated water, at 10 vols., then we cause it to flow gently into the flask, taking care to close the cock as soon as the last traces of oxygenated water have passed.

The action takes place at once without heat, and the escape of oxygen, which is at first very rapid, is completed in a few minutes if care is taken to shake the flask from time to time. Nothing then remains but to measure the volume of oxygen liberated.

To this end, it is sufficient to measure the increase of the total gaseous volume, ascertaining that the temperature and the pressure have remained the same as at the beginning of the experiment. The gas is lowered until the water is exactly at the same level within and without. The delivery-tube is withdrawn, and the volume of gas is read off, and brought anew exactly to the atmospheric pressure.

To find the total volume of oxygen liberated, or the increased volume of gas in the apparatus from the beginning to the end of the experiment, we must add to the volume, V, just read off the small volume of gas, v, which has filled the extremity of the delivery-tube originally full of water, a volume which is easily measured with water, once for all. On the other hand, we must deduct the volume, v', of the oxygenated water which has been introduced into the flask and has displaced an equal volume of oxygen.

The total increase of the gaseous volume, V<sub>t</sub>, is thus measured at the temperature, t, and the atmospheric pressure, H, observed at the outset. The gas is, moreover, saturated with moisture, the tension of which, h, is known according to the temperature.

Knowing that the weight of 1 litre of dry oxygen at 0° and at 760 m.m. is 1.4298 grm., and knowing the total volume, V<sub>t</sub>, expressed in c.c., we calculate in grms. the weight, p, of available oxygen in 1 kilo. of ore by means of the formula:—

$$p = \frac{1}{2} V_t \times 1.4298 \times \frac{H-h}{760} \times \frac{1}{1 + 0.00367.t}.$$

—Comptes Rendus, cxvi., 1295.

PREPARATION OF CERTAIN REFRACTORY METALS IN THE ELECTRIC FURNACE.

TUNGSTEN, MOLYBDENUM, VANADIUM.

By HENRI MOISSAN.

In this paper the author indicates the easy preparation of tungsten, and molybdenum, and vanadium carbides.

*Tungsten.*

It is known that tungsten may be easily obtained in the form of a powder by reducing tungstic acid at a red heat in a current of hydrogen. The metallic powder thus obtained has hitherto been fused only with great difficulty. Desprez has succeeded in melting small quantities of tungsten in the arc produced by 200 Bunsen elements. In the flame of the oxyhydrogen blowpipe tungsten is quickly oxidised, and soon disappears in fumes of tungstic acid.

The preparation of tungsten, either pure or as a carbide, is easily effected in the electric furnace. The mixture of tungstic acid and coke is placed in the crucible of the furnace, and in about ten minutes, with a current of 350 ampères and 70 volts, we obtain a metallic regulus of about 120 grms. If we have taken care to add a great excess of oxide, we may obtain the pure metal in the first experiment; but it is preferable to prepare first a metal slightly carbided, which is much more fusible, and to remelt it in a second operation in presence of a large excess of tungstic acid. In this manner we obtain a brilliant metal, very hard, and of the specific gravity 18.7. If the carbon is in excess, we obtain cast metals of very varying compositions. Four specimens gave on analysis the following percentages of carbon:—0.64, 2.74, 4.56, and 6.33. These cast metals have a brilliant fracture. They are stable on exposure to air, and are sometimes covered with a fine layer of blue tungsten oxide.

This metal has the curious property of fixing a large proportion of carbon. If the preparation of tungsten has been made in presence of an excess of coke, with a current of 1000 ampères and 70 volts, we obtain cast metals much richer in carbon, specimens of which were found to contain C 17.27, 17.61, 18.27, and 18.81 per cent.

*Molybdenum.*

Pure molybdenum has been regarded hitherto as infusible. Henri Debray had difficulty in melting with the oxyhydrogen blowpipe a molybdenum carbide containing from 4 to 5 per cent of carbon. In the electric furnace the operation requires only a few moments.

We set out with pure ammonium molybdate, which on ignition yields a grey pulverulent oxide. It is mixed with charred sugar, and heated for seven to eight minutes with a current of 350 ampères and 70 volts. We thus obtain a regulus of cast metal which is easily detached from the crucible. This molybdenum carbide is very hard, scratching glass and steel. The fracture is brilliant, and it is not affected by moist air. Its specific gravity is 8.6. Its composition is variable, according to the proportion of coke employed. The percentage of carbon ranged from 9.77 to 9.90.

*Vanadium.*

The important researches of Roscoe proved the difficulty of obtaining this elementary substance. By reducing vanadic acid with coke there was merely obtained a silicide scarcely fusible at the temperature of a good blast furnace. Ultimately he surmounted the numerous difficulties which this preparation presented, and he obtained metallic vanadium by reducing vanadium bichloride with pure dry hydrogen. He remarks, however, that the powder of metal thus obtained still contains a trace of oxygen, and 1.3 per cent of hydrogen.

In the preparation of cast vanadium in the electric furnace we set out with pure ammonium meta-vanadate, which on ignition yielded an easily fusible vanadic oxide of a yellowish brown colour. It was mixed with the charcoal of sugar, and when placed at some centimetres distance from the arc produced by a current of 350 ampères and 70 volts no reduction occurred. It was necessary to let the arc play in contact with the powder for twenty minutes, and then we only obtained on the surface of the mixture small metallic granules of the size of a lentil.

On employing an arc produced by a current at 1000 ampères and 70 volts, we obtained the complete reduction of the oxide, by the fusion of the carbide, in a few moments. The cast metals obtained under these conditions contained respectively C 25.47, 25.65, and 17.56.

It is a curious fact that as the temperature rises, we tend towards metallic carbides very rich in carbon.

The vanadium carbide has the specific gravity 5.3.

It appears from these experiments that pure chromium is more infusible than platinum, whilst higher than chromium we must place molybdenum, uranium, tungsten, and lastly vanadium.—*Comptes Rendus*, cxvi., p. 1225.

## THE VOLATILISATION OF SILICA AND ZIRCONIA, AND THE REDUCTION OF THESE SUBSTANCES BY CARBON.

By HENRI MOISSAN.

On submitting zirconia to the high temperature of the electric furnace, this oxide quickly enters into fusion. After the lapse of ten minutes, on operating with a current of 360 ampères, and 70 volts, there appear very abundant white fumes. These fumes consist of the vapour of zirconia, which earth at this high temperature is in full ebullition. If the vapours are condensed upon a cold substance we obtain a white powder, which is treated with very dilute hydrochloric acid to remove any lime present. After washing with boiling distilled water and desiccation there remains a white powder, which under the microscope appears as white rounded masses, without any transparent particles. This powder presents all the characters of zirconia. It scratches glass with ease, and its sp. gr. is 5.10.

After cooling, there remains in the crucible a mass of melted zirconia, with a crystalline fracture. Within the furnace, in the cooler parts, we sometimes find characteristic crystals of zirconia, of the form of transparent dendrites, of a vitreous lustre, not attacked by sulphuric acid, and capable of scratching glass.

This zirconia, when in fusion, is easily reduced by coke. If we place a quantity of zircon in a crucible of coke, we find below the residue of melted zirconia a metallic regulus of zirconium, containing neither carbon nor nitrogen, but containing variable quantities of zirconia.

On the contrary, on mixing zirconia with an excess of coke, we obtain a substance of a metallic appearance, not containing nitrogen, and which on analysis gave the following results:—

	1.	2.	3.
Carbon .. ..	4.22	4.60	5.10.

When the zirconium carbide is richer in carbon it is rapidly destroyed on exposure to the air.

This carbide may be refined so as to yield metallic zirconium by re-melting in presence of an excess of liquid zirconia. Zirconium is a very hard body, which easily scratches glass and ruby. Its sp. gr. is 4.25. It therefore approximates very closely to that of Troost's zirconium (4.15).

*Silica.*—Fragments of rock crystal in a crucible of coke were exposed to the action of the electric arc produced by a current of 350 ampères and 70 volts. In a few moments the silica enters into fusion, and in seven or eight minutes ebullition sets in.

There then issues from the furnace, by the apertures which give passage to the electrodes, a smoke of a bluish colour, lighter than that produced by zirconia. These vapours are given off plentifully as long as the experiment continues. They may be condensed by placing an inverted crystalliser at some distance from the apertures of the furnace. The interior of this crystalliser is rapidly coated with a slight layer of a scarcely transparent substance, of a slightly bluish white colour. On taking up the contents of the crystalliser in water, and examining this residue under the microscope with a very low power, we see that it is chiefly formed of opalescent spheres, quickly soluble in hydrofluoric acid. These small spheres of silica, visible to the naked eye, are solid. They sometimes present at one point a hollow, which seems to indicate that the melted silica has contracted in volume in passing from the liquid to the solid state. Along with these spheres there are numerous particles of amorphous silica.

If we wish to collect a notable quantity of this product it is better to use a furnace the cover of which has an aperture for the escape of the vapour of silica. A glass bell is placed over this aperture, and we may thus, in from ten to fifteen minutes, collect 20 grms. of a very light white powder, which is purified from lime by washing with dilute hydrochloric acid.

The form of the condensed silica depends of course on the more or less rapid refrigeration of the vapour. This process must not be too rapid if we wish to obtain numerous spherules of silica.

This silica is very soluble in hydrofluoric acid. It dissolves in the cold with a slight rustling noise. It is readily attacked by melting potassium hydrate and by alkaline carbonates. Its sp. gr. is 2.4, *i. e.*, a little lower than that of rock crystal. The spherules scratch glass with ease.

On studying the deposit formed in glass globes in which the electric arc has been caused to play for lighting, we have found small globules of silica identical with those just described. The opalescence of glass globes in which the arc has been in action for some time is therefore due to the volatilisation of silica. This silica is derived from the impurities of the electric carbons.

We will add that silica at this temperature is easily

reduced by carbon, and yields a crystalline silicon carbide which we are further examining.—*Comptes Rendus*, cxvi., p. 1222.

ON AMIDOPHOSPHORIC ACID.\*

By H. N. STOKES.  
(Continued from p. 11).



This is prepared by boiling the ether ten minutes with strong caustic soda, cooling and acidifying with acetic acid. It separates at once without adding alcohol as a crystalline powder, which is washed with dilute alcohol, dissolved in ammonia, and re-precipitated by acetic acid or carbon dioxide. It forms a heavy sandy powder, consisting of well-defined crystals belonging to the hexagonal system, occurring sometimes as hexagonal plates or prisms without pyramids, occasionally as very symmetrical double pyramids without prism surfaces. It is scarcely soluble in cold water, insoluble in alcohol. If boiled with water it dissolves, and is at once converted into acid sodium ammonium phosphate; the same change occurs slowly at ordinary temperature under water. Like all other amidophosphates, it is instantly converted into phosphoric acid by warm dilute acids. On ignition it loses ammonia, and leaves a vitreous residue of sodium hexametaphosphate. It contains small but varying amounts of water. The analysis of one preparation gave—

	Calculated for $\text{PO} \cdot \text{NH}_2 \cdot \text{ONa} \cdot \text{OH} + \frac{1}{2}\text{H}_2\text{O}$ .	Found.	
P	25.11	25.08	
N	11.36	11.49	11.34
Residue ( $\text{NaPO}_3$ )	82.54	82.43	

Other samples contained less water. This water is accounted for in part by the presence of a small amount of acid sodium ammonium phosphate; but the latter, when determined as in the acid potassium salt, was found to be only 2 to 2.5 per cent, while the whole amount of water present, if assumed to be in the form of ammonium salt, would make the amount 16.8 per cent. The water is therefore present mainly as such. It does not act on the amido group at 100°, as the quantity of ammonia expelled by alkali after heating at this temperature is not increased, and there is no loss of weight. At 150° it reacts, converting a portion of amide into ammonium salt, which at the same time loses ammonia, the residue being found to contain less nitrogen. The acid sodium salt dissolves rather difficultly in excess of ammonia, probably forming the sodium ammonium salt; from this solution it is re-precipitated by carbon dioxide, or even by expelling the ammonia by an air current or spontaneous evaporation. In this respect it resembles the neutral phosphates containing ammonia.

Neutral sodium amidophosphate,  $\text{PO} \begin{matrix} \text{NH}_2 \\ \text{O} \end{matrix} (\text{ONa})_2$ , is readily made by treating caustic soda solution with excess of acid salt, the excess remaining undissolved. It forms bunches of needles or prisms, extremely soluble in water, but not deliquescent. By the action of carbon dioxide, even that in the air, it is decomposed into acid salt and sodium carbonate. Alcohol precipitates it as a syrup from aqueous solution.

Acid lithium amidophosphate is precipitated by lithium chloride from a strong solution of the acid potassium salt, in the form of difficultly soluble crystalline granules. On boiling it is converted into phosphates of lithium.

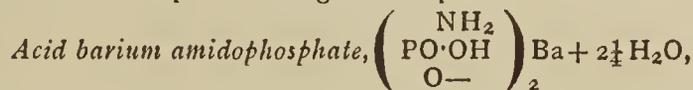
Acid ammonium amidophosphate is formed by decomposing either the acid or neutral silver salt with ammo-

onium sulphide and precipitating by alcohol. It forms a beautiful network of needles, crossing at angles of 60°, and is very soluble in water and permanent in the air. As it is formed by precipitating an ammoniacal solution by alcohol, it appears that the neutral salt is very unstable, if capable of existence.

Potassium ammonium amidophosphate is precipitated by alcohol from an ammoniacal solution of the acid potassium salt as a syrup, which is decomposed by washing with alcohol into acid potassium salt and ammonia.

Acid hydroxylamine amidophosphate, obtained by precipitating a moderately strong solution of the acid potassium salt with hydroxylamine hydrochlorate, is difficultly soluble in water, and forms brilliant rhombic plates and prisms. Its crystallising power is greater than that of any other salt obtained. A neutral salt could not be prepared.

The preparation of salts of the earths and heavy metals from the acid potassium salt is interfered with by the latter being contaminated with a small amount of phosphate. The contamination of the precipitate in the case of the salts is best avoided by adding to the ice-cold solution of the acid potassium salt, before precipitation, a very little dilute nitric acid, which effectively holds all phosphate in solution. In making neutral salts it is not so easy to get rid of the phosphate; the ways in which this was accomplished are given in special cases below.

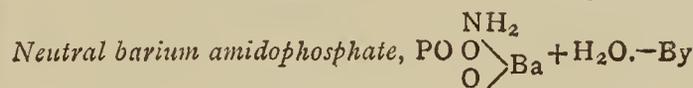


is obtained by adding to an ice-cold solution of acid potassium salt, faintly acidified with nitric acid, barium chloride in excess. It thus forms a supersaturated solution, which crystallises only on rubbing with a glass rod. The precipitate is washed with a little water and alcohol. It forms groups of radiating microscopic plates, and once formed is quite difficultly soluble in water. On boiling its solution, a scaly crystalline precipitate of acid barium phosphate,  $\text{BaHPO}_4$ , at once forms. It contains about 2½ mols. crystal water, the greater part of which is lost at 100°; but this cannot be directly determined, owing to its tendency to pass into ammonium salt with loss of ammonia. On ignition it fuses to a glass of barium hexameta-phosphate.

	Calculated for $\text{Ba}(\text{PO}_3\text{NH}_2)_2 + 2\frac{1}{2}\text{H}_2\text{O}$ .	Found.
Loss ( $2\text{NH}_3 + \text{H}_2\text{O}$ )	20.17	19.82

The residue gave—

	Calculated for $\text{Ba}(\text{PO}_3)_2$ .	Found.
Ba	46.43	47.12
P	21.03	21.38



mixing a dilute solution of acid potassium salt with ammoniacal barium chloride solution, and filtering quickly from the small amorphous precipitate of barium phosphate, the salt soon crystallises. It forms very characteristic hard and brittle rhombic plates, often with truncated angles, often superposed in coincident or partly turned position, sometimes also as fine prisms with many sharply defined faces. It is unchanged at 100°, but at 150° the crystal water is taken up to form ammonium salt, which at once loses ammonia, forming acid barium phosphate, which on ignition leaves a residue of pyrophosphate, giving off but little ammonia.

	Calculated for $\text{PO} \begin{matrix} \text{NH}_2 \\ \text{O} \end{matrix} \text{Ba} + \text{H}_2\text{O}$ .	Found.
Loss of 1 mol. $\text{NH}_3$ at 150°	6.80	6.84
Total loss on ignition, $\text{NH}_3 + \frac{1}{2}\text{H}_2\text{O}$	10.40	10.70

\* American Chemical Journal, vol. xv., No. 3.

The residue gave—

	Calculated for Ba <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	Found.
Ba	61.17	61.80
P	13.84	14.44

The salt is very difficultly soluble in water. Its solution, or the liquid from which it has not yet crystallised, gives on boiling, even in the presence of an excess of ammoniacal barium chloride, a scaly precipitate of acid barium phosphate.

	Calculated for BaHPO <sub>4</sub> .	Found.
Loss on ignition $\frac{1}{2}$ H <sub>2</sub> O	3.86	4.65

The residue gave—

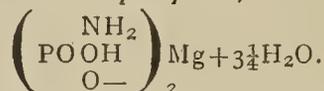
	Calculated for Ba <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	Found.
Ba	61.16	61.76

The salt shows a peculiar behaviour when formed in the presence of strong ammonia. By mixing a solution of the acid potassium salt with strongly ammoniacal barium chloride, an amorphous precipitate is formed, which dissolves (excepting traces of phosphate) on adding water. Strong ammonia re-precipitates it, and more water dissolves it; this process may be repeated several times. The solution soon deposits crystals of the neutral salt, and the precipitate itself soon turns to scales of the same substance. Filtered off and washed with ammonia, it gave on analysis figures corresponding to those of the neutral salt.

*Acid calcium amidophosphate*, obtained like the barium salt, is much less soluble than the latter, and forms spherical aggregations of needles.

*Neutral calcium amidophosphate* is formed like the neutral barium salt, but is much less soluble. Its crystallising power is also much less. From very dilute solutions it separates gradually in the form of microscopic groups of flat-pointed prisms; from concentrated solutions as an amorphous precipitate which does not become crystalline, while from solutions of intermediate strength it is at first amorphous, but gradually becomes crystalline.

*Acid magnesium amidophosphate*,—



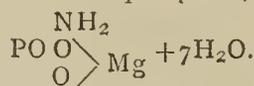
On mixing an ice-cold strong solution of acid potassium salt, acidified slightly with nitric acid, with magnesium chloride, nothing separates, even after many hours. On rubbing with a glass rod, crystallisation starts at once. Once separated it is almost insoluble in water, and forms microscopic granules consisting of radiating needles or prisms. It is insoluble in ammonium chloride. At 100° it retains 2 mols. water; on ignition it gives off ammonia and water, and leaves magnesium metaphosphate.

	Calculated for Mg(PO <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> + 3 $\frac{1}{2}$ H <sub>2</sub> O.	Found.
Loss (2NH <sub>3</sub> + 3 $\frac{1}{2}$ H <sub>2</sub> O)	33.71	33.86

The residue gave—

	Calculated for Mg(PO <sub>3</sub> ) <sub>2</sub> .	Found.
Mg	13.18	12.85
P	34.10	33.88

*Neutral magnesium amidophosphate*,—



This salt has the same empirical composition as crystallised ammonium magnesium phosphate,—



but differs entirely in its properties. It forms at once on adding magnesia mixture to a solution of acid potassium salt, or, better, by precipitating neutral sodium salt with a magnesium salt. Any phosphoric acid present is first thrown down by a little of the precipitant, either as magnesium or magnesium ammonium phosphate; even when phosphoric acid is in excess it is completely thrown down

by magnesia mixture before any amidophosphate forms, and the change can easily be followed by observing the crystals under the microscope. From solutions containing ammonium chloride (as when magnesia mixture is used) it crystallises in very characteristic plates, often nearly rectangular, but more frequently with truncated angles, forming oblong octagonal plates. In the absence of ammonium salts it forms thick prisms, in either case easily distinguishable from ammonium magnesium phosphate. It is difficultly but perceptibly soluble in water, and quite readily in dilute ammonium chloride solution, and may be separated from any accompanying ammonium magnesium phosphate in this way. From its aqueous solution ammonia precipitates magnesium hydroxide. On boiling its aqueous solution, ammonium magnesium phosphate is at once formed. It dissolves in acetic acid; from its solution in nitric acid, alcohol precipitates acid salt. Even when free from ammonium salt, caustic potash causes more or less evolution of ammonia in the cold. Over sulphuric acid it quickly loses most of its crystal water, but the last two or three molecules are given off very slowly, and constant weight could not be obtained. At 100° it loses somewhat more than 5 mols., but this cannot be accurately determined, as at this temperature partial decomposition of the amide with loss of ammonia occurs, as shown by analysis of the residue. On ignition it leaves magnesium pyrophosphate.

	Calculated for MgPO <sub>3</sub> NH <sub>2</sub> + 7H <sub>2</sub> O.	Found.
P	12.67	12.59
N	5.73	6.53
Mg	9.79	9.77
Loss on ignition	54.70	54.79

*Acid manganese amidophosphate*, prepared like the acid magnesium salt, forms faintly pinkish microscopic crystals, or granular and lenticular forms. It contains crystal water, is difficultly soluble, and shows no tendency to form supersaturated solutions.

*Neutral manganese amidophosphate*, from the neutral sodium salt, is an amorphous white precipitate.

*Acid zinc amidophosphate* is difficultly soluble in water; soluble in acetic acid and in ammonia. It crystallises readily in small but finely-formed rhombic prisms with pyramids, or in hexagonal plates.

*Neutral zinc amidophosphate* is an amorphous white precipitate, perceptibly soluble in water. Both salts are converted into phosphate by boiling.

*Cobalt amidophosphates*. The *acid* salt forms readily from the acid potassium salt with a cobalt salt, after adding a drop of nitric acid. It is difficultly soluble in water; soluble in ammonia, and forms pink granules. The *neutral* salt is an amorphous pink precipitate.

*Nickel amidophosphates*. The *acid* salt has a great tendency to supersaturation, and can only with great difficulty be made to crystallise. Once formed, it consists of minute crystalline granules, difficultly soluble in water. The *neutral* salt is an amorphous, nearly colourless precipitate, soluble in acetic acid and in ammonia.

*Ferrous amidophosphates*. The *acid* salt, formed as above, crystallises very readily in nearly colourless microscopic crystals, apparently of the regular system, and consisting of the dodekahedron or combinations of cube and octahedron. It is nearly insoluble in water or ammonium chloride; soluble in ammonia. The *neutral* salt is a dirty greenish, amorphous precipitate, soluble in much water, in acetic acid, and in ammonia.

*Ferric amidophosphates*. Both acid and neutral alkali salts give, with a neutral solution of ferric chloride, white, amorphous precipitates, soluble in excess of amidophosphate and in ammonia, insoluble in acetic acid.

*Aluminium amidophosphate*. Neutral sodium salt gives, with alum, a white, amorphous precipitate, completely soluble in ammonia.

*Chromic amidophosphate*, from neutral sodium salt, is

a very nearly colourless amorphous precipitate, soluble in ammonia on warming.

*Cupric amidophosphates.* The acid salt crystallises in rosettes and dumb-bell-like forms, nearly insoluble in water. The neutral salt is an amorphous precipitate, slightly soluble in water, and converted into phosphate by boiling.

*Mercuric amidophosphates.* Neither acid nor neutral salts are precipitated by mercuric chloride. On boiling, mercuric phosphate is formed.

*Cadmium amidophosphates.* By mixing solutions of acid potassium amidophosphate and cadmium chloride, crystalline precipitates somewhat soluble in water are obtained. These differ in form according as one or the other reagent is in excess; with excess of cadmium chloride a double salt is formed, which gives off ammonium chloride on heating.

*Lead amidophosphate.* Acid potassium salt and lead acetate give a precipitate consisting of groups of radiating plates, slightly soluble in water, presumably acid salt.

(To be continued).

### THE DEPOSITS OF NATIVE SODA, NEAR LARAMIE, WYOMING.\*

By H. PEMBERTON, Jun., and GEO. P. TUCKER.

PREVIOUS to the Civil War, and at a time when the line of civilisation extended as far only as the Mississippi River, very little was known of the part of the United States west of that limit. A vast region now comprising many large States was described in the geographies of the day as "the great American Desert." It constituted a part of the prairies or plains, so often mentioned in Cooper's novels. And while the prairies, as a general rule (and particularly in elevations not much above sea-level), are composed of a fertile and rich soil, their character changes as the approach is made to the Rocky Mountains, and when an elevation of 7000 feet is reached, as in Wyoming, the soil and climate resemble somewhat the soil and climate of Nevada and other parts of the Great Basin. On this high Wyoming plateau, particularly in the neighbourhood of the town of Laramie, one drives for miles over a perfectly flat country, with nothing but some distant hills to break the wide circle of the horizon—not even a single tree. A little thin grass grows in the gravelly soil, but no other form of vegetation, except when aided by irrigation. The region is nearly rainless, the relative humidity quite low, and all conditions favourable to the formation of the saline deposits peculiar to this portion of the United States.

About fourteen miles south-west of Laramie, there exists a deposit of sulphate of soda; such deposits are locally known as "lakes." The deposit in question is composed of three of these lakes lying within a stone's throw of one another. They have a total area of about sixty-five acres, the local names of the three being the Big Lake, the Track Lake, and the Red Lake. They are the property of the Union Pacific Railroad Company, are connected by a branch of that road with the main line at Laramie, and are generally known as the Union Pacific lakes.

In these lakes the sulphate of soda occurs in two bodies or layers. The lower part constituting the great bulk of the deposit, is a mass of crystals of a faint greenish colour, mixed with a considerable amount of black slimy mud. It is known as the "solid soda." We give an analysis of this below.

This solid soda is stated to have a depth of some 20 or 30 feet. Borings were made a number of years ago under the direction of the Union Pacific Railroad agents, but all

*Analysis of Solid Soda immediately under the Top Layer of White Sulphate of Soda on Red Lake and Track Lake (U. P. Lakes).*

	Anhydrous. Per cent.	Crystallised. Per cent.
Na <sub>2</sub> SO <sub>4</sub> .. .. .	36.00	81.63
CaSO <sub>4</sub> .. .. .	1.45	1.82
MgCl <sub>2</sub> .. .. .	0.77	1.64
NaCl .. .. .	0.21	0.21
	38.43	85.30
Insoluble residue (at 100° C.)		13.86
		99.16

Total chloride calculated as NaCl = 1.16 per cent.  
This calculated on 100 parts anhydrous: Na<sub>2</sub>SO<sub>4</sub> equals 3.22 per cent NaCl.

attempts to obtain the results of the same were futile, as the records have been mislaid or lost. There is nothing to prove that the depth is not shallower than stated above.

Above the solid soda occurs the superficial layer of *pure white crystallised sulphate of soda*. This is formed by solution in water of the upper part of the lower body—the crystals being deposited by evaporation or by cooling, or by the two combined. A little rain in the spring and autumn furnishes this water, as do also innumerable small sluggishly flowing springs present in all the lakes. But on account of the dry air of this arid region, the surface is generally dry or nearly so, and in midsummer the white clouds of efflorescent sulphate that are whirled up by the ever-blowing winds of Wyoming can be seen for miles. Even should there be a little water present, there is no difficulty in gathering the crystals by the train-load. The spring, however, is the worst season of the year, on account of the warm weather and of the rains—conditions unfavourable to the formation of crystals. The layer of this white sulphate is from 3 to 12 inches in thickness. When the crystals are removed, the part laid bare is soon replenished by a new crop.

The following is an analysis of the purest of this white sulphate of soda, calculated upon an anhydrous basis; that being the condition, of course, in which it would be used:—

Na <sub>2</sub> SO <sub>4</sub> .. .. .	99.73
MgCl <sub>2</sub> .. .. .	0.26
Insoluble .. .. .	trace
	99.99

Several hundred tons of this have been shipped by the railroad to the works at Laramie City. The plant there for dehydrating the crystals is not of the best, and the long exposure to the dust and smoke of the fire gases in the evaporation—and again in the calcining—introduces more or less impurity into the finished calcined sulphate of soda. The following is an analysis of the latter:—

Finished calcined sulphate of soda. (From U. P. Lakes).	
Na <sub>2</sub> SO <sub>4</sub> .. .. .	95.80
CaSO <sub>4</sub> .. .. .	0.76
NaCl .. .. .	1.84
Ignition .. .. .	0.19
SiO <sub>2</sub> .. .. .	1.48
Fe <sub>2</sub> O <sub>3</sub> .. .. .	0.06
Al <sub>2</sub> O <sub>3</sub> .. .. .	0.31
CaO .. .. .	0.20
MgO .. .. .	0.44
	101.08

This analysis represents the general run of the sulphate, as manufactured in Laramie. The sample was taken from a carload lot sold to the Wyoming Glass Company.

\* Read before the Chemical Section of the Franklin Institute.

It contains only a trace of iron, and, of course, no free acid.

At the time when we examined these lakes, in 1888, they were entirely under water. An irrigating canal—or "ditch"—had been located within a half mile of them, the water from which had gradually collected to the extent of several feet in the lakes. The course of the canal has since been changed, and the lakes are again in about their normal condition.

Samples of this water were collected by us, and analysed as giving a very fair idea of the average composition of the deposits. The ingredients are calculated to the anhydrous condition. The last item, it will be noticed, is given as anhydrous borax,  $\text{Na}_2\text{B}_4\text{O}_7$ . It represents the results of titration with standard acid, using methyl-orange as an indicator. It may be noted that, on account of the lime salts present in solution, alkaline carbonates and phosphates must be absent, and direct test proved the absence of soluble silicates. We have noticed the same titration reaction (if we may so call it) in a sample of sulphate of soda from a deposit near Rawlins, Wyoming, and, in general, it may be stated that the character of the climate, soil, and formation in Wyoming is very similar to that of such parts of the Pacific Slope as are known to contain deposits of borax.

*Water from Big Lake (U. P. Lakes).*

Density =  $9\frac{1}{4}^\circ$  Tw. (= 1.0487 sp. gr.).

10 c.c. contains:—

	Grms.	Per cent.
$\text{Na}_2\text{SO}_4$ .. .. .	0.4490	= 81.43
$\text{CaSO}_4$ .. .. .	0.0175	= 3.17
$\text{MgSO}_4$ .. .. .	0.0060	= 1.09
$\text{MgCl}_2$ .. .. .	0.0643	= 11.66
$\text{Na}_2\text{B}_4\text{O}_7?$ .. .. .	0.0146	= 2.65

Total solids .. .. . 0.5514 100.00  
(Total solids by evaporation 0.5417)

One cubic foot contains  $6\frac{3}{10}\%$  pounds of pure crystallised sulphate of soda.

*Water from Track Lake (U. P. Lakes).*

Density =  $14\frac{1}{2}^\circ$  Tw. (= 1.0725 sp. gr.).

10 c.c. contains:—

	Grms.	Per cent.
$\text{Na}_2\text{SO}_4$ .. .. .	0.7563	= 92.23
$\text{CaSO}_4$ .. .. .	0.0146	= 1.79
$\text{MgSO}_4$ .. .. .	0.0070	= 0.85
$\text{MgCl}_2$ .. .. .	0.0300	= 3.66
$\text{Na}_2\text{B}_4\text{O}_7?$ .. .. .	0.0121	= 1.47

Total solids .. .. . 0.8200 100.00  
Total solids by evaporation 0.8240

One cubic foot of this water contains  $10\frac{7}{10}\%$  pounds of pure crystallised sulphate of soda.

*Water from Red Lake (U. P. Lakes).*

Density =  $17\frac{3}{4}^\circ$  Tw. (= 1.0887 sp. gr.).

10 c.c. contains:—

	Grms.	Per cent.
$\text{Na}_2\text{SO}_4$ .. .. .	0.9307	= 91.77
$\text{CaSO}_4$ .. .. .	0.0201	= 1.98
$\text{MgSO}_4$ .. .. .	0.0143	= 1.41
$\text{MgCl}_2$ .. .. .	0.0416	= 4.10
$\text{Na}_2\text{B}_4\text{O}_7?$ .. .. .	0.0075	= 0.74

Total solids .. .. . 1.0142 100.00  
Total solids by evaporation 1.0320

One cubic foot of this water contains  $13\frac{1}{10}\%$  pounds of pure crystallised sulphate of soda.

We give, also, below analysis of sulphate of soda from lakes controlled by Col. S. W. Downey, of Laramie. Of these deposits we know but little other than that they are

situated about twenty-five miles south-west of Laramie, and, as indicated by the analyses, are contaminated by lime and magnesia salts to a considerable degree. Both analyses were made on samples previously calcined.

	S. W. Downey's Wilcox Lake.	S. W. Downey's Red Soda.
$\text{Na}_2\text{SO}_4$ .. .. .	43.12	69.55
$\text{MgSO}_4$ .. .. .	41.70	6.75
$\text{CaSO}_4$ .. .. .	—	11.24
$\text{NaCl}$ .. .. .	0.20	1.01
Ignition .. .. .	0.32	0.33
Insoluble .. .. .	16.15	10.50
	101.49	99.38

From a commercial standpoint these Wyoming deposits are interesting, inasmuch as they furnish cheaply and in large quantities quite a pure grade of sulphate of soda. This sulphate being free from iron, and also, of course, from free acid, is well adapted to use in the manufacture of glass. Freight rates from the East are in its favour, and allow a price that should yield a fair profit. Attempts have been made at Laramie on quite an elaborate scale, to manufacture soda-ash and caustic by the Leblanc process. These efforts were not remunerative.

## THE EFFECT OF DECOMPOSING ORGANIC MATTER ON NATURAL PHOSPHATES.

By Dr. N. T. LUPTON.

DURING the past two years especial attention has been called to the fertilising value of natural or raw phosphates, when applied alone in the form of floats and when mixed with organic matter, such as cotton-seed and cotton-seed meal.

If floats can be shown to produce as good results as acidulated phosphates, which is claimed by some, the cost of commercial fertilisers ought to be greatly reduced, and the extensive deposits of soft aluminous phosphates found in Florida and elsewhere find a ready sale. While the results of experiments are somewhat conflicting, there appear to be conditions under which floats, or ground raw phosphates, do produce as good, if not better, results than acid phosphates. The presence of decomposing organic matter is generally regarded as one of these conditions, but chemists are not agreed as to the precise nature of its action.

Liebig, in his letters on "Modern Agriculture," published in 1859, advances the theory that organic matter undergoing decay accumulates carbonic acid in the soil, and when rain falls it dissolves the carbonic acid, and thereby acquires the power of taking up phosphate of lime. This carbonic acid water does not withdraw from the soil the phosphate of lime contained in it, but wherever it meets with the granules of apatite or phosphorite, it dissolves a certain portion. Under these circumstances a solution of phosphate of lime must consequently be formed, which spreads in all directions around each granule. Wherever this solution comes in contact with soil not already saturated with phosphate of lime, the soil will take up and retain a certain portion of this salt. The portion of soil now saturated with phosphate will oppose no further obstacle to the wider diffusion of the solution.

Voelcker (*Bied. Centr.*, 1880, 866, 867), as quoted in the *Journal of the Chemical Society*, xxiv., Second Series, p. 640, draws the following conclusions:—

1. Phosphates are not readily taken up by plants in a soluble form, but must be returned to an insoluble condition before they yield their useful properties.

2. The efficacy of insoluble calcium phosphate corresponds with the minuteness of division in which it is found in a fertiliser.

3. The finer the particles in a phosphatic material, the more energetic its action as a manure.

Fleischer and Kissling (*Bied. Centr.*, 1883, 155, 161), on the application of insoluble phosphates to soils, found that the action of moorland soils when mixed with insoluble phosphates is to render a portion of the phosphate soluble in water, amounting to 5.5 per cent in one case of the total phosphoric acid; a portion at the same time was reduced to the di-calcium salt, and in one compost heap as much as 17 per cent of the total acid was brought into this form.

The general outcome of their experiments is that it is more advantageous to apply insoluble phosphate than superphosphate on humous soils, as they are capable of bringing insoluble phosphate into a soluble condition. This applies, however, only to peaty soils, as the presence of lime hinders this action.

In the *Journ. Chem. Soc.*, xxx., p. 774, is an abstract of an article from the *Journal of the Royal Agricultural Society*, 1884, by Dyer, which states that the first experiments made in 1882 in a stiff clay soil containing no calcium carbonate, ground and unground coprolites were used. The comparison was made with swedes both with and without manure; in each case the better result was from the undissolved phosphate. On the same plots, the following year, oats were grown without further addition of manure, and the produce was again, on an average, better where the undissolved phosphate had been employed. The following year 225 bushels of lime per acre were ploughed in before sowing. The same quantities of manure were applied as before. The season was dry and the crop small, but in this case the produce was better where the dissolved phosphate had been used. The ground coprolite contained more than twice as much phosphoric acid as the superphosphate.

Coming nearer home we find that experiments made at the Alabama Agricultural Station are of similar import.

In *Bulletin No. 22*, new series, January, 1891, we find the following statement:—"In several experiments previously conducted to ascertain the comparative agricultural value of the phosphate rock ground to impalpable powder, known as floats, with that of acidulated phosphate, the results have indicated that, used in conjunction with cotton-seed meal, floats are more profitable than the acid phosphate, taking into consideration the fact that floats contain nearly twice the percentage of phosphoric acid.

The soil used in these experiments was sandy drift that had been lying out many years. No commercial fertiliser had been previously applied to it."

To test more thoroughly the comparative productiveness of ground raw phosphate and acid phosphate under different conditions, and to determine whether decomposing organic matter converts insoluble into soluble phosphate, two sets of experiments were carried out, one on the farm and the other in the chemical laboratory, the results of which will now be given.

The materials used were carefully analysed by Dr. Anderson, assistant chemist, with the following results:—

The acid phosphate used gave—

Water-soluble phosphoric acid (P <sub>2</sub> O <sub>5</sub> ) ..	9.10	per cent.
Citrate-soluble ..	2.94	"
Acid-soluble ..	2.32	"
<hr/>		
Total phosphoric acid (P <sub>2</sub> O <sub>5</sub> ) .. ..	14.36	"

The Florida phosphate reduced to a fine powder, similar to floats, gave—

Moisture .. .. .	4.18
Insoluble matter .. .. .	32.39
Total phosphoric acid (acid-soluble)	16.54
Iron and aluminium oxides .. .. .	8.89

None of the lime phosphate was soluble in water, and only 0.32 was soluble in ammonium citrate. The analysis

shows an inferior grade of raw phosphate. The material purchased as "South Carolina floats" contained 2.26 per cent of available phosphoric acid in the form of citrate-soluble acid, and a total phosphoric acid of 28.73 per cent. The available phosphoric acid in each of the materials used in the experiments may be stated as follows:—

1. Cotton-seed meal, available acid (P <sub>2</sub> O <sub>5</sub> )	3.19	per cent.
2. Cotton-seed, .. .. .	1.03	"
3. Florida raw phosphate, .. .. .	0.32	"
4. South Carolina floats, .. .. .	2.26	"
5. Acid phosphate, .. .. .	12.04	"

Two qualities of land were selected at the station for the field experiments, one a strong red soil, the other a poor sandy soil. The results obtained were as follows; on the poor soil the fertilisers were sown broadcast:—

	Lbs. seed cotton per acre.
No. 1. 400 lbs. pulverised Florida phosphate ..	290.5
" 2. 800 .. .. .	219.8
" 3. 400 .. acid phosphate .. .. .	196.7
" 4. 800 .. .. .	144.2
" 5. No fertiliser .. .. .	106.4
" 6. 400 lbs. Florida phosphate with 400 lbs. cotton-seed meal .. .. .	249.2
" 7. 800 lbs. Florida phosphate with 800 lbs. cotton-seed meal .. .. .	322.7
" 8. 400 lbs. acid phosphate with 400 lbs. cotton-seed meal .. .. .	252.0
" 9. 800 lbs. acid phosphate with 800 lbs. cotton-seed meal .. .. .	320.6
" 10. No fertiliser .. .. .	233.8

Each plot was one-seventh of an acre, and the usual precautions were taken to remove disturbing elements and have the conditions of cultivation and growth as uniform as possible. The details of the work were under the immediate supervision of Mr. Clayton, assistant agriculturist. On the strong red soil the fertilisers were applied in the drill with results as follows:—

	Lbs. seed cotton per acre.
No. 1. 200 lbs. Florida phosphate with 200 lbs. cotton-seed meal .. .. .	1016.6
" 2. 400 lbs. Florida phosphate with 400 lbs. cotton-seed meal .. .. .	1105.6
" 3. 200 lbs. acid phosphate with 200 lbs. cotton-seed meal .. .. .	844.8
" 4. 400 lbs. acid phosphate with 400 lbs. cotton-seed meal .. .. .	1108.8
" 5. No fertiliser .. .. .	863.2
" 6. 200 lbs. Florida phosphate with 400 lbs. cotton-seed .. .. .	919.2
" 7. 400 lbs. Florida phosphate with 800 lbs. cotton-seed .. .. .	1182.4
" 8. 200 lbs. acid phosphate with 400 lbs. cotton-seed .. .. .	1178.4
" 9. 400 lbs. acid phosphate with 800 lbs. cotton-seed .. .. .	1387.2
" 10. No fertiliser .. .. .	931.2
" 11. 400 lbs. Florida phosphate .. .. .	892.8
" 12. 400 lbs. acid phosphate .. .. .	975.2
" 13. 400 lbs. cotton-seed meal .. .. .	1271.2
" 14. 800 lbs. cotton-seed .. .. .	1294.4

The land was not uniform in natural productiveness, but improved in quality from the first to the last plot. While the results are not perfectly uniform the pulverised raw phosphate evidently produced as good, if not better, results than the acid phosphate, whether used alone or mixed with cotton-seed and cotton-seed meal.

Anticipating these results, experiments were carried on in the laboratory during the summer to determine whether they are due to the fact that decomposing organic matter

converts insoluble or acid-soluble lime phosphate into the available or citrate-soluble condition. For this purpose half-gallon wide-mouthed glass jars were used, and the following mixtures placed in each:—

No. 1. 2 lbs. Florida phosphate with  $\frac{1}{2}$  lb. cotton-seed meal.

No. 2. 1 lb. Florida phosphate with  $\frac{1}{2}$  lb. cotton-seed meal.

No. 3. 2 lbs. South Carolina floats with  $\frac{1}{2}$  lb. cotton-seed meal.

No. 4. 1 lb. South Carolina floats with  $\frac{1}{2}$  lb. cotton-seed meal.

No. 5. 2 lbs. Florida phosphate with  $\frac{1}{2}$  lb. cotton-seed.

No. 6. 1 lb. Florida phosphate with  $\frac{1}{2}$  lb. cotton-seed.

No. 7. 2 lbs. South Carolina floats with  $\frac{1}{2}$  lb. cotton-seed.

No. 8. 1 lb. South Carolina floats with  $\frac{1}{2}$  lb. cotton-seed.

The contents of each jar were rubbed up in a porcelain mortar moistened with water, and mixed as thoroughly as possible. The mixtures were stirred frequently, in fact nearly every day. Fermentation began within a day or two, and continued during the whole period of the experiments. Samples for analysis, that is, for the determination of available phosphoric acid, were taken from the jars and analysed, with results as follows:—

Date of taking sample.	Per cent of available P <sub>2</sub> O <sub>5</sub> found.							
	1.	2.	3.	4.	5.	6.	7.	8.
July 2.	0.99	1.69	2.68	3.04	0.58	0.54	2.77	—
„ 9.	1.25	1.62	2.89	2.64	0.72	0.95	2.33	2.27
„ 16.	1.25	1.61	2.89	2.82	0.72	0.80	2.29	2.26
„ 23.	1.16	1.80	3.37	3.22	0.84	0.49	2.37	2.39
„ 30.	1.12	1.60	3.02	3.38	0.72	0.53	1.81	2.70
Aug. 6.	1.41	1.79	2.87	3.15	0.82	1.08	2.49	2.57
„ 20.	1.41	1.57	2.73	3.26	0.81	1.00	2.15	2.53
Sept. 3.	1.50	2.16	2.75	3.27	1.16	1.10	1.96	2.51
„ 17.	1.41	1.75	2.56	2.91	1.07	0.89	2.04	2.32
Oct. 1.	—	2.28	2.97	3.14	0.99	1.26	2.57	2.51

The above results seem to show that the fermentation of the cotton-seed and cotton-seed meal had very little, if any, effect on the Florida ground phosphate or the South Carolina floats in converting the insoluble into soluble phosphate. The slight variation in the results, though favouring to some extent the conclusion that there is a slight increase in the available phosphoric acid, may be accounted for on the ground of personal error or the want of uniformity in the mixing of the materials, since it is difficult, if not impossible, to secure perfect uniformity in a mixture of ground phosphate and cotton-seed.—*Journ. Amer. Chem. Soc.*, xiv., No. 10.

## NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.\*

By Lieut.-General C. A. McMAHON, F.G.S.

### PART I.—General Remarks.

ALL petrologists who have worked much with the microscope must have felt the want of a system of micro-chemical analysis at once simple and reliable. Having devoted some time to the study of micro-chemical reactions, I think it may save the time and labour of students who propose to take up the subject if I give them the result of the experience I have gained up to date.

In order to shorten this paper as far as possible, I have limited myself to the bases that commonly enter into the composition of rock-making minerals, and have excluded those which relate to ores.

Micro-chemical analysis is not only an essential adjunct to micro-petrological research, but it is capable of rendering some aid to the ordinary chemist. Not only does it afford a ready means of testing precipitates, but it is even more essential as a method for testing the purity of reagents.

Until I took up this inquiry I had no idea of the extent to which the reagents supplied by some good firms contain chemical impurities. I was astonished to find, for instance, that my bichloride of platinum invariably showed the presence of potash in every mineral I tested with it; that my fluosilicic acid always indicated the existence of an appreciable amount of soda; and my aluminium sulphate, delusively labelled "purified," contained so much potash that it crystallised on my glass slides as an alum. I mention these cases as mere illustrations. I have succeeded in obtaining some chemicals sufficiently pure to work with; but in other cases I have failed to do so. Pure uranium acetate, for instance, is said to belong to the rhombic system, and to crystallise in long prisms; but though I have had uranium acetate specially made for me, all that I have obtained crystallises in the cubic system in forms identical with those of the double salt of acetate of sodium and uranium. As a test for soda, therefore, by the microscopic method, it is worse than useless.

In micro-chemical analysis I have found the following system the most convenient to pursue. I convert the bases present in the minerals under examination into sulphates,\* and, with one or two exceptions to be noted further on, work with these sulphates in aqueous solution without the aid of heat. There is considerable advantage, it seems to me, in working with salts in the form of sulphates; most of them are soluble in water; they are all insoluble in absolute alcohol, and Canada balsam diluted with benzole or chloroform does not corrode them. Scarcely any of those entered in Part II. are deliquescent; whilst the alums are the only ones that crystallise in the cubic system.

All the sulphates can be mounted in Canada balsam with the greatest ease, and preserved for any number of years for future study. The microscopist therefore can dispense with the aid of figured illustrations; he can form, what is far better, an imperishable collection of typical specimens of the salts themselves to be always at hand for ready reference.

Other salts besides the sulphates can be mounted in Canada balsam, but the mounting and preservation of some of them are extremely difficult. Many of the chlorides, for instance, deliquesce, rendering the use of heat in some form necessary; many are corroded by Canada balsam; and many crystallise in the cubic system, rendering their identification more difficult. Potassium chloride, for instance, cannot be distinguished from sodium chloride under the microscope.

Having obtained a solution of a sulphate, or a mixture of sulphates, I place a drop of the solution on a glass slide and allow it to evaporate spontaneously in a place free from wind, draught, or dust. I find a shelf in a glass book-case a suitable place. Five or six slides should be prepared at the same time. The next day two or three of the most perfect of these should be selected for mounting, but it is material to preserve an unmounted specimen for subsequent comparison with the mounted

\* Silicates, insoluble in sulphuric but soluble in hydrofluoric acid, I convert into sulphates by dissolving them in a state of fine powder in hydrofluoric acid, in a platinum vessel, with the aid of heat. I then add sufficient sulphuric acid to convert the bases into sulphates. On evaporation to dryness the silica is driven off in the form of fluosilicic acid, and the sulphates are left behind. These can now be dissolved in water, or, in the case of barium or strontium, in hot sulphuric acid. A similar process can be used to test the purity of the hydrofluoric acid employed, viz., add concentrated sulphuric acid to the HF aq. and evaporate to dryness. If the HF contains bases in any appreciable quantity they will be left behind as sulphates, and may be detected under the microscope. In the case of minerals not soluble in hydrofluoric acid they must be decomposed by fusion with carbonate of soda or some other flux. See *Zircon*, Part III.

\* *Mineralogical Magazine*, vol. x., No. 46, p. 79.

ones. The unmounted slide enables us to observe whether the salt effloresces, deliquesces, becomes opalescent, or has a silky lustre. Information regarding its refraction can also be obtained, for salts, like gypsum, whose index of refraction is very close to that of balsam, will, when mounted in that medium become invisible, or nearly so, in ordinary transmitted light.

The material I use for mounting is Canada balsam diluted with chloroform until it flows freely. I keep it in a small stoppered bottle, and find one of about  $\frac{1}{2}$  an oz. capacity very convenient. I pour this balsam very carefully, drop by drop, on the crystals to be mounted, place a thin cover-glass over the balsam, and allow the latter to consolidate by the spontaneous evaporation of the chloroform without subjecting the preparation to pressure or heat. From one to three days is sufficient, in ordinary cases, for the consolidation of the balsam.

I have found it convenient to divide this paper into three parts. The present part (Part I.) is devoted to remarks of an explanatory character. Part II. contains, in a tabular form, a list of sulphates with the most important or best known of their hydrates and double salts. It contains chemical information gleaned from various standard works on chemistry. The optical system to which each salt belongs, and its chemical formula, are given in Cols. 1 and 4 on the authority of either Fock (*Krystallographisch-Chemische Tabellen*, 1890) or Roscoe and Schorlemmer ("A Treatise on Chemistry," vol. ii. The Metals. New Edn.). Col. 5 indicates the form in which the salt appears when crystallised on a glass slide by the method above described, and embodies in every case the result of my own observations.

The forms described in col. 5 will not be found to agree, in every case, with the crystals figured in mineralogical or ordinary chemical works. The crystals figured in such works are often natural minerals formed in the laboratory of Nature under conditions that cannot be reproduced by the micro-chemical student; in other cases they are typical examples of exceptionally perfect crystals selected from a large number obtained by the crystallisation of a considerable quantity of material from saturated solutions. For our purposes we must be content with the results that can be obtained by allowing a drop of an aqueous solution to crystallise on a glass slide by spontaneous evaporation. The conditions under which crystallisation takes place in the latter case differ from those which obtain in the cases above referred to, and the results are therefore sometimes considerably modified. The material at the disposal of the microscopist is often extremely small, and his methods, to be of any value, must be capable of dealing with small quantities.

Cols. 6, 7, and 8 contain optical observations for which I am responsible. Cols. 6 and 7 require a few words of explanation. I have given the order of colours exhibited by the crystals according to Newton's scale,\* as I think this affords a rough mode of determining the double refraction of these salts which is of some practical value. Colours, no doubt, depend not only on the strength of the double refraction, and the direction taken by the light in its passage through a crystal, but also on the thickness of the crystal. But in dealing with the results of the spontaneous evaporation of an aqueous solution on a glass slide, I think it will be generally found that each salt has a habit of its own in respect of the general size and general thickness of its crystals as well as of the faces on which they commonly lie, and that therefore they will generally yield fairly similar results as regards colours in polarised light. It will be found that whilst certain salts habitually yield colours as high as the 7th order, others never give colours higher than those of the 1st, 2nd, or 3rd order, as the case may be. By discarding from consideration specially thin and attenuated crystals deposited when nearly the whole of the material in the drop had

been exhausted, and by selecting for observation the crystals that exhibit the strongest double refraction, we obtain data of some value. Treated in this way the colours afford a rough practical guide to aid us in determining the identity of the salt. The order of colour recorded in Col. 6 is the maximum observed by me.

In Col. 7 the direction of the major axis of elasticity has been determined with the aid of the quartz wedge. When it is said to be " $\parallel$  to  $e$ " it is intended to imply that when the axis of the quartz wedge is parallel to the axis of elongation of the crystal the phenomenon of *thinning* is produced. I have employed ( $e$ )\* as an abbreviation for the ordinary direction of elongation because it excludes any pretence of absolute precision. Some salts habitually lie on one face on the glass slide and are elongated in one direction. In practice I find the direction of the major axis, as indicated in Col. 7, an aid to the determination of salts of great practical value.

In Col. 8 I have alluded to a phenomenon observed when the polariser is used without the analyser which is usually attributed to "absorption." Calcite, and some other colourless minerals, when examined in transmitted light with the polariser alone, exhibit dark lines, shadows, and dark markings, in a certain position of the polariser (or when the polariser is rapidly revolved) which disappear altogether when the plane of vibration of the nicol is altered relatively to the plane of vibration of the light passing through the mineral. Some salts possess this property in a high degree—others in a much less degree or not at all. When a colourless salt, or mineral, possesses this absorption conspicuously, it marks it off from other minerals that do not display the property. We have here therefore a mode of distinguishing colourless minerals from one another which I have endeavoured to utilise in Col. 8.

(To be continued.)

## NOTICES OF BOOKS.

*Foundations of the Atomic Theory*: comprising Papers and Extracts. By JOHN DALTON, WILLIAM HYDE WOLLASTON, M.D., and THOMAS THOMSON, M.D. (1802—1808). Edinburgh: W. F. Clay. London: Simpkin, Marshall, Hamilton, Kent, and Co. 1893.

THIS publication is the second of the interesting series known as the "Alembic Club Reprints." It comprises John Dalton's "Experimental Enquiry into the Proportion of the several Gases or Elastic Fluids constituting the Atmosphere." This memoir was originally read on November 12th, 1802, before the Literary and Philosophical Society of Manchester, and may be found in the second series of their *Transactions* (vol. i., 1805, pp. 244—258). It is of capital importance as presenting the first definite example of the law of multiple importance.

A second paper, read also by Dalton on October 21st, 1803, treats of the absorption of gases by water and other liquids, and includes the author's earliest Table of Atomic Weights. Here hydrogen is taken as = 1.

Two short papers follow from Dalton's "New System of Chemical Philosophy,"—"On the Constitution of Bodies" (pp. 141—143), and on "Chemical Synthesis" (pp. 211—216 and 219—220). Here the author seems to adopt the view that analysis and synthesis go no farther than to the separation of particles, one from another, and to their reunion. Dalton's system of chemical symbols is also included.

A paper on Super-acid and Sub-acid Salts, by W. H. Wollaston, M.D., next follows. It was originally read before the Royal Society, Jan. 28th, 1808, and may be found in the *Phil. Trans.* (vol. xcvi., 1808, pp. 96—102).

\* For the mode of ascertaining the order see my paper on Double Refraction of Minerals, *Geol. Mag.*, 1888, p. 548. Also p. 65 of "Rosenbusch's Microscopical Physiography," by Iddings.

\* I have occasionally given  $c$  when the vertical crystallographic axis is intended.

Here we find a fore-shadowing of stereo-chemistry. The author thinks that we shall be obliged to acquire a geometrical conception of their (the atoms) relative arrangement in all the three dimensions of solid extension.

Lastly, come extracts from a paper on Oxalic Acid, by Dr. Thomas Thomson, F.R.S.E., and inserted in the *Phil. Trans.* (vol. xcvi., 1808, p. 63). This brief paper is an appreciative notice of Dalton's atomic theory.

We think that our brief remarks may draw attention to these fundamental documents of chemistry, especially as they are not universally accessible in their original forms.

## CORRESPONDENCE.

### THE CHICAGO EXHIBITION.

*To the Editor of the Chemical News.*

SIR,—I send you manuscript of an invitation to be issued especially to English speaking chemists, inviting them to take part in the Chemical Congress of the World's Auxiliary of the World's Columbian Exposition, to be held in Chicago in August next.

Special invitations have been sent to nearly all prominent English chemists, but it is believed that the publication of the enclosed circular in the CHEMICAL NEWS will reach a number of chemists who otherwise would fail to get an invitation.—I am, &c.,

U.S. Dept. of Agriculture,  
Division of Chemistry,  
Washington, D.C.,  
June 24, 1893.

H. W. WILEY,  
Chief of the Chemical Division,  
and Chairman of the  
General Committee on  
World's Chemical Congress.

### THE WORLD'S CONGRESS AUXILIARY OF THE WORLD'S COLUMBIAN EXPOSITION.

Department of Science and Philosophy.  
General Division of Chemistry.

The Committees in charge of the Congress have selected Monday, August 21st, as the date of the opening of the Congress of Chemistry to be held in connection with the Columbian Exposition in Chicago.

The chairman of the committee appointed for co-operation in this Congress by the American Association for the Advancement of Science, Chemical Section, is Prof. Ira Remsen, Johns Hopkins University, Baltimore, Md. The chairman of the committee appointed by the American Chemical Society is Dr. Wm. McMurtrie, 106, Wall Street, New York, N.Y. The chairman of committee of the World's Congress Auxiliary, on Congress of Chemists, is Prof. John H. Long, 2421, Dearborn Street, Chicago, Ill. The various committees have organised by selecting Dr. H. W. Wiley, Chief Chemist of the Department of Agriculture, Washington, D.C., as Chairman, and Prof. R. B. Warder, Howard University, Washington, D.C., as Secretary.

The work of the Congress has been divided into ten sections and a temporary chairman has been selected for each section, as follows:—

Agricultural Chemistry—H. W. Wiley, Department of Agriculture, Washington, D.C.

Analytical Chemistry—A. B. Prescott, Michigan University, Ann Arbor, Mich.

Didactic Chemistry—W. E. Stone, Lafayette, Ind.

Historical Chemistry and Bibliography—H. Carrington Bolton, University Club, New York.

Inorganic Chemistry—F. W. Clarke, Geological Survey, Washington, D.C.

Organic Chemistry—I. Remsen, Johns Hopkins University, Baltimore, Md.

Physical Chemistry—R. B. Warder, Howard University, Washington, D.C.

Physiological Chemistry—V. C. Vaughan, Michigan University, Ann Arbor, Mich.

Sanitary Chemistry—H. Leffmann, 715, Walnut Street, Philadelphia, Pa.

Technical Chemistry—Wm. McMurtrie, 106, Wall Street, New York, N.Y.

General and special invitations have already been issued to foreign chemists and many replies have been received, indicating a large attendance of chemists from abroad at the Congress.

The following distinguished foreign chemists have already promised to present papers to the Congress, and the list will without doubt be increased many fold before the date of the opening:—

Prof. L. G. Ernest Milieu, Marseilles—On Standard Methods of Oil Analysis.

Mr. Farnham Maxwell Lyte, London—On the Production of Chlorine.

Mr. H. Droop Richmond, London—On the Accuracy of the Methods of Analysis of Dairy Products.

M. Pierre Manhes, Lyon—Subject to be announced later.

Prof. B. Tollens, Göttingen—Researches on the Synthesis of Polyatomic Alcohols.

Prof. Ferd. Tiemann, Berlin—Subject to be announced later.

M. H. Pellet, Brussels—On the Methods of Determining the Percentage of Sugar in Beets.

Mr. H. R. Procter, Leeds—On the Examination of Tanning Materials.

M. O. Kemna, Antwerp—On the Purification of Water.

Mr. Otto Hühner, London—Subject to be announced.

Prof. C. A. Bischoff, Riga—Subject to be announced.

Prof. G. Lunge, Zürich—On the Method of Teaching Technological Chemistry at Universities and Polytechnic Schools.

Prof. Ludwig Mond, Rome—Subject to be announced.

Prof. W. N. Hartley, Dublin—Subject to be announced.

This circular is specially intended to reach American chemists, inviting them to take an active interest in the Congress, and to be present; or, if that is not possible, to send papers on some of the subjects indicated in the classification above mentioned.

Chemists specially interested in each of the subjects for discussion are invited to correspond with the chairmen of those sections in regard to the character of the work and of the papers expected. All chemists who expect to read papers at the Congress are earnestly requested to send the titles thereof to the Chairman of the General Committee, Dr. H. W. Wiley, Department of Agriculture, Washington, D.C., on or before the 1st day of August. It will be difficult to arrange for a position on the programme for the titles of any papers which may be received after that date. The time required for each paper should also be noted so that daily programmes can be provided for in advance. In all cases the place of honour on the programme will be given to foreign contributors. Papers or Addresses can be presented in English, French, or German, as the author may select; but where convenient, the English language will be preferred.

The Committee desires to ask those chemists who propose to attend the World's Congress to make an excursion, during the week previous to the meeting, to Madison, Wisconsin, for the purpose of attending the meetings of the Chemical Section of the American Association for the Advancement of Science. This will not only be a delightful excursion, as Madison is distant only about four hours from Chicago, but will also enable the participants in the Congress to make the acquaintance of the scientific men of the United States and other countries engaged, not only in chemical, but also in other branches of science.

Other attractions in Chicago will be meetings of different Chemical Societies. Among these may be mentioned the American Chemical Society, the Annual

Meeting of which will begin August 21st, and the Association of Official Agricultural Chemists, which will hold its Annual Meeting in Chicago, beginning Thursday, August 24th. The Sessions of these Societies will be so ordered as not to conflict with the business of the Congress. The American Pharmaceutical Association, which has a strong Chemical Section, will also meet in Chicago at or near this time. It is hoped that the Institute of Mining Engineers may also hold its meeting about this time, although no definite announcement can be made in regard to this matter. It is thus seen that this occasion will bring together the active workers in all branches of chemical science in the United States, and enable American chemists to make the acquaintance of distinguished co-labourers from abroad, and the visiting chemists to meet the largest possible number of their fellow labourers here.

Every possible arrangement will be made for the convenience and comfort of visitors. Intending participants in the Congress should address Prof. John H. Long, 2421, Dearborn Street, Chicago, Ill., for information in regard to quarters and other accommodations. On arrival in Chicago, visitors should report at once to the Congress Headquarters, Art Institute Building, Lake Front and Adams Street, where full information will be given them in regard to matters connected with their personal comfort. Wherever possible, intending visitors should write a few days before their arrival to the Committees above-mentioned, in order that special provision may be made for their comfort when they reach Chicago.

In regard to the climate of Chicago in August much can be said in praise. While warm days may sometimes be expected, the situation of the city on the edge of a vast open prairie extending for nearly a thousand miles north and west without a break, secures, even in the hottest day, refreshing breezes which cool the atmosphere and mitigate the heat of summer. The lake breezes also do much to render the climate moderate. No one need be deterred from attending the Congress on account of fear of severe heat.

It is especially urged that all chemists who intend visiting the World's Fair take this occasion to do so, by which they can combine the pleasure of visiting the Exposition with the benefit derived from attendance at the Congress. To American chemists an especial appeal is made to be present for the purpose of welcoming our foreign visitors, and showing them the progress of Chemical Science in the United States.

HARVEY W. WILEY.

### THE ORGANISATION OF SCIENCE.

To the Editor of the Chemical News.

SIR,—Mr. Swinburn's letter in *Nature* of June 29, is one more piece of evidence to show that workers in the various branches of Science are at last waking up to a realisation of the necessity of replacing the present happy-go-lucky machinery of science by a thorough re-organisation—a necessity which I pointed out at some length in my pamphlet on the "Organisation of Science" over a year ago. Since that pamphlet appeared, we have had long letters from zoologists, geologists, and now from a physicist, all groaning at the waste and inefficiency involved in the present unsystem, and supporting, to a large extent, practically the same reforms as those suggested in my pamphlet.

To comment upon Mr. Swinburn's letter at the length which the subject deserves, would be to make an unreasonable demand upon your space; and there is the less necessity for this, since most of his difficulties are answered by anticipation in my pamphlet; but perhaps you will permit me a few words in reply to him.

If Mr. Swinburn will refer to pp. 19—23 of my essay, he will find a scheme worked out by which a decentralisa-

tion of scientific meetings (that is to say, a provision for meetings in the provinces and not in London only) would be secured, together with a complete centralisation of the publishing—in effect a federation of all the societies concerned in any one branch of science; and a splitting up of all societies and journals of proceedings, concerned with half a dozen different subjects.

With regard to the Royal Society, which I am relieved to find myself not alone in considering a stumbling-block to scientific organisation in the present day, I have already pointed out a simple remedy, viz., that it should refuse to receive any papers that come within the scope of the various specialist sciences, and should, instead, co-ordinate and collate the work of all the sub-societies (pp. 6—14).

I am sorry that Mr. Swinburne has seen fit to adopt the specialised tone of a simple physicist, since the evil is common to all branches of science, and reform is necessary for Physics no more than for the rest of science; but I am still more sorry he has seen fit to put forward the dignity of the Physical Society as a hypothetical obstacle to reform. I must emphatically protest against the notion that the Physical or any other society has any single interest to consult other than how best to subserve that science which it was founded to minister unto. The only true dignity of any such society consists in loyally ministering to the wants of science, and in a complete readiness to, at any time, even efface itself, if such proceeding be advantageous to science. Therein lies the whole duty and dignity of the Physical, as of every other society; and any suggestion contrary to this cometh of evil. The Physical Society exists for the advancement of Physics; not Physics for the promotion of the Physical Society's dignity.—I am, &c.,

A FREE LANCE.

London, June 30, 1893.

## 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. cxvi., No. 25, June 19, 1893.

Extraction of Zirconia and Thoria.—L. Troost.—This paper will be inserted in full.

Study of certain Novel Phenomena of Fusion and Volatilisation produced by the Heat of the Electric Arc.—Henri Moissan.—This memoir requires full insertion.

Study on the Filtration of Liquids.—R. Lezé.—The author's method is to submit the liquid in question to very rapid rotation in a porous vessel. The speed of efflux of distilled water being taken as unity, the following values were found for:—

	Rate of efflux.
NaCl .. .. .	5 per cent 1'023
KCl .. .. .	5 " 1'043
Sodium nitrate .. ..	5 " 1'051
Ammonium sulphate..	5 " 0'993
Alcohol at 20° .. ..	0'590
" " 40° .. ..	0'50
" " 90° .. ..	0'67
Milk .. .. .	0'03
Sewage .. .. .	0'10

Combinations of Molybdates and Sulphurous Acid.—E. Péchard.—It results from the facts stated that sulphurous acid does not act upon alkaline molybdates in the manner of ordinary reducing agents, the difference depending on the formation of molybdosulphites. Reduc-

tion occurs only if the liquid is strongly acid. Selenious acid yields with the molybdates analogous compounds, but much more stable.

**On the Bromoboracites.** Iron and Zinc Bromoboracites.—G. Rousseau and H. Allaire.—The composition of iron bromoborate is shown by the formula  $6\text{FeO}, 8\text{B}_2\text{O}_3, \text{FeBr}_2$ . It always contains a small quantity of lime, which replaces, isomorphically, an equivalent proportion of ferrous oxide. It appears as a greyish white powder, consisting of a mixture of cubes and tetrahedra, acting upon polarised light like natural boracite. The zinc compound,  $6\text{ZnO}, 8\text{B}_2\text{O}_3, \text{ZnBr}_2$ , forms white microscopic crystals of a pseudocubic symmetry, acting upon polarised light.

**Copper Fluorides.**—M. Poulenc.—The hydrated fluoride,  $\text{CuFe}_2\text{H}_2\text{O}$ , has been already obtained by Albiano. The author has succeeded in obtaining the cuprous fluoride  $\text{Cu}_2\text{Fe}_2$  in the anhydrous state by the action of gaseous hydrofluoric acid upon cuprous chloride. When fused it appears as a transparent mass, of a ruby-red colour, and of a crystalline fracture. Cupric fluoride,  $\text{CuFe}_2$ , is obtained by the action of melted ammonium fluoride upon hydrated cupric fluoride. It is a white crystalline powder, which gradually turns blue on exposure to the air.

**Action of Electricity upon the Carbide of Iron by Cementation.**—Jules Garnier.—At about  $1000^\circ$ , under the action of a very weak current (50 ampères and 2.5 volts) the conversion of iron into steel takes place with great rapidity.

**Rotatory Power of Bodies belonging to a Homologous Series.**—Ph. A. Guye.—This paper does not admit of abstraction.

**Rotatory Power of the Ethers of Valerianic and Glyceric Acid.**—Ph. A. Guye and L. Chavanne.—This paper also is not adapted for abstraction.

**Formation-heat of certain Derivatives of Indigo.**—R. d'Aladern.—The formation-heat of indigotine is given as  $+41.0$  cal.; that of isatine =  $+59.0$  cal.; that of isathyde is  $+145.0$ ; and that of dioxyindol  $+80.2$  cal.

**On Dextro-licareol.**—Ph. Barbier.—Licareol exists in two modifications, dextro-rotatory and lævo-rotatory.

**New Apparatus for Measuring the Intensity of Perfumes.**—Eugene Masnard.—The author proposes the use of a general method and a new apparatus for determining the intensity and persistence of perfumes, founded on the property of oil of turpentine to prevent the luminosity of phosphorus in darkness.

*Bulletin de la Société Chimique de Paris.*  
Series 3, Vols. ix. and x., No. 11.

**A Study on the Rate of Decomposition of the Diazo-Compounds.**—J. Hausser and P. Th. Müller.—The authors have examined the diazotoluene sulphate and the diazobenzenecarboxylated sulphates. The para-compounds are the most stable, the meta-compounds the least stable, whilst the ortho-compounds take an intermediate position.

**The Odoriferous Power in the Fatty Series.**—Jacques Passy.—Already inserted.

**Action of Acetic Acid and of Formic Acid upon Turpentine.**—MM. Bouchardat and Oliviero.—The action of formic acid upon turpentine in presence of water is distinguished by its violence, destroying the rotatory power, and by the abundant formation of free terpine, which, with acetic acid, is observed only to a very slight extent.

**Convenient and Expeditious Process for Saponifying the Nitriles.**—L. Bouveault.—This paper is not adapted for useful abstraction.

**Preparation of Triphenylacetone and Triphenylcarbinol.**—L. Bouveault.—The author prepares

triphenylcarbinol by decomposing triphenylbromomethane with water. Triphenylbromomethane is best obtained by the process of Allen and Kölliker, which consists in letting the calculated quantity of bromine fall drop by drop upon melted triphenylmethane heated to  $130^\circ$ .

**Hydrazone of Cyanacetone.**—L. Bouveault.—A critique of the process of Mr. Burns (*Journ. Prakt. Chemie*).

**Pyruvic Ether and its Product of Condensation in Presence of Hydrochloric Acid.**—P. Genviessé.—The author has obtained pure pyruvic ether, and studied its action upon gaseous ammonia. He has obtained for the first time methyl-2-pentene-2-one-4-dioic acid, prepared its copper and silver salts and its ethylic ether, and shows that pyruvic ether behaves like acetylacetic ether with hydrochloric acid.

**Oxyhæmatine, Reduced Hæmatine, and Hemochromogen.**—H. Bertin-Sans and J. Moitessier.—The direct action of reducing agents upon alkaline solutions of oxyhæmatine produces not hemochromogen, but a compound not as yet described, which we shall call reduced hæmatine, and which is characterised by a special spectrum. Pure oxyhæmatine, prepared by Cazeneuve's process and dissolved in soda at 1 per cent, presents an absorption-spectrum consisting of a single band with blunted margins, situate between C and D, the middle of which coincides with  $\lambda=618$ . The addition of a reducing salt, such as neutral potassium sulphide, causes the rapid disappearance of this band and the appearance of an analogous band, the middle of which coincides with the ray D. The authors ascribe this spectrum to the formation of reduced hæmatine. If to reduced hæmatine we add a slight excess of ammonia or of an amine, the band of reduced hæmatine disappears, and the solution gives very distinctly the spectrum of hemochromogen.

**Action of Carbon Monoxide upon Reduced Hæmatine and Hemochromogen.**—H. Bertin-Sans and J. Moitessier.—The authors have obtained a compound of carbon monoxide with hæmatine by setting out directly from reduced hæmatine without the intervention of hemochromogen. Without absolutely asserting that the compound formed under these conditions differs decidedly from the compounds described by Popoff, Jaegerholm, and Hoppe-Seyler, it seems to present greater guarantees of purity.

ERRATA.—Vol. lxxvii., p. 313, col. 1, in every case, for "Olouchoff" read "Obouchoff." Line 31, for "Pfaltzer" read "Holtzer."

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# THE CHEMICAL NEWS.

VOL. LXVII., No. 1756.

## AN IMPROVED METHOD OF PURIFYING TOLUOL, BENZOL, &c.

By R. J. FRISWELL

OF late years the demand for toluol has so much increased that large quantities of the by-products from the oil gas factories have been worked up to recover the toluol and benzol which Armstrong some years back discovered in them.

This has caused much trouble in separating traces of paraffins, which, though not so troublesome with benzol, render toluol almost unworkable, unless treated in a special manner. These substances are not indicated by any variation of the boiling-points which are now uniformly good, but can be at once detected by vigorously shaking the sample with an equal volume of pure sulphuric acid of 1.842 sp. gr.

Under these circumstances a sample made from pure coal oils separates sharply into two layers when allowed to rest after shaking, and the acid is colourless, or of a very faint brown tint, and so remains for twenty-four hours or more.

On the contrary, the samples contaminated with these bodies form an emulsion, which takes five to ten minutes to separate completely, and the acid is more or less bright orange-coloured. In about one hour the surface of the acid is deep green, and this tint gradually spreads through the liquid, so that in ten to twelve hours the whole is deep green, or even black, while a distinct odour of sulphurous acid is easily detected.

A sample of toluol behaving in this way may be at once rejected by anyone desiring to avoid an immense amount of trouble in working it.

It is, however, an easy matter to render toluol quite equal to the best samples prepared from pure coal oils by a very simple and inexpensive treatment.

It is, of course, well known that agitation with concentrated oil of vitriol will effect the removal, by solution, of most of these bodies; but unfortunately at the same time great loss of toluol occurs, owing to its easy solubility in the acid. Its recovery by hydrolysis is, needless to say, an expensive operation.

It is no secret that many makers have used fuming acid, and have alleged that, notwithstanding increased loss, it has proved cheaper to use than ordinary vitriol. The use of oxidising agents dissolved in the vitriol has been found quite ineffective.

The movement in the direction of stronger acid is an entirely erroneous one, and the secret of success lies in an opposite direction.

It is quite possible to employ an acid too weak to dissolve the toluol, but quite strong enough to wash out the paraffins; but this treatment is rendered expensive by reason of the large volume of acid and number of treatments required. It is, however, possible to make use of an acid which shall act in a different manner, viz., render the paraffin-like bodies, part of which it dissolves, much less volatile by polymerising them.

This may be carried out as follows:—Crude toluol boiling between 110°—130° C. is agitated thoroughly for four hours with 10 per cent by volume of sulphuric acid of sp. gr. 1.803. It is allowed to rest, and drawn off from the acid in the usual manner, and washed once with enough caustic soda to remove traces of acid. Very thorough agitation is necessary, and certain samples may require more acid or a longer time of treatment. The loss should not exceed 5 per cent.\*

\* About half of this is due to the paraffins removed.

It is then at once transferred to the rectifying still, and the pure toluol taken off. This will be found by the acid test quite equal to the best toluol made from coal oils. In fact 95 per cent of the distillates will pass this test.

The residues in the still consist partly of the polymerised bodies, their boiling-points lying between 260° and 285° C.

The waste acid on dilution deposits a deep green oil, which, when nearly free from acid, is soluble in water. When distilled with water a very heavy oil comes over with the distillate. The acid cannot be recovered unless this substance is separated by dilution, as, if heated directly as drawn from the toluol, it evolves large volumes of sulphurous oxide and becomes nearly solid from separation of carbon.

## THE AVAILABILITY OF THE FLUORESCENCE REACTION FOR THE DETECTION OF SACCHARINE IN BEER.

By F. GANNTER.

BÖRNSTEIN has recommended in the *Zeit. für Analyt. Chemie* (xxvii., 167), as a very sensitive reaction for saccharine, the formation of fluorescein on heating saccharine with concentrated sulphuric acid and resorcin. The value of this reaction has been contested by Hooker (*Berichte*, xxi., 3395), since on treating resorcin alone with concentrated sulphuric acid, a reaction occurred apparently the same as that described by Börnstein as characteristic of benzoic sulphide.

Börnstein, in a reply, admitted that many organic compounds, on suitable treatment, yielded liquids with a greenish surface-reflection, but that these were all so far inferior in intensity to the fluorescence caused by sulphinide that the latter—on a proper management of the experiment—may serve very well for establishing the presence of saccharine. According to these enlargements, the reaction appeared not alone very sensitive; but, in comparison to the other methods, by conversion into a sulphate or salicylic acid, very simple and convenient. As I had to test a great number of samples of beer for saccharine, I was induced to study the reaction more closely.

In the first place, to test the behaviour of pure resorcin, a few grms. of it were heated with from 3 to 5 drops of concentrated sulphuric acid in the manner described by Börnstein. The solution became at first light red, then dark brown, and finally dark greenish black. After diluting with water and adding soda-lye until the reaction became alkaline, no change of colour was observed, the solution remained reddish brown, had on its surface scarcely a greenish reflection, and displayed certainly no fluorescence. In various other experiments repeated with the addition of various organic substances an unmistakable fluorescence was never observed. Ten m.grms. of a saccharine tablet (saccharine + sodium bicarbonate) was treated in exactly the same manner: the reaction ensued exactly as described by Börnstein. The solution became yellowish red, then deep green, and on dilution with water had a deep reddish brown colour, which on the addition of soda-lye displayed a distinct sharp change to dark green. On further dilution the liquid appeared yellowish red by transmitted light, but by reflected light intensely green fluorescent; which even on dilution to 1 and upwards retained this property. Repeated experiments with still smaller proportions of saccharine always gave the same very strong fluorescence, not to be mistaken even on great dilution.

The reaction can therefore without doubt serve for the recognition of the smallest quantities of saccharine.

Börnstein further mentions that the phenomenon of fluorescence in the reaction occurs only further in presence of phthalic anhydride and phthalimide; and I

thence on the basis of the above experiments concluded that the reaction might be directly used for the detection of saccharine in beer. Therefore the beer was evaporated down, extracted with ether in the manner described below, and the reaction was effected with the residue left after the evaporation of the ether, which must contain any saccharine present. Twelve beers treated in this manner gave, without exception, a very intense fluorescence, so that on the faith of this reaction alone an addition of saccharine must have been assumed as beyond all doubt. But in each of these beers I had tested the ethereal residue with the tongue, and in eleven cases I had found a sharply burning strongly bitter taste, without any sweetness. One sample, however, gave at first an unmistakable sweetness, followed by a strongly bitter taste. On account of the intense sweetness of saccharine, this tongue-test must be accepted as decisive, as even the smallest quantity of saccharine in the ethereal residue would be at once manifested by the taste.

Thus the ethereal residue of eleven samples which contain no saccharine on heating with resorcin and concentrated sulphuric acid gave as intense and distinct fluorescence as a sample containing saccharine. This remarkable circumstance led to the conjecture that there is present in beer some compound which behaves with resorcin as does saccharine. Of the constituents of beer which pass into the ethereal extract the most prominent are tannin, the resin, and the bitter principle of the hop. The reaction was first tried with tannin which gave not a trace of fluorescence. It was then tried with a few m.grms. of ordinary colophonium, which gave the same intense green fluorescence as pure saccharine.

The fluorescence reaction therefore cannot be used for the direct recognition of saccharine in the ethereal extract of beer.—*Zeitschrift für Analytische Chemie*.

#### ON THE EXTRACTION OF ZIRCONIA AND THORIA.

By L. TROOST.

In the Session of the Academy (vol. cxvi., p. 1227) I have shown that zircon (zirconium silicate) heated under the same conditions as zirconia to the temperature of the electric arc produced by a current of 30 to 35 ampères and 70 volts quickly gives long filaments of silica which gradually interlace so as to form a true felt.

As this experiment permits us to get rid of nearly all the silica contained in zirconium silicate, I will detail all its conditions.

The powdered zircon is intimately mixed with an excess of finely sifted charcoal and compressed into small cylinders, which are submitted, on a coke cupel, to the action of the electric arc in a closed vessel traversed by a slow current of carbonic acid. Under these conditions, the production of the filaments of silica is effected rapidly; it is accompanied by a thick black smoke, showing that there is not merely evaporation of the silica, but also, in part, a reduction of the silica by the coke, and consequently the production of pulverulent silicon, which is carried away, and is re-oxidised beyond the electric arc. Hence, along with the evaporation, properly so-called, there is an apparent volatilisation of silica resulting from the double phenomenon of successive reduction and re-oxidation.

In these circumstances, the zircon which before the experiment contained about 33 per cent of silica, leaves a product not containing more than from 1 to 1½ per cent. A part of the zirconia is reduced, and if the furnace is opened before it is completely cold the zirconium resulting from the reduction takes fire, and is re-converted into zirconia. The extraction of zirconia from zircon is thus notably simplified.

If, instead of a mixture of zircon and coke, we expose

zircon alone to the temperature of the arc, it melts, but the evaporation of the silica is slow and incomplete, and carries away with it a notable proportion of zirconia.

I have obtained analogous results for the elimination of the silica contained in thorite and orangite (thorium silicate).

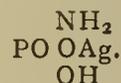
This procedure may be generalised so as to facilitate the preparation of the bases contained in the silicates.—*Comptes Rendus*, cxvi., p. 1428.

#### ON AMIDOPHOSPHORIC ACID.\*

By H. N. STOKES.

(Concluded from p. 19).

*Acid Silver Amidophosphate*,—



—This may be obtained by precipitating the acid potassium salt with silver nitrate, but, thus obtained, it contains too much silver (about 2 per cent), due, perhaps, to a small amount of neutral salt or to a trace of phosphate. By previously adding a very little nitric acid to the cold solution, it is obtained pure. As it is somewhat soluble in water, the theoretical yield cannot be obtained. It is also formed by dissolving the neutral salt in cold dilute nitric acid and precipitating by alcohol, or by adding alcohol to a solution of the free acid and silver nitrate. It forms a heavy crystalline powder, consisting of short needles, or, oftener, of very thick, short, hexagonal prisms with pyramidal ends, united into groups or twins; also, by precipitating with alcohol, as hexagonal stars. The forms are very characteristic. It is difficultly, but appreciably, soluble in water, easily in dilute nitric or acetic acid, and in ammonia; from the latter solution it crystallises on evaporation. The aqueous solution is at once converted into phosphate by boiling. Light does not discolour it. The air-dried salt is anhydrous. Analysis gave—

	Calculated for PO	NH <sub>2</sub> OAg. OH	Found.
P .. ..	15.22		15.23
Ag .. ..	52.90		53.35

On ignition it loses ammonia and leaves an easily fusible glass of silver hexametaphosphate.

	Calculated for PO	NH <sub>2</sub> OAg. OH	Found.
Loss (NH <sub>3</sub> ) .. ..	8.36		8.17

*Neutral Silver Amidophosphate*,—



—This is obtained either by adding silver nitrate and then ammonia to the filtrate from the acid salt, or (with much loss) by dissolving the acid salts in very dilute nitric acid, and adding silver nitrate and ammonia. It forms at first a turbidity, which in a few moments turns to a quickly subsiding crystalline precipitate. The ammonia must be added cautiously, and stopped as soon as the salt ceases to subside quickly. At this point a nearly white amorphous substance of unknown composition is formed, which remains in suspension, and may be re-dissolved by a drop of nitric acid. Further addition of ammonia to the filtrate gives the same amorphous salt, which is faintly yellow, and rapidly blackens in the light. It may also be obtained from the neutral sodium salt, but this method is not to be recommended, as the product is slightly yellow. The best method is the first mentioned,

\* *American Chemical Journal*, vol. xv., No. 3.

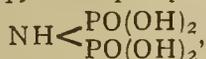
and if very dilute solutions of acid potassium salt have been used, nearly all the acid silver salt remains in solution, and can be converted into neutral salt as described. The neutral salt forms characteristic microscopic rhombic plates, with angles of nearly 60°, often united to bunches. It is colourless and unaffected by light. The crystalline powder is soft, and can thus be distinguished from the acid salt, which is gritty. It is almost insoluble in water; soluble in nitric acid, from which solution alcohol precipitates acid salt; soluble in ammonia, and deposited unchanged on spontaneous evaporation. The air-dried salt is anhydrous.

	Calculated for PO.NH <sub>2</sub> (OAg) <sub>2</sub> .	Found.
P .. .. .	9.98	10.03
N .. .. .	4.52	4.51
Ag .. .. .	69.40	69.18

It remains unchanged at 150°; at 180° it loses weight, the loss corresponding to one-half the total nitrogen calculated as ammonia. On heating to constant weight at 180°—

	Calculated for 2PO.NH <sub>2</sub> (OAg) <sub>2</sub> —NH <sub>3</sub> .	Found.
Loss .. .. .	2.74	2.82

The residue is brownish, but may be fused over the blast with but slight loss, whereby a little oxygen escapes, and a small amount of metallic silver is formed. In the above case this was weighed, and found to be only 5.61 per cent out of a total of 69.40 per cent. The loss between 180° and red heat was 0.34 per cent, and this is exactly the amount of oxygen which would be given off by the silver oxide corresponding to 5.61 per cent silver. The residue on ignition consists, besides metallic silver, of a yellow glass soluble in ammonia. Probably there is formed at 180° the silver salt of *pyrimidophosphoric acid*,—



which is not decomposed by fusion. Attempt will be made to isolate the free acid.

If the salt be heated at once over the blast, without previous heating at 180°, the decomposition is markedly different, much more metallic silver being formed.

	Calculated for $\frac{1}{2}$ N as NH <sub>3</sub> .	Found.
Loss .. .. .	2.74	4.63
Free silver .. .. .	—	25.75

This amount of silver corresponds to 1.91 per cent oxygen, which with 2.74 per cent ammonia makes 4.65 per cent loss, the amount actually found. The formation of silver oxide is due to the liberated ammonia, which splits off silver oxide and water, forming a higher amide. The action of dry ammonia gas on the salt is scarcely appreciable at 180°, as was found by experiment, hence the salt may be heated at this temperature without the ammonia which is given off liberating any considerable amount of silver oxide, as seen in the first case. At 200° and higher, dry ammonia forms large amounts of silver oxide and water, and therefore on heating rapidly, as in the second case, the liberated ammonia is able to act, and the large amount of silver formed is accounted for. The products of the action of dry ammonia on this salt will be described in a future article, when it will also be shown that amidophosphates may be made from neutral silver phosphate in this way. Experiments towards forming other inorganic amides by this method are also in progress.

*Free Amidophosphoric Acid.*

The isolation of the free acid is attended with difficulties, owing to its unstable nature. It has not yet been obtained perfectly pure, and the yield is always far

below the theoretical. The silver salts may be decomposed by hydrochloric acid in the cold, and the solution precipitated by alcohol, but a deficiency of acid causes the solution to be contaminated with acid salt, and an excess destroys the amido-acid completely, or at least prevents its precipitation. The decomposition of the silver salts by sulphuretted hydrogen gives better, but unsatisfactory, results. The best results are obtained by suspending the lead salt in a little ice-water, and decomposing by sulphuretted hydrogen. It is essential to have the latter in excess, as otherwise the solution contains some lead salt. The filtrate is run into four or five volumes of alcohol, whereby the acid is at once precipitated in the form of microscopic crystals. These consist sometimes of thick plates, sometimes of forms which appear to be cubes, but which are anisotropic. It is insoluble in alcohol, easily soluble in water, the solution having a sweetish taste. It gives no precipitate with silver nitrate, unless on addition of ammonia or alcohol. It evolves no ammonia with caustic alkalis, and is easily converted into the characteristic sodium, magnesium, barium, and silver salts, hence there can be no question as to its nature. It may be exposed to the air for a long time without change, but gradually alters, becoming pasty, in which condition it precipitates silver nitrate directly, and hence has become converted into an ammonium salt. The precipitate is white and amorphous, hence not phosphate. Its solution, if boiled but a moment, also gives a white silver precipitate, but on boiling several minutes it is completely converted into phosphate. It does not lose weight at 100°, but is slowly converted into ammonium salt, giving a white silver precipitate direct. Whether the product is one of the isomeric ammonium metaphosphates has not yet been determined. At 150° it also loses nothing, but fuses partially, and on higher heating it gives off ammonia. The silver salt from the acid which has been heated just to fusion becomes pasty under boiling water, like silver hexametaphosphate. The free acid obtained as above did not give satisfactory results on analysis, and such data are therefore postponed.

The alcoholic filtrate from the free acid contains an abundance of ammonium salts, giving amorphous, white, silver precipitates.

The action of amidophosphoric acid towards indicators is not sharp. The free acid gives acid reaction, the acid alkali salts have neutral reaction, but no sharp transitions can be obtained either with litmus, methyl orange, or phenolphthalein. It also differs from phosphoric acid in the uniformity with which its acid alkali salts precipitate acid salts, and its neutral alkali salts give neutral salts. No exception to this was observed. Soluble acid phosphates, as is well known, give, with silver and many other metals, precipitates of neutral salt.

The investigation will be continued in the directions indicated.

The above data were worked out, for the most part, in the chemical laboratory of the United States Geological Survey, in Washington, and I am indebted to the director, Major Powell, and to Professor F. W. Clarke for the opportunity of so doing.

Determination of Total Nitrogen in Urine.—C. Arnold and K. Wedemeyer (*Pflüger's Archiv*).—The authors compared the time required for the complete decomposition of urine on Kjeldahl's process if they used a mixture of 1 part potassium sulphate and 2 parts sulphuric acid, or sulphuric acid with 1 grm. each mercury and copper sulphate, or the exclusive use of one of the latter additions. In all three cases the oxidation was equally rapid, but in presence of potassium sulphate the frothing was stronger, unless sulphuric acid was added in excess. Arnold and Wedemeyer condemn the process of Schneider-Sugen, as less convenient and less accurate.

## POLARISATION OF PLATINUM ELECTRODES IN SULPHURIC ACID.\*

By JAMES B. HENDERSON, B.Sc.

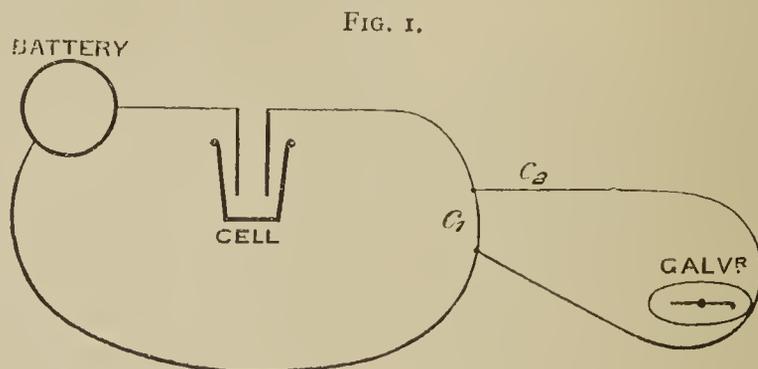
THIS investigation was begun about the beginning of February, 1893, at the instigation of Lord Kelvin, and was conducted in the Physical Laboratory of Glasgow University. The object of the investigation was to obtain the difference of potential between two platinum electrodes immersed in a solution of sulphuric acid immediately after the stoppage of a current which had been electrolysing the solution, and to find how this difference varied with a variation in the intensity of the current or in the strength of the solution.

Former experiments by Buff (*Poggendorff*, vol. cxxx., p. 341, 1867) and Fromme (*Wiedemann*, vol. xxxiii., p. 80, 1888) have given for the maximum polarisation with platinum wires of very small surface in the electrolysis of dilute sulphuric acid 3.5 and 4.6 volts.

Dr. Franz Richarz, in a paper "On the Polarisation of Small Electrodes in Dilute Sulphuric Acid," read before

wire electrodes, and also got the same maximum with large platinum plates.

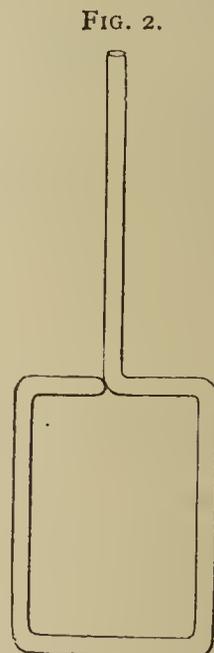
The cell used in the present investigation was a cylindrical glass vessel 10 c.m. diameter and 12 c.m. deep. The electrodes were rectangular plates of platinum foil, 7 c.m. long by 5.5 c.m. broad, and were stiffened by being mounted on rectangular frames made by bending glass tubing (Fig. 2). The tubing of these frames also served to support the plates in vertical planes by being passed through holes in a bar of wood placed across the mouth of the vessel. The plates were immersed in the solution to a depth of 5 c.m., having their planes parallel and about 1 c.m. apart. There were thus 55 sq. c.m. of surface of each plate wetted. To find the polarisation one of Lord Kelvin's quadrant electrometers were used, and by an arrangement, described later, the breaking of the electrolysing current circuit and the switching of the electrodes on to the terminals of the electrometer were done simultaneously. Before switching as above, however, the needle of the electrometer was deflected by making a difference of potential between the pairs of quadrants, and this deflection was so adjusted by trial



the British Association at Bath (1888), says of the above:—

"In these experiments the polarisation is calculated from measurements of the intensity of the galvanic current during the electrolysis, tacitly assuming that the resistance of the decomposition cell is independent of the intensity of the galvanic current. The correctness of the supposition has not been proved. I tried experiments by similar methods, and obtained yet greater values of the polarisation; it was calculated with a current density of 12 ampères per square centimetre as 4.4 daniells (4.7 volts), and increased more and more with increasing intensity of the galvanic current. It is very improbable that this can be right. By supposing, however, that the resistance of the decomposition cell is not independent of the intensity, but decreases in a fixed manner with increasing intensity, the calculation of the same experiment gives small and constant values of polarisation."

The method Dr. Richarz used to find the polarisation in his investigation was independent of the resistance of the electrolytic cell. The battery electrolytic cell and a switch,  $c_1$ , were joined in closed circuit. A branch circuit containing a very high resistance, a galvanometer, and another switch,  $c_2$ , joined the two sides of the switch  $c_1$  ( $c_1$  and  $c_2$  were the two contacts of a Helmholtz's pendulum interrupter). When  $c_1$  was made there was a very small current through the galvanometer. To determine the polarisation,  $c_1$  was broken, and immediately after  $c_2$  also. In the short time between the interruption of  $c_1$  and  $c_2$  a current strong for the sensibility of the galvanometer went through it. The polarisation was calculated from the deflection given to the galvanometer needle by the impact of the current, which was proportional to the electromotive force of the battery minus the polarisation. In this way, Dr. Richarz found values for the polarisation never greater than 2.6 volts with small

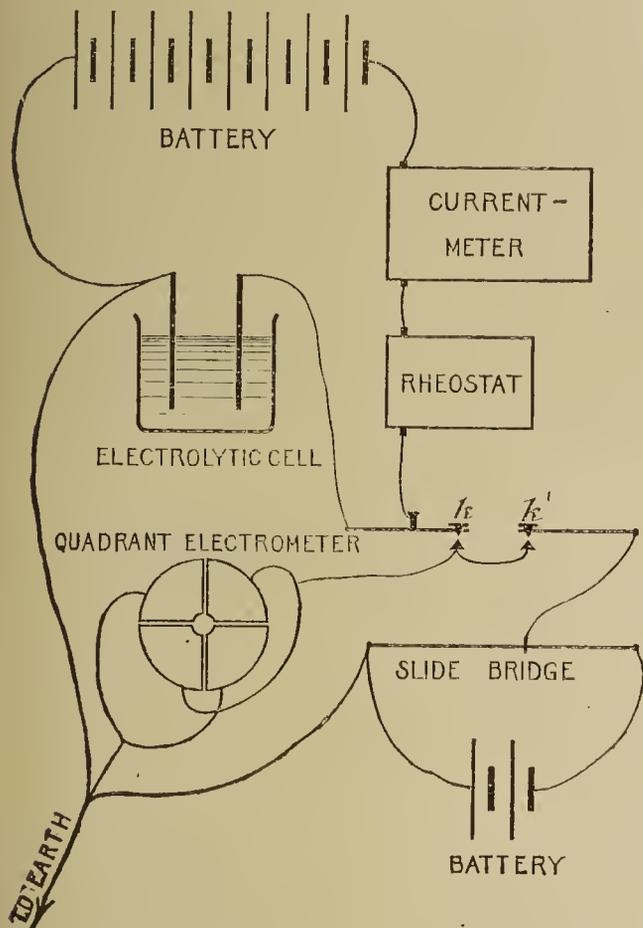


and error that, when the electrodes were switched on, the needle was no further deflected. For deflecting the needle of the electrometer a high resistance slide bridge was used. A difference of potential was maintained between its two ends, and the difference of potential between one end and the slider was used to deflect the needle, so that by moving the slider one way or the other the deflection could be increased or diminished at will. The electrolysing current was kept constant throughout each experiment, being measured by one of Lord Kelvin's electric balances and adjusted by a rheostat. One terminal of the electrometer, one electrode, and one end of the slide bridge were connected together and then put to earth. The current for the electrolysis was got from eight large

\* A Paper read before the Royal Society, June 15, 1893.

secondary cells, and the difference of potential between the ends of the slide bridge was maintained by two small secondary cells. The arrangement of keys can be best understood from the diagram. By pressing the key *k'*, connection was made between the slider and the unearthed

FIG. 3.



quadrants, and when the key *k* was free, the circuit was complete for the electrolysing current, but when *k* was pressed down the circuit was broken, and the unearthed electrode was connected to the unearthed quadrants.

The order of an experiment was the following:—

After carefully standardising the electrometer, the electrolysis was started and the unearthed electrode connected by a wire (not shown in the diagram) to the unearthed quadrants. The deflection of the needle thus produced, which showed the difference of potential between the electrodes, continued to increase steadily until, after the lapse of an interval of time depending on the strength of the current, it became constant. When this stage was reached the wire mentioned above was removed and the key *k'* pressed and kept down, thus making connection between the slider and the quadrants. The slider was then moved along until the deflection was nearly equal to that which would be given by the polarisation, and the key *k* momentarily pressed, thereby breaking the current circuit and connecting the electrode to the quadrants. An impulsive deflection immediately followed, unless the potential of the quadrants was equal to that of polarisation. If this deflection was negative (which indicated that the potential of polarisation was less than that of the quadrants) the slider was moved so as to reduce the potential of the quadrants below that of polarisation, thereby making the impulsive deflection positive, and then the experiment was continued as below. When the positive deflection was obtained its amount was noted, and the slider was moved so as to increase the steady deflection nearly up to the point on the scale reached by the impulsive one, and another trial then made. In this way, by watching the point reached by each impulsive deflection, and then increasing the steady one almost up to that point, the latter was increased until the former vanished, that is,

until the potential of the quadrants was that of polarisation. The magnitude of this deflection was then noted, and the polarisation calculated from it. In these trials the key *k* was kept down only for about two seconds, just sufficient time to allow the extent of the deflection to be seen, and at least two minutes were allowed to elapse between one trial and the next.

After the maximum deflection had been reached, a considerable interval of time was allowed to elapse, and then the key *k'* raised and *k* simultaneously lowered and kept down, and the rate of fall of the deflection noted. The above motion of the keys threw the slider off and put the electrode on to the quadrants, at the same time stopping the current. The deflection was therefore due to polarisation alone, and its rate of fall was therefore the rate of fall of the polarisation.

The results of one series of experiments are given in the accompanying Table.

All the results point to the polarisation being constant with large electrodes, being independent of the strength of the solution and the intensity of the current. The variations in the figures do not occur in any order, and are all such as might be expected in experimental results of this nature. Some of the greatest variations were obtained in exactly similar experiments performed at different times.

The mean of all the values of the polarisation in this Table is 2.09 volts.

The rate of fall of the polarisation depends on the time the current has been electrolysing the solution, and also on its intensity, but in every case the fall is very rapid at first, being in some cases as much in the first minute as it is in the next five minutes, and the fall in the first minute is never less than one-fourth of the polarisation.

Percentage strength of solution.	Strength of current in ampères.	Time the current had been passing.		Polarisation in volts.
		H.	M.	
30	0.2	3	25	2.066
30	0.5	0	45	2.060
30	1.0	0	35	2.060
30	1.0	0	45	2.124
20	0.1	3	22	2.126
20	0.5	1	25	2.139
20	1.0	0	25	2.090
20	1.0	0	35	2.124
10	0.1	17	40	2.139
10	0.5	1	19	2.066
10	1.0	0	44	2.066
5	0.1	18	30	2.116
5	0.5	1	36	2.078
5	1.0	1	0	2.083
5	1.0	3	15	2.054

Mean polarisation = 2.09 volts.

#### NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.\*

By Lieut.-General C. A. McMAHON, F.G.S.

(Continued from p. 23).

IN a previous page I assumed that we had reduced the chemical constituents of a mineral to the form of soluble sulphates, and had crystallised a mixture of these sulphates on glass slides for microscopic examination. An inspection of these slides, with the information contained in Part II. before us, will often give us important information regarding the character of the mineral under examination. For instance, if we have treated a piece of serpentine in the manner described it will be at once seen that the principal chemical constituent of the mine-

\* *Mineralogical Magazine*, vol. x., No. 46, p 79.

ral is magnesia, for unmistakable crystals of magnesium sulphate will occupy a prominent position on the slide. But supposing that we wish to confirm this determination, or to ascertain what other sulphates are contained in our solution, we can pass on to the reactions based on Part II., or to those detailed in Part III.

The double sulphates, recorded in Part II., supply us with a valuable means of detecting the presence of many metallic salts. Suppose, for instance, that we are seeking for evidence of the presence of sodium, we examine our original slides to see whether they contain any cubic crystals of alum. If they do not do so, there is a strong probability that the mineral under examination does not contain either aluminium or chromium as well as sodium. We then place a few drops of the original aqueous solution on several glass slides and add two or three drops of an aqueous solution of aluminium sulphate to some of the slides, and two or three of chromic sulphate to the other slides, and allow these to evaporate spontaneously without the application of heat. If soda be present in the mineral, crystals of alum will be found on the slides.

Then we can further test for soda (without going beyond methods based on Part II.) by employing, in the way described, the sulphates of calcium, magnesium, or manganese, with each of which sodium sulphate forms double salts.

The above illustration refers to the detection of sodium only, but a reference to Part II. will show that the sulphates of many other metals may be detected by the employment of sulphates that form double salts with them. Cold solutions, combined with spontaneous evaporation, have yielded me the best results.

In Part III. I have given some selected tests *supplementary* to those suggested by Part II. Most of these reactions, due originally to Haushofer, Behrens, Boricky, and others, have been taken from the works of Klement and Renard ("Reactions Microchimiques," par C. Klement et A. Renard, 1886), and Behrens ("Contributions to Micro-chemical Analysis," by H. Behrens; CHEMICAL NEWS, 1891). I have tried and can recommend all the reactions entered in Part III. In one or two cases I have given my reasons for rejecting some reactions that have been suggested by various authorities; but I think it unnecessary to specify my grounds for excluding other reactions which I have tried, but which, from their requiring great heat, great expertness on the part of the operator, or reagents that I could not obtain sufficiently pure, or for some other reason, were found unsuitable for ordinary use.

In Part III. I have noted facts that seem to me of interest regarding some of the salts alluded to therein, and I will now conclude with a few observations of more general character.

Several interesting facts will be apparent on a consideration of Part II. The first is that the addition of a single molecule of water to the formula of a hydrate is sufficient, in some cases, to completely alter the physical properties of the salt, involving not only a change in its optical properties, and in its solubility, but in some cases even a change of colour.

Conversely the loss of water, even when heat has not been employed, may result in a change of molecular structure, as in the interesting instance noted in Part III., iron, where a salt changes from a glass into a crystal on losing some of its water.

The formation of one hydrate rather than another depends in some cases on the temperature at which crystallisation takes place, and in others on other considerations—solubility being probably a dominating factor. That is to say, as evaporation proceeds, and the volume of water present is reduced, one hydrate may be thrown down first and another later on.

The student may sometimes be disconcerted by the diversity of forms presented to him by micro-chemical reactions; but fundamental diversity of form in such

cases is, I suspect, more often the result of minute difference in chemical composition than an instance of polymorphism. Hydrates, basic salts, or double salts, of which little or nothing is yet known, may be formed under special conditions. These salts reveal themselves under the microscope in forms that are new to the student, and invite him to future excursions into unexplored fields of research.

Another thing that has interested me as a student of igneous rocks is the presence in these salts of aqueous origin of twinning, zonal structure, and cleavage lines.

Many kinds of twinning—penetration twins, ordinary binary twins, and polysynthetic twinning, combined with macles analogous to those on the pericline plan—are to be found in crystals formed on glass slides in the manner above described, and they appear to be congenital in origin. They are by no means confined to crystals formed round the margin of a drop, where it might possibly be alleged that they had suffered strains from molecular tension, or from crowding; but they appear quite as commonly in discrete crystals standing by themselves in the centre of the area originally covered by the liquid.

The following abbreviations are used in Part II. :—

<i>R.L.</i>	for right angle.
	parallel.
<i>e</i>	direction of elongation.
<i>c.p.l.</i>	converging polarised light.
<i>Q.W.</i>	quartz wedge.
<i>C.</i>	cubic.
<i>T.</i>	tetragonal.
<i>H.</i>	hexagonal.
<i>R.</i>	orthorhombic.
<i>M.</i>	monoclinic.
<i>Tr.</i>	triclinic.

(To be continued).

#### TURACIN, A REMARKABLE ANIMAL PIGMENT CONTAINING COPPER.\*

By Prof. A. H. CHURCH, M.A., F.R.S.

THE study of natural colouring-matters is at once peculiarly fascinating and peculiarly difficult. The nature of the colouring-matters in animals and plants, and even in some minerals (ruby, sapphire, emerald, and amethyst, for example), is still, in the majority of cases, not completely fathomed.

Animal pigments are generally less easily extracted and are more complex than those of plants. They appear invariably to contain nitrogen—an observation in accord with the comparative richness in that element of animal cells and their contents. Then, too, much of the colouration of animals, being due to microscopic structure, and therefore having a mechanical and not a pigmentary origin, differs essentially from the colouration of plants. Those animal colours which are primarily due to structure do, however, involve the presence of a dark pigment—brown or black—which acts at once as a foil and as an absorbent of those incident rays which are not reflected.

Many spectroscopic examinations of animal pigments have been made. Except in the case of blood- and bile-pigments, very few have been submitted to exhaustive chemical study. Spectral analysis, when uncontrolled by chemical, and when the influence of the solvent employed is not taken into account, is very likely to mislead the investigator. And, unfortunately, the non-crystalline character of many animal pigments, and the difficulty of purifying them by means of the formation of salts and of separations by the use of appropriate solvents, oppose

\* A Lecture delivered at the Royal Institution of Great Britain, Friday, February 17th, 1893.

serious obstacles to elucidation. Of blood-red or hæmoglobin it cannot be said that we know the centesimal composition, much less the molecular weight. Even of hæmatin the empirical formula has not yet been firmly established. The group of black and brown pigments to which the various melanins belong still awaits adequate investigation. We know they contain nitrogen ( $8\frac{1}{2}$  to 13 per cent, and sometimes iron, but the analytical results do not warrant the suggestion of empirical formulæ for them. The more nearly they appear to approach purity the freer the majority of them seem from any fixed constituent such as iron or other metal. It is to be regretted that Dr. Krukenberg, to whom we are indebted for much valuable work on several pigments extracted from feathers, has not submitted the interesting substances he has described to quantitative chemical analysis.

I must not, however, dwell further upon these preliminary matters. I have introduced them mainly in order to indicate how little precise information has yet been gathered as to the constitution of the greater number of animal pigments, and how difficult is their study.

And now let me draw your attention to a pigment which I had the good fortune to discover, and to the investigation of which I have devoted I am afraid to say how many years.

It was so long ago as the year 1866 that the solubility in water of the red colouring-matter in the wing-feathers of a *plantain-eater* was pointed out to me. [One of these feathers, freed from grease, was shown to yield its pigment to pure water.] I soon found that alkaline liquids were more effective solvents than pure water, and that the pigment could be precipitated from its solution by the addition of an acid. [The pigment was extracted from a feather by very dilute ammonia, and then precipitated by adding excess of hydrochloric acid.] The next step was to filter off the separated colouring-matter, and to wash and dry it. The processes of washing and drying are tedious, and cannot be shown in a lecture. But the product obtained was a solid of a dark crimson hue, non-crystalline, and having a purple semi-metallic lustre. I named it *turacin* (in a paper published in a now long-defunct periodical, *The Student and Intellectual Observer*, of April, 1868). The name was taken from "*Touraco*," the appellation by which the *plantain-eaters* are known—the most extensive genus of this family of birds being *Turacus*.

From the striking resemblance between the colour of arterial blood and that of the red touraco feathers, I was led to compare their spectra. Two similar absorption-bands were present in both cases, but their positions and intensities differed somewhat. Naturally I sought for iron in my new pigment. I burnt a portion, dissolved the ash in hydrochloric acid, and then added sodium acetate and potassium ferrocyanide. To my astonishment I got a precipitate, not of Prussian blue, but of Prussian brown. This indication of the presence of copper in turacin was confirmed by many tests, the metal itself being also obtained by electrolysis. It was obvious that the proportion of copper present in the pigment was very considerable—greatly in excess of that of the iron (less than 0.5 per cent) in the pigment of blood.

Thus far two striking peculiarities of the pigment had been revealed, namely, its easy removal from the web of the feather, and the presence in it of a notable quantity of copper. Both facts remain unique in the history of animal pigments. The solubility was readily admitted on all hands, not so the presence of copper. It was suggested that it was derived from the Bunsen burner used in the incineration, or from some preservative solution applied to the bird-skins. And it was asked, "How did the copper get into the feathers?" The doubters might have satisfied themselves as to copper being normally and invariably present by applying a few easy tests and by the expenditure of half-a-crown in acquiring a touraco wing. My results were, however, confirmed (in 1872) by several independent observers, including Mr. W.

Crookes, Dr. Gladstone, and Mr. Greville Williams. And in 1873 Mr. Henry Bassett, at the request of the late Mr. J. J. Monteiro, pushed the inquiry somewhat further. I quote from Monteiro's "*Angola and the River Congo*," published in 1875 (vol. ii., pp. 75–77). "I purchased a large bunch of the red wing-feathers in the market at Sierra Leone, with which Mr. H. Bassett has verified Professor Church's results conclusively," &c., &c. Mr. Bassett's results were published in the *CHEMICAL NEWS* in 1873, three years after the appearance of my research in the *Phil. Trans.* As concentrated hydrochloric acid removes no copper from turacin, even on boiling, the metal present could not have been a mere casual impurity; as the proportion is constant in the turacin obtained from different species of touraco, the existence of a single definite compound is indicated. The presence of traces of copper in a very large number of plants, as well as of animals, has been incontestably established. And, as I pointed out in 1868, copper can be readily detected in the ash of banana fruits, the favourite food of several species of the "*turacin-bearers*." The feathers of a single bird contain on the average 2 grains of turacin, corresponding to 0.14 of a grain of metallic copper; or, putting the amount of pigment present at its highest, just one-fifth of a grain. This is not a large amount to be furnished by its food to one of these birds once annually during the season of renewal of its feathers. I am bound, however, to say that in the blood and tissues of one of these birds, which I analysed immediately after death, I could not detect more than faint traces of copper. The particular specimen examined was in full plumage; I conclude that the copper in its food, not being then wanted, was not assimilated.

Let us now look a little more closely at these curious birds themselves. Their nearest allies are the cuckoos, with which they were formerly united by systematists. It has, however, been long conceded that they constitute a family of equal rank with the Cuculidæ. According to the classification adopted in the Natural History Museum of the order Picariæ contains eight sub-orders, the last of which, the Cocyges, consists of two families, the Cuculidæ and the Musophagidæ. To the same order belong the Hoopoes, the Trogons, the Woodpeckers. The plantain eaters or Musophagidæ are arranged in six genera and comprise twenty-five species. In three genera—*Toracus*, *Gallirex*, and *Musophaga*—comprising eighteen species, and following one another in zoological sequence, turacin occurs; from three genera (seven species)—*Corythæola*, *Schizorhis*, and *Gymnoschizorhis*—the pigment is absent. [The coloured illustrations to H. Schlegel's Monograph (Amsterdam, 186c) on the Musophagidæ were exhibited.] The family is confined to Africa; eight of the turacin-bearers are found in the west sub-region, one in the south-west, two in the south, two in the south-east, four in the east, two in the central, and two in the north-east. It is noteworthy that, in all these sub-regions save the south-east, turacin-bearers are found along with those plantain-eaters which do not contain the pigment. Oddly enough two of the latter species, *Schizorhis africana* and *S. zonura*, possess white patches destitute of pigment in those parts of the feathers which in the turacin-bearers are crimson. These birds do not—I will not say cannot—decorate these bare patches with this curiously complex pigment. [Some extracts were here given from the late Mr. Monteiro's book on Angola (vol. ii., pp. 74–79), and from letters by Dr. B. Hinde. These extracts contained references to curious traits of the touracos.]

Usually from twelve to eighteen of the primaries or metacarpo-digitals and secondaries or cubitals, amongst the wing-feathers of the turacin-bearers have the crimson patches in their web. Occasionally the crimson patches are limited to six or seven of the eleven primaries. I have observed this particularly with the violet plantain-eater (*Musophaga violacea*). In these cases the crimson head-feathers, which also owe their colour to turacin, are few in number, as if the bird, otherwise healthy, had

been unable to manufacture a sufficiency of the pigment. I may here add that the red tips of the crest-feathers of *Turacus meriani* also contain turacin.

In all the birds in which turacin occurs this pigment is strictly confined to the red parts of the web, and is there unaccompanied by any other colouring-matter. It is therefore found that if a single barb from a feather be analysed, its black base and its black termination possess no copper, while the intermediate portion gives the blue-green flash of copper when incinerated in the Bunsen flame. [A parti-coloured feather was burnt in the Bunsen flame, with the result indicated.

Where it occurs, turacin is homogeneously distributed in the barbs, barbels, and crochets of the web, and is not found in granules or corpuscles.

To the natural question "Does turacin occur in any other birds besides the touracos?" a negative answer must at present be given. At least my search for this pigment in scores of birds more or less nearly related to the Musophagidæ has met with no success. In some of the plantain-eaters (species of *Turacus* and *Gallirex*) there is, however, a second pigment closely related to turacin. It is of a dull grass-green colour, and was named Turacoverdin by Dr. Krukenberg in 1881. I had obtained this pigment in 1868 by boiling turacin with a solution of caustic soda, and had figured its characteristic absorption-band in my first paper (*Phil. Trans.*, vol. clix., 1870, p. 630, fig. 4). My product was, however, mixed with unaltered turacin. But Dr. Krukenberg obtained what certainly seems to be the same pigment from the green feathers of *Turacus corythaix*, by treating them with a 2 per cent solution of caustic soda. I find, however, that a solution of this strength dissolves, even in the cold, not only a brown pigment associated with turacoverdin, but ultimately the whole substance of the web. By using a much weaker solution of alkali (one part to a thousand of water) a far better result is obtained. [The characteristic absorption-band of turacoverdin, which lies on the less refrangible side of D, was shown; also the absorption-bands of various preparations of turacin.] I have refrained from the further investigation of turacoverdin, hoping that Dr. Krukenberg would complete his study of it. At present I can only express my opinion that it is identical with the green pigment into which turacin when moist is converted by long exposure to the air or by ebullition with soda, and which seems to be present in traces in all preparations of *isolated* turacin, however carefully prepared.

A few observations may now be introduced on the physical and chemical characters of turacin. It is a colloid of colloids. And it enjoys in a high degree one of the peculiar properties of colloids, that of retaining, when freshly precipitated, an immense proportion of water. Consequently, when its solution in ammonia is precipitated by an acid, the coagulum formed is very voluminous. [The experiment was shown.] One gm. of turacin is capable of forming a semi-solid mass with 600 grms. of water. Another character which turacin shares with many other colloids is its solubility in pure water and its insolubility in the presence of mere traces of saline matter. It would be tedious to enumerate all the observed properties of turacin, but its deportment on being heated and the action of sulphuric acid upon it demand particular attention.

At 100° C., and at considerably higher temperatures, turacin suffers no change. When, however, it is heated to the boiling-point of mercury it is wholly altered. No vapours are evolved, but the substance becomes black and is no longer soluble in alkaline liquids, nor, when still more strongly heated afterwards, can it be made to yield the purple vapours which unchanged turacin gives off under the same circumstances. This peculiarity of turacin caused great difficulty in its analysis, for these purple vapours contain an organic crystalline compound in which both nitrogen and copper are present, and which resist

further decomposition by heat. [Turacin was so heated as to show its purple vapours, and also the green flame with which they burn.] This production of a volatile organic compound of copper is perhaps comparable with the formation of nickel- and ferro-carbonyl.

The action of concentrated sulphuric acid upon turacin presents some remarkable features. The pigment dissolves with a fine crimson colour, and yields a new compound, the spectrum of which presents a very close resemblance to that of hæmatoporphyrin [Turacin was dissolved in oil of vitriol; the spectrum of an ammoniacal solution of the turacoporphyrin thus produced was also shown], the product obtained by the same treatment from hæmatin; in other respects also this new derivative of turacin, which I call turacoporphyrin, reminds one of hæmatoporphyrin. But, unlike this derivative of hæmatin, it seems to retain some of its metallic constituent. The analogy between the two bodies cannot be very close, for if they were so nearly related as might be argued from the spectral observations, hæmatin ought to contain not more but less metal than is found to be present therein.

The percentage composition of turacin is probably:—Carbon, 53.69; hydrogen, 4.6; copper, 7.01; nitrogen, 6.96; and oxygen, 27.74. These numbers correspond pretty nearly to the empirical formula,  $C_{82}H_{81}Cu_2N_9O_{32}$ . But I lay no stress upon this expression.

I have before said that copper is very widely distributed in the Animal Kingdom. Dr. Giunti, of Naples, largely extended (1881) our knowledge on this point. I can hardly doubt that this metal will be found in traces in all animals. But besides turacin only one organic copper compound has been as yet recognised in animals. This is a respiratory, and not a mere decorative, pigment like turacin. Léon Fredericq discovered this substance, called hæmocyanin. It has been observed in several genera of Crustacea, Arachnida, Gastropoda, and Cephalopoda. I do not think it has ever been obtained in a state of purity, and I cannot accept for it the fantastic formula— $C_{867}H_{1369}CuS_4O_{258}$ —which has recently been assigned to it. On the other hand, I do not sympathise with the doubts as to its nature which F. Heim has recently formulated in the *Comptes Rendus*.

It is noteworthy, in connection with the periodic law, that all the essential elements of animal and vegetable organic compounds have rather low atomic weights,—iron, manganese, and copper representing the superior limit. Perhaps natural organic compounds containing manganese will some day be isolated, but at present such bodies are limited to a few containing iron, and to two—hæmocyanin and turacin—of which copper forms an essential part.

If I have not yet unravelled the whole mystery of the occurrence and properties of this strange pigment, it must be remembered that it is very rare and costly, and withal difficult to prepare in a state of assured purity. It belongs, moreover, to a class of bodies which my late master, Dr. A. W. von Hofmann, quaintly designated as "dirts" (a magnificent dirt truly!)—substances which refuse to crystallise and cannot be distilled. I have experienced, likewise, during the course of this investigation, frequent reminders of another definition propounded by the same great chemist, when he described organic research as "a more or less circuitous route to the sink"!

I am very glad to have had the opportunity of sharing with an audience in this Institution the few glimpses I have caught from time to time during the progress of a tedious and still incomplete research into the nature of a pigment which presents physiological and chemical problems of high if not of unique interest.

Let my last word be a word of thanks. I am indebted to several friends for aid in this investigation, and particularly to Dr. MacMunn, of Wolverhampton, the recognised expert in the spectroscopy of animal pigments.

THE PROBABLE DESTRUCTION OF  
BACTERIA IN POLLUTED RIVER WATER  
BY INFUSORIA.\*

By D. HARVEY ATTFIELD, M.A., M.B., B.C., D.Ph., Cantab,  
Demonstrator in the Public Health Laboratories, King's College.

TOWARDS the end of June, 1892, Professor Dr. Emmerich, of the Hygienic Institute of the Royal University of Munich, suggested that possibly infusoria had something to do with that self-purification of impure water which is well known to occur in many circumstances. With the object of investigating this matter I carried on the following series of experiments in the laboratories of the Institute:—

On July 1st two 1-litre flasks, which may be designated A and B, were sterilised. Into each of these was introduced about 500 c.c. of water drawn from a certain disused well. This water contained an average of 10,000 bacteria per c.c., as estimated by counting the colonies on gelatin plates in the usual manner, but was almost free from infusoria. To A was added 10 c.c. of River Isar water. The latter was collected about 150 metres below the influx of one of the main Munich sewers. The Isar water contained much *Beggiatoa alba*, and swarmed with infusoria as well as with the bacteria of the sewage. The infusoria were for the most part *Paramœcia aurelia* and *P. caudatum*. After diluting a portion of A with sterilised water three gelatin plates were made containing respectively:—

(1) 0'008 c.c. of A. (2) 0'016 c.c. of A. (3) 0'024 c.c. of A.

Three plates were also made from the contents of B—that is, the well water without Isar water:—

(1) 0'010 c.c. of B. (2) 0'020 c.c. of B. (3) 0'050 c.c. of B.

The plates and the two flasks were then placed in the cellar of the Institute, because the temperature there resembled that of the well from which the water was drawn.

July 2nd.—No colonies were as yet found on the plates. The infusoria in A were observed to be in active movement. More plates were prepared from A and B.

July 4th.—From the counting of the colonies on the plates prepared on July 1st—

A had 259,000 bacteria per c.c.  
B had 10,000 bacteria „

Additional plates were made from A and B. The plates prepared from A on July 2nd showed that A had on that day an average of 364,000 bacteria per c.c.

July 5th.—The plates made on July 4th had not developed sufficiently for counting the colonies. Further plates were prepared from A and B.

July 6th.—The plates made from A on July 4th showed 48,500 bacteria per c.c.

July 8th.—The plates made on July 5th from A showed a bacterial contents of 47,500 per c.c.; from B, 5,450.

These results may be thus tabulated:—

A, 10,000 Bacteria per C.c.—Isar Water Added.

July 1st, per c.c.	.. ..	259,000 bacteria.
„ 2nd „	.. ..	364,000 „
„ 4th „	.. ..	48,500 „
„ 5th „	.. ..	47,500 „

B, 10,000 Bacteria per C.c.—No Isar Water Added.

July 1st, per c.c.	.. ..	10,000 bacteria.
„ 5th „	.. ..	5,450 „

It thus appears that in the water (A) swarming with

infusoria, the bacteria had decreased to less than one-fifth of their original number in six days; whereas in the water (B) containing very few, if any, infusoria, the decrease of the bacteria in six days was only one-half of their original number.

I now made another series of experiments, using in the one case Isar water taken from *above*, and, in the other, from *below*, a point of inflow of sewage. A suggestion having been made that in the previous experiments perhaps light had something to do with the destruction of the bacteria—for a certain amount of direct sunlight had access to the cellar—in this series of experiments similarly prepared vessels were protected from light by means of appropriate covers of black cardboard.

The contents of the two bottles were kept in constant movement by blowing a slow current of air through each bottle by means of a forcing air-pump, the air being filtered through plugs of sterilised cotton-wool. The water used was, for A, collected 150 metres below the influx of the main Munich sewer into the Isar. It contained some *Beggiatoa alba* and infusoria. For B, the water was collected, as I have said, from the Isar above Munich. The methods of procedure, namely, making plate cultures and counting the colonies, were carried out as in the previous series of experiments.

The figures obtained from these results may be tabulated as follows:—

A.—Isar water from below Munich with a little *Beggiatoa alba* and many *Paramœcia*.

B.—Isar water from above Munich, containing no apparent infusoria.

		A.	Bacteria per c.c.
Plates of July 11	.. ..	637,000	
„ „ 13	.. ..	462,000	
„ „ 14	.. ..	3,300	
„ „ 15	.. ..	11,000	
„ „ 16	.. ..	1,200	
		B.	Bacteria per c.c.
Plates of July 11	.. ..	5,900	
„ „ 13	.. ..	23,800	
„ „ 14	.. ..	33,300	
„ „ 15	.. ..	26,500	
„ „ 16	.. ..	2,000	

In all these cases, with one exception, the plates were counted after from thirty-six to forty-eight hours. The exception is that of the A plates dated July 15th, when, owing to unavoidable absence, the counting was not done till about seventy-two hours after preparation; hence, perhaps, the increase noted.

Here again the proportional amount of decrease of bacteria between the water with infusoria and that without them will be observed to be very marked. In A the decrease is from 637,000 to 1200,—that is, as from 500 to 1,—while in B it is from 33,300 to 2000—that is, nearly 17 to 1.

On July 19 a fresh series of experiments was started. As before, samples of water from below Munich with infusoria and from above the town without them were collected in sterilised bottles.

In this series, however, each water, A and B, was divided into two equal portions, which may be designated as A<sub>1</sub> and A<sub>2</sub>, and B<sub>1</sub> and B<sub>2</sub>; the two former being from below and the two latter from above Munich, as before. At the time of taking these samples the Isar was in flood, and in consequence the water was very turbid from suspended matter. Through A<sub>1</sub> and B<sub>1</sub> air was blown, while A<sub>2</sub> and B<sub>2</sub> were not so treated.

From these samples six sets of plate cultures were prepared in the course of fourteen days, and from the data thus afforded the following Tables are compiled:—

\* From the *British Medical Journal*, June 17, 1893.

A, with Infusoria.

July 19.	3,000,000 Bacteria per c.c.	
	A <sub>1</sub> with Air.	A <sub>2</sub> without Air.
July 21.. ..	215,000	567,000?
" 23.. ..	101,250	196,000
" 25.. ..	35,552	58,000
" 28.. ..	42,920	97,000
Aug. 1 .. ..	13,200	Not counted.

B, without Infusoria.

July 19.	700 Bacteria per c.c.	
	B <sub>1</sub> with Air.	B <sub>2</sub> without Air.
July 21.. ..	1,470,000	354,900
" 23.. ..	1,285,000	797,550?
" 25.. ..	504,000	228,159
" 27.. ..	250,500	80,800
Aug. 1 .. ..	121,500	Not counted.

Examining this Table, we find there is very little difference in the proportional decrease of bacteria, whether sterilised air be driven through the fluid or not.

Secondly, in this series some very interesting ocular evidence of the purification that was going on was noticed—namely, the water in the A bottles became quite bright and clear, while the water in the B bottles became thicker and more turbid. Prof. von Pettenkofer, to whom I showed these bottles, was particularly struck by this point.

Thirdly, in this last series the presence of Infusoria seemed to have a more marked effect than in the foregoing experiments. For, in ten days, a water containing 3,000,000 bacteria per c.c. decreased in bacterial contents to a little over 13,000, while the water containing no Infusoria not only gave no decrease in numbers, but rose in bacterial contents from 700 per c.c. to 121,500 in the same time, namely ten days.

From all of these experiments it would seem that Infusoria have some powerful influence in the getting rid of bacteria, and, possibly, so aiding in the "self-purification" of water.

## PROCEEDINGS OF SOCIETIES.

### ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, July 3, 1893.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.,  
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—His Royal Highness The Duke of Connaught, K.G. (Honorary Member), and Alfred Walter Soward, F.C.S.

The special thanks of the Members were returned for the following donations to the Fund for the Promotion of Experimental Research at Low Temperatures:—Ludwig Mond, £500; Robert Hannah, £50; Sir Walter Gilbey, Bart., £21; Henry Arthur Blyth, £21; James Blyth, £21.

The special thanks of the Members were returned to Mr. William Schooling for his present of portraits of Sir George B. Airy, Professor J. Crouch Adams, Professor Cayley, and Dr. William Huggins.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

A Burette Float.—R. Benedikt (*Chemiker Zeitung*).—The mark is inside, so that it cannot be obliterated by use.

## 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. cxvi., No. 26, June 26, 1893.

**Formation of Natural Aluminium and Iron Phosphates. Phenomena of Fossilisation.**—Armand Gautier.—Ammonium phosphate has its origin in the bacterial decomposition and the oxidation of nitrogenous matter, animal or vegetable, or it may be originally derived from the phosphorus of the igneous rocks and from the ammonia derived from the reactions of the elements of the central nucleus. This ammonium phosphate, as soon as it is dissolved in water, attacks the oxides and the carbonates which it encounters. Thus there are formed not merely the calcium phosphates of the phosphates, but the aluminium, copper, and iron phosphates. Thus minervite,  $P_2O_5, Al_2O_3, 7H_2O$ , is produced by the action of a layer of guano upon a subjacent stratum of hydrargillite. The same reaction gives rise to the mixed aluminium and calcium phosphates found in the small islands of Alta Vela, Redonda, and Commandeur. The author has reproduced these reactions experimentally. In contact with ferrous carbonate dissolved in water containing carbonic acid or of siderose in fine powder, ammonium phosphate produces ferrous phosphate, though very slowly. This is one of the sources of vivianite and of dufrenite. The simultaneous formation of ammonia, hydrogen sulphide, and other products of slow bacterial fermentation, with the intervention of the air dissolved in the waters generally, involves the simultaneous formation—in soils at once calcareous and ferruginous—of calcium phosphates and of pyrites. These substances accompany each other, as in the green-sand of the pas de Calais and the Ardennes, where beds and nodules of phosphates are enclosed among strata rich in pyrites.

**Combinations of Oxalic Acid with Titanic and Stannic Acids.**—E. Péchard.—Oxalic acid yields with mineral acids, such as the titanate and stannate, definite compounds. The author has previously demonstrated this property for molybdic acid, and Rosenheim has pointed it out for tungstic and vanadic acids. In the salts studied there are always 2 mols. of oxalic acid to 1 mol. of titanate acid.

**Researches on the Arsenic and Antimony Chlorosulphides.**—L. Ouvrard.—Dry hydrogen sulphide reacts at common temperatures upon arsenic chloride, giving a yellow precipitate like arsenic sulphide with an abundant escape of hydrochloric acid. The precipitate, when washed with carbon disulphide, has the composition  $As_2S_5Cl$ . Three antimony chlorosulphides have been already obtained by Cloez and Schneider. The author has obtained the compound  $SbS_2Cl$  in reddish brown crystals, and on prolonging the action of the current of hydrogen sulphide there is obtained another compound,  $Sb_2S_5Cl$ .

**Action of Carbon Monoxide upon Sodiammonium and Potassiammonium.**—A. Joannis.—The author has obtained with carbon monoxide and potassium a compound potassium carbonyl,  $C_2O_2K$ . Sodiammonium,  $C_2O_2Na$ , has a faint lilac tint, and detonates in presence of small quantities of air or water. The temperature of 90° occasions an explosion.

**Combinations of Boron Bromide with Phosphorus Bromides.**—M. Tarible.—Boron bromide combines easily with the two phosphorus bromides, forming the compounds  $PBr_3BBr_3$  and  $PBr_5BBr_3$ . Both these substances are well crystallised, and are decomposed in the cold by water, chlorine, and gaseous ammonia.

**Action of Zinc and Magnesium upon Metallic Solutions, and on the Determination of Potassa.**—A. Villiers and Fr. Borg.—This paper will be inserted in full.

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*Bulletin de la Société Chimique de Paris.*  
Series 3, Vols. ix. and x., No. 10.

**Thio-derivatives of Cellulose.**—C. F. Cross, E. J. Bevan, and C. Beadle.—The substance of this paper has already appeared in an English organ.

**Qualitative and Quantitative Analysis of Formaldehyd.**—A Trillat.

**Electric Crucible.**—MM. Ducretet and Le Jeune.—Already noticed.

**Different Toxicities of Stereoisomeric Bodies.**—At the meeting of the Société Chimique, April 28th, °C. Chabré expressed the opinion that stereoisomeric bodies may have different toxicities. He reserved the question of the two conicines, and had studied the four tartaric acids. He showed that the lævo-rotatory acid was more poisonous than the dextro-rotatory acid, both being more poisonous than racemic acid, and the inactive acid incapable of being split up. He represented the relative portions of these acids required to produce a fatal effect as 34·26, 104·24, 165·25, and 196·27. He concludes with the consideration that the spores of *Penicillium*, mixed with a solution of racemic acid, split it up into dextro-rotatory acid, which they destroy, and into a lævo-rotatory acid, which they tolerate for a time. Hence it results that a slightly poisonous solution has become more poisonous under the influence of micro-organisms without the production of a chemical compound of a new species. This will be poisoning without a poison. If, instead of a racemic solution, we have a solution of the inactive acid which cannot be split up, the spores have not increased its toxicity; and the author asks if the intangible differences between an individual enjoying immunity against certain pathogenic microbes and another individual which does not possess this immunity, may not depend on the circumstance that the one has in its liquids the same products as the other, but in a different stereoisomeric condition. The author purposes to study pathological bloods and those of vaccinated and non-vaccinated subjects to verify this hypothesis.

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*Zeitschrift für Analytische Chemie.*  
Vol. xxxii., Part 2.

**Detection of Ammonia by the Nessler Reaction.**—L. L. de Koninck.—An alcoholic solution of ammonia gives no yellowish brown precipitate, nor even a colouration, with the Nessler test. Alcohol does not, however, prevent the reaction of ammonia with mercuric chloride (Bohlig's reaction).

**Systematic Method for the Detection and Separation of the more common Acids.**—F. Harrison.—From the CHEMICAL NEWS.

**Micro-chemical Analysis of Rocks.**—Frey (*Pharm. Schweiz. Wochenschrift*).—Already inserted.

**Various Applicability of the Centrifugal Machine for Analytical Purposes.**—Various machines have been described by W. Thörner (*Chemiker Zeitung*), C. G. Haubold, F. Heynemann, and Fr. Hegershof (trade circulars).

**Prevention of Bumping in Boiling Liquids.**—G. Craig (CHEMICAL NEWS); also Pellagio, Winkelhofer, and H. Müller in former issues of the *Zeit. Anal. Chemie*.

**Production of the Sodium Light.**—H. Kräl (*Chem. Zeitung*).—Already inserted.

**New Rings for Retort-stands, &c.**—Morris and Hicks.—From the *Chemist and Druggist*.

**Arrangement for Decantation and Filtration.**—W. Saulmann (*Zeit. f. Angew. Chemie*).—This article requires the accompanying figure.

**A New Colorimeter.**—Gallenkamp (*Chem. Zeitung*).—The apparatus consists of two troughs of mirror-glass placed side by side. One of the troughs has the form of a parallelepipedon and contains the liquid in question. The other, which is wedge-shaped downwards, contains the normal solution.

**Laboratory Heating Appliances.**—Various spirit-lamps are described by Barthel (*Chemiker Zeitung*), Muencke (*Ibid.*), and a furnace for organic combustions designed by F. Fuchs (*Zeit. für Angewandte Chemie*).

**Universal Economical Gas-burner.**—R. Röher (*Chemiker Zeitung*).—A safety burner is proposed by Porges. (From a trade circular).

**Laboratory Apparatus for Speedily Heating Liquids.**—Wiesneg.—From the *Journal des Usines à Gaz* and the *Chemiker Zeitung*.

**Preservation of Solutions of Metaphenyldiamine for the Detection of Nitriles and Hydrogen Peroxide.**—G. Denigès (*Journ. de Pharmacie et de Chemie*).—The author dissolves 2 grms of the hydrochloric substance in 100 c.c. of ammonia and places the solution in a bottle fitted with a ground glass stopper. To this solution he adds 5 grms. pulverised animal charcoal, shakes up vigorously several times, allows it to settle, repeats the shaking hourly three or four times, and allows the liquid to subside over night. If the supernatant liquid is not sufficiently decolourised, the shaking must be repeated. In this manner there may be obtained a liquid almost entirely colourless. It keeps for an indefinite length of time in contact with animal charcoal if not more than from 2 to 4 parts of metaphenyldiamine have been used with 100 parts of ammonia. Aqueous and alcoholic solutions cannot be preserved. For detecting nitrous acid 5 drops of the reagent are mixed with 5 c.c. of dilute sulphuric acid (1:5). To this mixture, which should be colourless, the author adds 100 c.c. of the water under examination, and heats for five minutes in the water-bath. A yellow colouration, which appears distinct if seen in the direction of the axis of the test-glass, indicates nitrous acid.

**Determination and Separation of the Xylols.**—J. M. Crafts.—From the *Comptes Rendus*.

**Examination of, and Judicial Decision upon, Animal Matter designed for Human Food.**—W. Eber.—From a work published by the author, and already inserted.

**Detection of Extracted Tea used as a Sophisticant.**—W. A. Tichomeirow.—Already inserted.

**Two Air-baths for Heating Substances in Glass Tubes under Pressure.**—H. Pemberton and D. Woodman.—From the *American Chemical Journal* and the *Four. Soc. Chem. Industry*.

**A Thermometer of Precision.**—Porges.—From a circular.

**Sources of Error in Analyses Owing to the Use of Gas.**—E. von Meyer (*Journal für Prakt. Chemie*), Van Leeuwen (*Trav. Chim. des Pays-Bas* and *Chem. Zeitung*), Ad. Nieben (*Akad. der Wissenschaften in Wien*), Privoznik (*Berichte*), U. Collan (*Chemiker Zeitung*).

**Presence of Lead in Commercial Ammonia said to be pure.**—W. F. Lowe (*Journal Soc. Chem. Industry*).

**Determination of Vanadic Acid.**—A. Ditte (*Comptes Rendus*).

**Reactions of the three Isomeric Amidobenzoic Acids.**—Oechsner de Coninck.—Noticed under *Comptes Rendus*.

**Detection of Phenoles.**—L. M. A. Lambert (*l'Union Pharmaceutique*).—Already inserted.

**Detection of Nitrobenzene.**—J. Marpurgo (*Pharm. Post*).—Already inserted.

**Determination of Nitrogen in Organic Substances.**—Notices of papers by Association of Official Agricultural Chemists (CHEMICAL NEWS), E. B. Voorhees (*Ibid.*), J. H. Smith (*Chemiker Zeitung*), J. O'Sullivan (*Journal Soc. Chem. Industry*), Frankland (*Phil. Trans.*), Keating Stock (*Analyst*), Hugnet (*Journal de Pharmacie and Chemiker Zeitung*), Vincent Edwards (CHEMICAL NEWS), H. Synder (*Four. Amer. Chem. Soc.*), E. Fricke (*Zeit. Angewandte Chemie*), Stutzer (*Zeit. Ang. Chemie*), Ulsch (*Chem. Centralblatt*), Boyer (*Comptes Rendus*), Arnold and Wedemeyer (*Amer. Journ. Pharmacy*).

**Determination of Vanilline.**—F. X. Moerk (*American Journal of Pharmacy*).—The author has previously shown that facitious vanilline, on treatment with bromine-water and addition of ferrous sulphate, takes a bluish green colour. He now finds that natural vanilla extract, if previously purified with recently precipitated lead hydroxide, gives the same reaction.

**Gottlieb's Modification of Röse's Method of Determining Milk Fat.**

**Examination of Olive Oil and of Butter.**—Roaul Brulte.—From the *Comptes Rendus*.

**Execution of the Reaction for Sesame Oil.**—G. Ambübl (*Schweiz. Wochen. f. Pharm.*).—The author dissolves 0.1 to 0.2 grm. of white sugar in 20 c.c. hydrochloric acid of sp. gr. 1.18, adds 10 c.c. of the oil, and shakes it well up. Sesame gives an intense red colour. Olive oil, containing only 10 per cent of oil of sesame, gives a pure deep rose colour. Pure olive oil (Tuscan, San Remo, Nice, and Provence) gives no red colour, only the Bari oils after some minutes turn a more violet-blue shade. Old, very rancid sesame oil gave an indigo-blue colour.

**New Normal Hydrometer for Must.**—Barth (*Weinlaube*).—The author states the degrees of the must of different grapes in degrees of Oechsle's scale.

**Agreements on the Analysis of Malt.**—(*Dingler's Polytech. Journal*).

**Lavender Oil and Bergamot Oil.**—J. Bertram and H. Waldbaum.—The editors refer to a commercial report by Schimmel and Co.

**Determination of Quinine in Cinchona Barks.**—J. H. Schmidt.

**Micro-chemical Distinction of Alkaloids and Protein Substances.**—Errera.—From the *Pharm. Journal and Transactions*.

**Valuation of Ipecacuanha.**—G. Kottmeyer (*Pharm. Post*).—Already inserted.

**Micro-chemical Detection of Phosphorus in the Tissues.**—L. Lilienfeld and A. Monti (*Zeit. f. Physiol. Chemie*).

**Determination of Uric Acid.**—F. G. Hopkins.—From "Guy's Hospital Reports."

**Action of Benzoyl Chloride upon Ammonia, Urea, and Kreatinin.**—V. Lehmann (*Zeit. Physiol. Chemie*).—No deposition of benzamid is observed on treating human urine with benzoyl, though it is obtained from the urine of some of the lower animals. Further papers on the detection of sugar in urine, on that of the carbohydrates in general in urine and in the blood, are not adapted for useful abstraction.

**Determination of Glycogen in the Liver and the Muscles.**—S. Fränkel (*Pflüger's Archiv*).—The author simplifies the ordinary process by using trichloroacetic acid instead of mercury-potassium iodide for the precipitation of the albumenoids.

**Identification of Coniin in a Toxicological Case.**—Launcelot W. Andrews.—From the *American Chemical Journal*.

**Researches on Cobalt.**—Hugo Remmler (*Zeit. für Anorganische Chemie*).—Already inserted.

## MISCELLANEOUS.

**The New Heidelberg Laboratory.**—We perceive that in the new chemical laboratory of the University of Heidelberg a special room is set apart for chemico-legal investigation.

**Quantitative Detection of Bacteria.**—Dr. Gottstein proposes the use of hydrogen peroxide for recognising the presence of bacteria. If the number of bacteria in a specimen of water reaches 10,000 per c.c., there is a brisk evolution of oxygen, and there is an appreciable liberation of this gas even with 1000 per c.c.

**Owens College, Manchester.**—Bishop Berkeley Research Fellowships have been awarded by the Council as follows:—H. B. Pollard, M.A. (Oxon), in Zoology; Albert Griffiths, M.Sc. (Vict.), and J. A. Harker, D.Sc. (Tübingen), in Physics; Bevan Lean, B.A., B.Sc. (Lond.), in Chemistry; and a Fellowship has been renewed to Stanley Dunkerley, M.Sc. (Vict.), in Engineering.

## 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.

C. S. will be glad to know of the best *small* book on the analysis of steel and iron, and the analysis of ores, in English or French.

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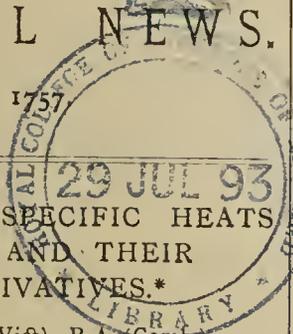
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ON THE RATIO OF THE SPECIFIC HEATS OF THE PARAFFINS AND THEIR MONOHALOGEN DERIVATIVES.\*

By J. W. CAPSTICK, M.Sc. (Vi&), B.A. (Camb.),  
Scholar and Coutts-Trotter Student of Trinity College, Cambridge.

THE experiments were undertaken to find whether the internal energy of the molecules of organic gases, as deduced from the ratio of the specific heats, showed any regularities corresponding to the chemical resemblances symbolised by the graphic formulæ.

The paraffins and their monohalogen derivatives are very suitable for the purpose, as their chemical relations to each other are simple, they are easily volatile, and are stable enough to be unaffected by ordinary purifying agents.

For the ratio of the specific heats we can calculate the relative rates of increase of the internal energy and the energy of translation of the molecules per degree rise of temperature, and, the aim of the experiments being to compare the rates of increase of the internal energy of different gases, it was decided to keep the translational energy constant by working at a constant temperature. Consequently the determinations were all made at the temperature of the room.

The ratio of the specific heats was calculated from the velocity of sound in the gases. This was determined by Kundt's method, using a double-ended form of apparatus, in all essential features the same as that described in *Pogg. Ann.*, vol. cxxxv. The tube in which the dust figures were made was 125 c.m. long and 26 m.m. in diameter, which Kundt showed to be great enough to avoid any lowering of the velocity of sound from the influence of the walls of the tube.

Lycopodium was used for forming the figures in the hydrocarbons and in methyl and ethyl chlorides, but in the heavier gases it became sticky, and would not move readily, so for these silica was used.

To measure the figures a piece of apparatus was constructed, consisting of a pair of parallel platinum wires, carried by a framework which slides along a steel slide graduated to millimetres. The tube was placed on V-shaped supports, parallel to the scale, and between the wires, which were so adjusted that their plane passed through the centre of the nodes. The position of the framework was then read on the scale, tenths of a millimetre being estimated with the help of a lens. With figures of average quality the setting of the wires could be repeated so as to agree within two or three tenths of a millimetre. The greatest divergence of the observed length of any one figure from the mean of the series was usually about five or six tenths of a millimetre.

The calculation of the ratio of the specific heats from the velocity of sound requires the density of the gas to be known, a circumstance which makes the method very sensitive to small amounts of impurity in the material.

Regnault's value was used for methane, and every precaution was taken to secure pure gas. Two methods of preparation were used, Gladstone and Tribe's, by the action of the copper-zinc couple on methyl iodide and alcohol, and Frankland's, by the action of zinc methyl on water. After each experiment an analysis of the gas was made to test its purity and to determine the amount of air present, for which a correction was made.

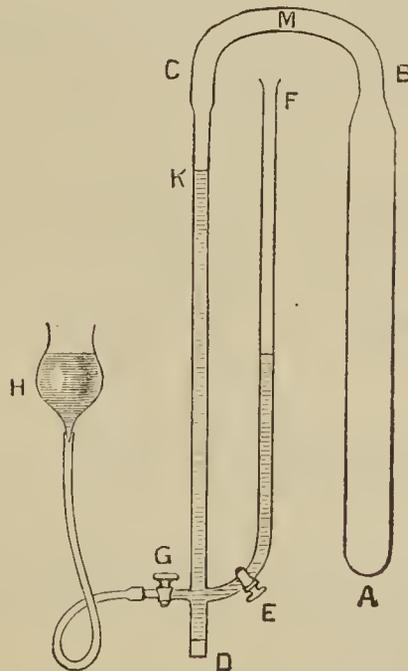
The ethane was prepared by the action of zinc ethyl on water, and for it the theoretical density calculated from the molecular weight was used.

For the preparation of propane, isopropyl iodide was reduced by zinc and hydrochloric acid, and the gas was freed from air by liquefaction in a freezing mixture of ether and solid carbonic acid, after passing through fuming sulphuric acid and potash, and over 30 grms. of palladium.

Methyl and ethyl chlorides were prepared in the usual way, by passing hydrochloric acid into a boiling solution of zinc chloride in the corresponding alcohol, and purified by re-distillation through suitable reagents. All the rest of the compounds were purchased from Kahlbaum, and were dried and fractionated before being used.

The vapour densities of propane and all the halogen compounds were determined at various pressures for the material, as it was used in the velocity of sound experiment, thus avoiding to a great extent any error arising from impurity.

The apparatus used for this purpose is shown in figure. Before joining the parts together, the tube, c d, is calibrated, and after it has been attached, but before the side tubes are fixed on, the volume of the whole is determined



by filling with water and weighing. Then, from the calibration of c d, the volume is known between A and a file mark at k.

A weighed quantity of the liquefied gas whose vapour density is required is sealed up in a small tube with capillary ends, and introduced at d, and, by inclining the apparatus, is made to slide over the bend and rest at M. The end, d, is then closed with a cork, and the apparatus exhausted through the three-way tap, G; on the completion of which operation mercury is allowed to flow in from the reservoir, H, and the tap, E, is opened. The difference of the levels of the mercury in the two tubes is read with a cathetometer, and, subtracted from the height of the barometer, gives the pressure of the residual air. On tilting the apparatus, the tube slides over into the wider part, and the end breaks off, allowing the liquid to evaporate. By reading the levels again we get the pressure of the gas, and knowing its weight and volume, we have all the materials required for calculating its specific gravity.

In the experiments the reservoir was always adjusted so that the level of the mercury in c d stood near the mark at k, thus simplifying the calculations a little.

The apparatus was found to give values of the vapour density concordant to about 1 part in 1000.

\* Abstract of a Paper read before the Royal Society, June 15, 1893.

The formula used in calculating the ratio of the specific heats was—

$$\gamma = 1.408 \times \rho \times \left(\frac{l}{v}\right)^2 \left(1 + \frac{1}{p} \frac{d}{dv}(pv)\right),$$

the last factor being added to the ordinary formula to correct for the divergence of the gas from Boyle's law.

The correction is obtained at once by putting in the equation—

$$u^2 = -\gamma v^2 \left(\frac{dp}{dv}\right)_t \text{ the value of } \left(\frac{dp}{dv}\right)_t \text{ given by}$$

$$\left(\frac{dp}{dv}\right)_t = p + v \left(\frac{dp}{dv}\right)_t.$$

From the vapour-density determinations a curve is constructed giving  $pv$  in terms of  $v$ , and the slope of this curve at any point gives the value of  $\frac{d}{dv}(pv)$  in arbitrary units. Dividing by the corresponding value of  $p$  in the same units, we obtain the amount of the correction.

The correction increases the ratio of the specific heats by from 1 to 2 per cent in most cases.

Observations varying in number from three to nine were made on each gas, the extreme range of the values being 2 per cent for marsh gas,  $1\frac{1}{2}$  per cent for methyl iodide, and 1 per cent, or less, for the rest.

The mean values are shown in the following table:—

Methane .. .. .	CH <sub>4</sub> .. ..	1'313
Methyl chloride .. .. .	CH <sub>3</sub> Cl .. ..	1'279
Methyl bromide .. .. .	CH <sub>3</sub> Br .. ..	1'274
Methyl iodide .. .. .	CH <sub>3</sub> I .. ..	1'286
Ethane .. .. .	C <sub>2</sub> H <sub>6</sub> .. ..	1'182
Ethyl chloride .. .. .	C <sub>2</sub> H <sub>5</sub> Cl .. ..	1'187
Ethyl bromide .. .. .	C <sub>2</sub> H <sub>5</sub> Br .. ..	1'188
Propane .. .. .	C <sub>3</sub> H <sub>8</sub> .. ..	1'130
Normal propyl chloride .. .. .	nC <sub>3</sub> H <sub>7</sub> Cl .. ..	1'126
Isopropyl chloride .. .. .	iC <sub>3</sub> H <sub>7</sub> Cl .. ..	1'127
Isopropyl bromide .. .. .	iC <sub>3</sub> H <sub>7</sub> Br .. ..	1'131

From this Table we have the interesting result that the gases fall into four groups, the members of any one group having within the limits of experimental error the same ratio of the specific heats.

These groups are—

- I.—Methane.
- II.—The three methyl compounds.
- III.—Ethane and its derivatives.
- IV.—Propane and its derivatives.

If the members of a group have the same ratio of the specific heats, we know, from a well-known equation in the kinetic theory of gases, that the ratio of the internal energy absorbed by the molecule to the total energy absorbed, per degree rise of temperature, is the same for all. Hence we have the result that, with the single exception of marsh gas, the compounds with similar formulæ have the same energy-absorbing power, a result which supplies a link of a kind much needed to connect the graphic formula of a gas with the dynamical properties of its molecules.

From the conclusion we have reached it follows with a high degree of probability that the atoms which can be interchanged without effect on the ratio of the specific heats have themselves the same energy-absorbing power, their mass and other special peculiarities being of no consequence. Further, the anomalous behaviour of methane confirms what was clear from previous determinations, namely, that the number of atoms in the molecule is not in itself sufficient to fix the distribution of energy, and suggests that perhaps the configuration is the sole determining cause,

If this is so, it follows that ethane and propane have the same configuration as their monohalogen derivatives, but that methane differs from the methyl compounds, a conclusion that in no way conflicts with the symmetry of the graphic formulæ of methane and its derivatives, for this is a symmetry of reactions, not of form.

## ON THE IODOMETRIC DETERMINATION OF THE NITRATES.\*

By HIPPOLYTE GRUENER.

DR. KONINCK and Nihoul (*Zeitschr. f. Angewandte Chem.*, 1890, p. 477) describe a method for the iodometric determination of nitrates, in which the decomposition of the nitrates is effected by the action of gaseous hydrochloric acid, the gases evolved being passed into potassium iodide; but the method is a cumbersome one. In a former paper (*Amer. Journ. Sci.*, xlv., p. 117), by Prof. Gooch and myself, a method was described according to which nitrates were decomposed successfully and easily by a solution of manganous chloride in hydrochloric acid, the products of decomposition being passed into potassium iodide, and the liberated iodine titrated with sodium thiosulphate. The ease with which hydriodic acid has been applied in this laboratory as a reducing agent in the determination of arsenic, chloric, and antimonic acids (*Amer. Journ. Sci.*, xl., p. 66; xlii., p. 220; xlii., p. 213) has suggested its application for the same end to nitric acid, and the present paper is the account of attempts in this direction.

*The Action of Phosphoric Acid and Potassium Iodide upon Nitrates.*—The decomposition of the last traces of nitrates in presence of potassium iodide and sulphuric acid does not occur except at very great concentrations, and, as at great concentrations sulphuric acid in presence of hydriodic acid itself liberates iodine, the use of syrupy phosphoric acid to bring about the required decomposition naturally suggested itself. Various attempts to simplify the process while still registering the amount of reduction by arsenic acid in the residue proved futile, and a distilling apparatus was found to be necessary. For this purpose a small retort was used, the neck of which was bent downward about 2 inches from the body, so that the retort itself might be tipped backward, allowing the unbenched portion of the retort to run upward, thus guarding against loss from spattering. Into the tubulature of the retort was ground a glass tube drawn out at both ends to serve as a perforated stopper for the entrance of carbon dioxide. The neck was passed through a rubber stopper into a side-neck Erlenmeyer flask, the exit tube of which was prolonged and dropped into a side-neck test-tube used as a trap. The retort was covered with a simply contrived hood which kept the upper parts warm and prevented the iodine from settling anywhere. In the retort was placed the nitrate with an excess of potassium iodide, and in the receiver a known amount of decinormal solution of arsenious oxide strongly alkaline with hydrogen sodium carbonate and diluted to a convenient bulk. The trap contained nothing but water. The phosphoric acid used was at first 10 c.m.<sup>3</sup> of strong acid, sp. gr. 1.7, with varying amounts of water; but when it was found that the amount of water present was an essential feature, a definite mixture was used as designated in the Tables. The acid was added to the retort last of all, and after carbon dioxide had been passed for a sufficient length of time heat was applied. The carbon dioxide was evolved in a Bonn generator from materials which had been carefully boiled, and cuprous chloride was added to the acid in the generator to take up the oxygen from any traces of air. Between the introduction

\* *American Journal of Science*, xlv., July, 1893.—Contributions from the Kent Chemical Laboratory of Yale College.

of phosphoric acid into the retort and the application of heat a good stream of gas was passed for ten minutes, at the end of which time the bubbles escaping at the last trap were completely absorbed in potassium hydrate of the requisite strength.

The first experiments were in blank with no nitrate present. Upon warming the mixture of phosphoric acid and 2 grms. of the iodide, signs of free iodine were developed; and by titration of the contents of the receiver at the end, iodine to the amount of 0.0014 gm. was found to have been liberated, either by residual traces of air or by dissociation. The experiment was repeated; but in this case all the water used had been boiled immediately before the experiment, and here iodine to the extent of 0.0009 gm. only was found to have been liberated. The cause and remedy for this liberation of iodine are discussed presently. A series of experiments was performed to study the action of the reagents when nitrates were present.

The method of procedure was as follows:—The nitrate was taken for convenience from a solution of 5 grms. in 500 c.m.<sup>3</sup> of water. The iodide was introduced dry or in solution, according to the bulk of water allowable. This mixture was boiled a moment to drive out all air, the phosphoric acid was then added, and carbon dioxide was passed as described, the receiver containing the arsenious oxide and the trap being already in position. It had been found that all but a trace of iodine was caught in the first receiver, so that the rubber stopper closing it could do no harm. When large amounts of nitrate were used, the clots of solid iodine settling out in the receiver were dissolved by means of a crystal or two of potassium iodide. The solution in the retort was boiled until it was clear that all the iodine had distilled over, and usually until the boiling in the retort had ceased. It was found advisable to empty the retort so soon as it was cool enough, else the phosphoric acid became unmanageable. The retort after each experiment was washed out with ammonia and water.

The results of these first experiments are shown in Table I.

TABLE I.

KNO <sub>3</sub> taken.	KI taken.	Water added to 10 c.m. <sup>3</sup> of phosph. acid, sp. gr. 1.7.	KNO <sub>3</sub> found.	Error in KNO <sub>3</sub> .	Error in HNO <sub>3</sub> .
Grm.	Grm.	C.m. <sup>3</sup> .	Grm.	Grm.	Grm.
Series 1.					
1 0.0005	0.2	2	0.0009	0.0004+	0.0002+
2 0.0010	0.2	2	0.0012	0.0002+	0.0001+
3 0.0020	0.2	2	0.0021	0.0001+	0.0001+
4 0.0050	0.2	2	0.0055	0.0005+	0.0003+
5 0.0100	0.2	2	0.0093	0.0007-	0.0004-
6 0.0100	0.2	2	0.0103	0.0003+	0.0002+
7 0.0200	0.3	3	0.0216	0.0016+	0.0010+
8 0.0200	0.3	3	0.0192	0.0008-	0.0005-
9 0.0200	0.3	3	0.0205	0.0005+	0.0003+
10 0.0200	0.3	3	0.0205	0.0005+	0.0003+
11 0.0500	0.5	6	0.0496	0.0004-	0.0002-
12 0.0500	0.5	6	0.0499	0.0001-	0.0001-
13 0.0300	0.5	4	0.0293	0.0007-	0.0004-
Series 2.					
14 0.0616	1.5	1	0.0682	0.0066+	0.0039+
15 0.0570	2.5	1	0.0643	0.0073+	0.0045+
16 0.1030	1.1	1	0.1061	0.0031+	0.0018+
17 0.1062	1.1	1	0.1197	0.0135+	0.0081+

With one or two exceptions the results of Series 1 are fairly good. Those of Series 2 are very bad. The only essential difference between the two series is in the dilution of the phosphoric acid used. In the first series there is always enough water present to make the specific gravity of the phosphoric acid no higher than 1.6 for small amounts of iodide and nitrate, and lower than that number when these amounts are increased. The suggestion is obvious that dissociation of the hydriodic acid

may occur at the boiling-point of the stronger acid. According to Berthelot (*Ann. de Chim. et Phys.* [IV.], xx., p. 392) aqueous solutions of hydriodic acid under pressure begin to dissociate at 275°, or even under. The temperature of the retort at the end of an experiment was taken and found to be far beyond the range of a thermometer reading to 360°. It is evident, then, that under the conditions there should be opportunity for dissociation. Four experiments in which potassium iodide was treated with phosphoric acid, sp. gr. 1.7, undiluted, gave of liberated iodine caught in arsenious acid 0.0030 gm., 0.0044 gm., 0.0049 gm., 0.0030 gm. of iodine, corresponding to 0.0008 gm., 0.0012 gm., 0.0013 gm., 0.0008 gm. of potassium nitrate respectively. These results would account only in part for the errors noted, but they are in the same direction. Chapman (*Fourn. Chem. Soc.*, xx., 1867, p. 166) has found that concentrated hydriodic acid acting upon organic nitrates and nitrites reduces them not alone to nitric oxide, but even in part to ammonia. The conditions of the experiments in Series 2 approximate to concentration of the hydriodic acid, and the reaction that Chapman found probably takes place here to a limited extent. Concentration of the hydriodic acid then must be avoided, both to eliminate dissociation and excessive reduction of the nitrate.

Therefore the plan was adopted of diluting the solution, so that the temperature and concentration should be effective in decomposing the nitrate, but should not bring about the complications just mentioned. A blank experiment made thus, 18 c.m.<sup>3</sup> of a solution of phosphoric acid of specific gravity 1.39, being used, gave of liberated iodine only 0.0004 gm. corresponding to 0.0001 gm. of potassium nitrate. So that under these conditions we may be assured that dissociation occurs, if at all, to only a slight extent. In the following experiments, therefore, the nitrate is decomposed in presence of dilute phosphoric acid, the dilution and the quantity taken being included in Table II.

TABLE II.

KNO <sub>3</sub> taken.	KI taken.	Found.	Sp. gr. of solution of phosphoric acid.	Amount of sol. used.	Error KNO <sub>3</sub> .	Error HNO <sub>3</sub> .
Grm.	Grm.	Grm.		C.m. <sup>3</sup> .	Grm.	Grm.
Series 3.						
18 0.0500	1	0.0500	1.43	17	0.0000	0.0000
19 0.0200	0.5	0.0201	1.43	17	0.0001+	0.0001+
20 0.0200	1	0.0198	1.43	17	0.0002-	0.0001-
21 0.0250	1	0.0250	1.43	17	0.0000	0.0000
22 0.0300	1	0.0307	1.43	17	0.0007+	0.0004+
23 0.0300	1	0.0312	1.43	17	0.0012+	0.0007+
24 0.0350	1	0.0353	1.43	17	0.0003+	0.0002+
25 0.0400	1	0.0409	1.35	20	0.0009+	0.0006+
26 0.0450	1	0.0444	1.35	20	0.0006-	0.0004-
27 0.0500	1	0.0499	1.37	20	0.0001-	0.0001-
Series 4.						
28 0.0600	1	0.0568	1.37	20	0.0032-	
29 0.0600	1	0.0575	1.37	20	0.0025-	
30 0.0600	1	0.0576	1.37	20	0.0024-	
31 0.0600	2	0.0588	1.37	20	0.0012-	
32 0.0600	2	0.0605	1.37	18	0.0005+	
33 0.0700	2	0.0708	1.37	18	0.0008+	
34 0.0800	2	0.0811	1.37	18	0.0011+	
35 0.0900	2	0.0842	1.37	18	0.0058-	
36 0.1000	2	0.0996	1.37	18	0.0004-	
37 0.1000	2	0.1012	1.37	18	0.0012+	
38 0.1000	1.5	0.0909	1.37	18	0.0091-	
39 0.1000	2.5	0.0979	1.37	18	0.0021-	
40 0.1021	3	0.1005	1.43	17	0.0016-	
41 0.1032	2	0.0949	1.43	17	0.0085-	

The iodine of 41 was collected in potassium iodide and titrated with thiosulphate. Series 3 requires little special comment. The experiments ran along smoothly, the manipulation was easy, the care required in watching

very little, and the results are fairly satisfactory. The causes leading to the high results of Series 2 seem entirely eliminated by the dilution. Series 4 is a direct continuation of Series 3, differing in the single point that larger amounts of nitrate are handled. These results with some exceptions are decidedly low. It appears that with a fair percentage of water present, as the amounts of nitrate grew larger, the error became a negative one. The explanation for this seemed to be that the last portions of nitric acid must have distilled before decomposition, whenever the original amount was large. Nitric acid was accordingly tested for in the distillate, and to this end all the conditions of the experiment were repeated, except that the receiver contained only water. Of the nitrate 0.4 gm., and of the iodide 4 grms., twice the amount theoretically necessary, were put into the retort, and at the end of the experiment the solution in the receiver was boiled with hydrogen peroxide to decompose the hydriodic acid and drive out the iodine, care being taken to keep enough water to hold any nitric acid present. When all the iodine was gone sodium carbonate was added, the solution evaporated, and the residue ignited and tested with a saturated solution of manganous chloride in hydrochloric acid, as described in the previous paper above mentioned. By this means 0.002 gm. potassium nitrate are very easily detected in 10 c.m.<sup>3</sup> of solution. Nitric acid was found in the distillate of this experiment as well as in two others conducted with 0.2 gm. and 0.1 gm. of the nitrate respectively. The residues in the retorts of these three tests showed no trace of nitric acid.

The process seems reliable enough, then, for estimating nitrates in small quantities not exceeding an equivalent of 0.04 gm. or 0.05 gm. of potassium nitrate. Every experiment performed with quantities not larger than 0.05 gm. has been given here, except four in which an imperfection in the apparatus showed an obvious mechanical loss. The errors in these experiments lie between the extremes of 0.0016 gm. + and 0.0008 gm. - on the nitrate, with an average error of 0.00016 gm. If Series 3 alone is taken, in which the dilution of the phosphoric acid was regulated, we have as extreme errors 0.0012 gm. + and 0.0006 gm. -, with a mean error of 0.0002 gm. +. With quantities of nitrate above 0.05 gm. the process does not seem a safe one, inasmuch as with a moderate amount of water present some nitric acid distils over undecomposed, and with little water present other complications as seen above arise.

The method so far as it is applicable may be summed up as follows:—The nitrate not to exceed in amount 0.05 gm. of potassium nitrate, is introduced into a retort, together with ten times its weight of potassium iodide, and 17 to 20 c.m.<sup>3</sup> of phosphoric acid, of specific gravity 1.43. All water used should be recently boiled. Carbon dioxide is passed from a receiver carefully set up. The neck of the retort passes into a receiver containing a known amount of decinormal arsenious oxide, alkaline with a good excess of hydrogen sodium carbonate, and diluted to a convenient bulk. To this flask is attached for additional safety a simple trap containing water. The solution in the retort is boiled until it is clear that no more iodine remains, when the receiver, after proper washing and addition of the liquid in the trap, is titrated with iodine to find the amount of arsenious oxide still left. This gives the measure of the iodine evolved and consequently of the nitrate present, according to the equation—



(To be continued).

Borings at Paruschowitz.—In May last the borings at Paruschowitz, in Upper Silesia, reached the depth of 2000 metres. Geothermic experiments are being made with very sensitive thermometers.—*Revue Universelle des Mines.*

## CONGRESS OF THE SOCIETY OF GERMAN NATURALISTS AND PHYSICIANS.

THIS Association, founded by the illustrious Lorenz Oken, will hold its 65th Congress at Nürnberg, from Sept. 11th to 15th inclusive. It is well known that this body was the model on which the British Association and similar societies in France, America, &c., were afterwards formed. The original German body differs, however, in many respects from imitators in other countries. It includes, in addition to the "Naturforscher,"—a term much more comprehensive than its English equivalent "Naturalist,"—the medical practitioners of all grades. This combination would not, we think, prove desirable in Britain, as we have an annual Medical Congress. It is free from the worst defect of the British Association—the so-called Economical and Statistical Section. The Germans know that statistics must be considered not as a science, but merely as a method applicable in various sciences, and that political economy borders perilously upon party politics and finds sufficient scope in Chambers of Commerce.

The German Association is also free from that phenomena of technological considerations by which its French colleague is unfavourably characterised.

The Nürnberg meeting will comprise 32 sections—namely, 1, mathematics and astronomy; 2, physics; 3, chemistry; 4, botany; 5, zoology; 6, entomology; 7, mineralogy and geology; 8, ethnology and anthropology; 9, anatomy; 10, physiology; 11, pathology; 12, pharmacology; 13, pharmacy and pharmacognosia; 14, internal medicine; 15, surgery; 16, obstetrics and gynaecology; 17, medical treatment of children; 18, neurology and psychiatry; 19, medical treatment of the eyes; 20, medical treatment of the ears; 21, laryngology and rhinology; 22, dermatology and syphilis; 23, hygiene and medical police; 24, forensic medicine; 25, medical geography, climatology, tropical hygiene; 26, military sanitation; 27, dentistry; 28, veterinary medicine; 29, agricultural chemistry; 30, instruction in mathematics and natural science; 31, geography; 32, instrumental knowledge.

Men of science who purpose visiting this Congress may learn all further particulars on application to Herr Medicinalrath Merkel, Nürnberg, Josephsplatz 3, and may engage apartments in hotels or private lodgings through the medium of Herr J. Gallinger, Nürnberg, Burgstrasse 8. Such applications should be made as early as possible, as rooms cannot be guaranteed after August 31st.

### NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.

By Lieut.-General C. A. McMAHON, F.G.S.

(Continued from p. 32).

#### PART II.

##### Table of Sulphates.

It will be convenient and will save space to preface the Table of Sulphates with the general formula of the *alums*. Omitting the selenates and mixed selenates and sulphates, the general formula is  $\text{M}_{23}\text{SO}_4 \cdot \text{N}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ; where M=Al, Cr, Mn, Fe, In, or Ga; and N=Na, K, Rb, Cs, NH<sub>4</sub>, Ag, or Tl.

The best known combinations are—

M	with N.
Al	„ Na, K, NH <sub>4</sub> , Rb, Cs, NH <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> ), Ag, or Tl.
Cr	„ Na, K, or NH <sub>4</sub> .
Mn	„ — K or NH <sub>4</sub> .
Fe	„ — K or NH <sub>4</sub> .
Ga or In	„ — — NH <sub>4</sub> .
M <sub>2</sub>	„
CrAl	„ — K or NH <sub>4</sub> .

The *alums* are strictly isomorphous. They crystallise in forms belonging to the cubic system, usually in cubes or octahedra, or in octahedra combined with cubes.

	No.	Name.	System.	Form.	Double refraction shows colours of.	Direction of major axis.	Other optical characters.
<b>ALUMINIUM.</b>							
$Al_2(SO_4)_3$ .. ..	1						
$Al_2(SO_4)_3 + 18H_2O$ ..	2	Alunogen. <i>See alums ante.</i>	M	(a) In six-sided tablets. (b) Radiating tufts like horse tails and grasses.	1st order.	About $45^\circ$ from <i>e</i> .	Boundaries of platy crystals marked by fine dark lines.
<b>BARIUM.</b>							
$BaSO_4$ .. ..	3	Barytes.	R	(a) Modified rhombic and rectangular prisms.	1st order.	(a)    to <i>e</i> .	(b) Extinguish at $45^\circ$ from the arms of skeleton.
$(BaSr)SO_4$ .. ..	4	<i>See Sr.</i>		(b) X-shaped skeleton crystals resembling ice crystals.			
<b>BERYLLIUM.</b>							
$BeSO_4 + 4H_2O$ . . .	5		T	(a) Prisms with pyramidal terminations. (b) In radiating and star-shaped arborescent forms.	7th order.	(a) <i>R.L.</i> to <i>e</i> . (b)    to fibres.	Axial sections in <i>c.p.l.</i> cross well seen. Negative.
$BeSO_4 + 7H_2O$ . . .	6	—	M	In prisms, sometimes twinned.	3rd order.	At a high angle to <i>e</i> and to twinning plane.	
$BeSO_4K_2SO_4 + 2H_2O$	7	—	—	Globulites either isolated or in perlitic looking base.	1st order.	In quadrants at <i>R.L.</i> to <i>Q.W.</i>	
<b>CALCIUM.</b>							
$CaSO_4$ .. ..	8	Anhydrite.	R	Usually combinations of the prism, pinacoids and basal planes. Microscopic crystals often boat-shaped.	4th order. In micro-crystals, usually not higher than 2nd order.	to <i>e</i> .	Interference fig. in <i>c.p.l.</i> is seen when prism lies on its macropinacoidal face.
$CaSO_4 + 2H_2O$ . . .	9	Gypsum.	M	(a) Acicular prisms often in radiating groups. (b) Swallow-tailed twins. (c) Short prisms with rhombic outline. Acute angle about $50^\circ$ . See Part III.	1st order.	(a) About $38^\circ$ from <i>e</i> , measured in direction of acute angle of rhomb.	Refraction nearly the same as Canada balsam, viz., Gypsum $n = 1.52$ . Balsam $n = 1.54$ .
$CaSO_4K_2SO_4 + H_2O$	10	Syngenite.	M	Small tabular crystals generally showing 6 or 8 sides in outline.	1st order.	About $3^\circ$ from (100).	No. 10. Refraction not far from balsam.

Remarks.

No. 2.—Dissolves in two parts of water. The tablets overlap each other and form platy masses, in which six-sided micaceous crystals can be distinguished. Two angles of  $92^\circ$  and four of  $134^\circ$ . When not mounted in Canada balsam the crystals have a peculiar pearly gloss. The pearly appearance is produced by a granular salt white in reflected and opaque in transmitted light, reminding one of the beginning of kaolinisation in felspar. Query, is this one of the basic sulphates  $Al_2O(SO_4)_2 + H_2O$  or  $Al(OH)SO_4$ ?

No. 3.—Almost insoluble in  $H_2O$  (soluble 1 in 400,000). The precipitate formed by adding  $H_2SO_4$  to an aqueous solution of a Ba salt does not yield definite crystals under the microscope. A Ba salt heated with concentrated  $H_2SO_4$  dissolves in part, and deposits on cooling crystals of  $H_2SO_4 + BaSO_4$ . If exposed to moist air, crystals of  $H_2SO_4 + BaSO_4 + 2H_2O$  are deposited. See Part III.

No. 5.—Beryllium readily forms basic sulphates. They may be obtained by boiling the normal sulphate (No. 5) with beryllium carbonate. They form gelatinous masses. The normal salt dissolves at the ordinary temperature in its own weight of water.

No. 6.—Separates out from an acid solution of the normal salt.

No. 7.—The outer margins of the globulites are hard black lines. They do not possess a radiate structure. The centres are often white in reflected, and brown and opaque in transmitted, light. The ground-mass may be either glassy or micro-granular.

No. 8.—Forms when concentrated  $H_2SO_4$  is used. With dilute  $H_2SO_4$  No. 9 forms.

No. 9.—See Part III.

No. 10.—Soluble in water 1 in 400 with separation of some gypsum. Slide shows numerous needles and prisms of gypsum with stumpy crystals of syngenite, roughly speaking resembling augite in habit. Twinning very common. Extinction between twins  $15^\circ - 24^\circ$ , sometimes less. Of the natural mineral Dana says it is elongated in the direction of vertical axis, and that the plane (100) always predominates.

	No.	Name.	System.	Form.	Double refraction shows colours of.	Direction of major axis.	Other optical characters.
CALCIUM.							
$\text{CaSO}_4\text{Na}_2\text{SO}_4$	.. 11	Glauberite.	M	(a) Crystals of approximately rhombic outline with a strong rib down centre radiating like the petals of a flower. (b) Radiating fibrous groups.	(a) Blue of 2nd order. (b) Double refraction feeble.	(a) At a high angle to rib. (b) Sometimes at high angles at low angle to fibre.	
CERIUM.							
$\text{Ce}(\text{SO}_4)_2+7\text{H}_2\text{O}$	.. 12	Ceric sulph.	—	Reniform mass.	—	—	—
$\text{Ce}_2(\text{SO}_4)_3$	.. .. 13	Cerous „	—	Small crystals and long needle-shaped prisms badly terminated.	—	—	No. 13. Straight extinction.
$\text{Ce}_2(\text{SO}_4)_3+8\text{H}_2\text{O}$	.. 14	„ „	M	Prisms terminated by clinodomes.	7th order.	At a very high angle to plane of twinning and to <i>e</i> .	No. 14. Prisms extinguished 25° from vertical edge. Some crystals exhibit absorption with single Nicol.
$\text{Ce}_2(\text{SO}_4)_3+9\text{H}_2\text{O}$	.. 15	„ „	H	(a) Prisms with pyrl. terminations. (b) Radiating fibres like spherulites. (c) Radiating tables with the habit of a zeolite.	1st order.	(a) and (b) at <i>R.L.</i> to <i>e</i> .  (c)    to <i>e</i> .	
COBALT.							
$\text{CoSO}_4+4\text{H}_2\text{O}$	.. 16		—	A peach-blossom coloured powder.			
$\text{CoSO}_4+6\text{H}_2\text{O}$	.. 17		M	In crystals.			
$\text{CoSO}_4+7\text{H}_2\text{O}$	.. 18	Bieberite or cobalt vitriol.	M	Crystalline crusts made up of obscurely-shaped granular crystals, with occasional 4- or 6-sided tabular crystals.	2nd order.	About 30° from <i>e</i> .	Dichroic. Rose-pink to amber. Relief sharp.
$\text{CoSO}_4\text{K}_2\text{SO}_4+2\text{H}_2\text{O}$	19	—	Tr				
$\text{CoSO}_4\cdot\text{K}_2\text{SO}_4+6\text{H}_2\text{O}$	20	—	M	Large tabular crystals with six, eight, or more faces, two or more corners often truncated; edges sometimes bevelled.	So high that a double <i>Q.W.</i> is sometimes required.	(a) Within a few degrees of <i>R.L.</i> to <i>e</i> in approximately rectangular prisms. (b) Within a few degrees of a line bisecting the acute angles in prisms of sphenic habit.	Extinction in (a) within a few degrees of <i>e</i> , in (b) within a few degrees of line bisecting acute angles. Dichroic in rose-pink and amber colours. Zonal structure. Twinning not uncommon.

## Remarks.

No. 11.—The crystals (a) have one of the acute angles pointing outwards: the other is at the centre of radiating group. The rib approximately bisects the acute angles. Many of the crystals strongly recall fig. 528 Dana's system, 5th Edn. The rib is apparently the junction of  $-\bar{1} : -\bar{1}$  and  $1 : 1$ .

No. 12.—Is obtained by dissolving the dioxide in dilute  $\text{H}_2\text{SO}_4$  and evaporating in a vacuum over  $\text{H}_2\text{SO}_4$ . Ceric sulphate is decomposed by water with formation of basic salts, which vary in composition according to the quantity of water present. It forms double salts with sulphates of the alkali metals, such as  $\text{Ce}(\text{SO}_4)_2+2\text{K}_2\text{SO}_4+2\text{H}_2\text{O}$ , small yellow monoclinic crystals.

No. 13.—Separates from a warm solution. It dissolves in six parts of cold and sixty parts of hot water. Also in hot  $\text{H}_2\text{SO}_4$ , which on cooling throws down small crystals and long needle-shaped prisms, which are re-dissolved after standing for some hours.

No. 14.—Separates from a concentrated solution. It occasionally exhibits multiple twinning.

No. 15.—Separates principally from dilute solution, but generally both 14 and 15 will be found on the same slide.

Solution 1 in 6. Cerous sulphate forms several potassium cerous double salts, as—  
 $3\text{K}_2\text{SO}_4+\text{Ce}_2(\text{SO}_4)_3$  and  $\text{Ce}_2(\text{SO}_4)_3+2\text{K}_2\text{SO}_4+3\text{H}_2\text{O}$  and  $\text{Ce}_2(\text{SO}_4)_3+\text{K}_2\text{SO}_4$ .

Sodium and ammonium sulphates also form double salts with cerous sulphate.

No. 16.—Deposited when a concentrated solution of cobalt sulphate is passed into  $\text{H}_2\text{SO}_4$ .

No. 18.—Soluble in twenty-four parts of cold water. Rose colour deepens on heating; crystal becomes opaque.

No. 20.—On heating, the rose-coloured crystals become reddish violet. Some of the rose-red crystals show a positive bisectrix.

(To be continued).

ORIGIN OF OXYGEN IN THE EARTH'S  
ATMOSPHERE.

By Dr. T. L. PHIPSON, F.C.S., &amp;c.,

Graduate of the Faculties of Science and Medicine of the  
University of Brussels.

IN 1791, when Priestley's house was burnt by the Birmingham mob, and he saved his life by escaping in my grandfather's\* carriage, a considerable amount of valuable silver plate, &c., was carried off at the same time, but none of the still more valuable MSS., the results of years of labour. These were destroyed, together with the entire library and laboratory. It is therefore impossible to say how far he may have pushed his investigations with regard to the mutual dependency of plants and animals, after discovering, some twenty years previously, that a sprig of mint vegetating for a few days in air vitiated by a burning candle, restored the purity of that air sufficiently to allow the candle to burn in it again.

In the seventh edition of the "Introduction to Botany," by Sir J. E. Smith, F.R.S., edited by William Hooker (1833, p. 104), the author, alluding to the absorption of carbonic acid by plants and its replacement by oxygen, says:—"This beautiful discovery, for the main principles of which we are indebted to the celebrated Dr. Priestley, shows a mutual dependence of the animal and vegetable kingdoms on each other which had never been suspected before his time."

It is not probable, however, that Priestley could have made much further advance owing to the backward state of chemistry in his day, and to his zeal for religious and political discussions. It was reserved for the persevering researches of the Swiss chemist, Theodore de Saussure, and to the splendid genius of Justus von Liebig, to demonstrate this mutual dependency in all its striking realities. Yet it is greater than even Liebig imagined.

In discussing recently the views of the late Prof. C. J. Koene, of Brussels University, on the Chemical Constitution of the Earth's Atmosphere from remote geological periods to the present time, I have mentioned the results of certain experiments which I had made with the view of elucidating this interesting question.

I found that minute microscopic plants (*Protococcus pluvialis* and *P. palustris*) could be easily transformed, so to speak, into manufacturers of oxygen gas. I grew several kinds of plants in pure carbonic acid, and found that it did not kill them at once, as it would kill an animal, but that they lived in it for some time, though they did not prosper. In an atmosphere of hydrogen gas they lived and prospered, but the hydrogen was slowly absorbed until it had all disappeared, or nearly so, and the plants got covered with water.

In the next place I exposed my plants to an atmosphere of pure nitrogen, and to Koene's primitive atmosphere (nitrogen and carbonic acid), and I found that, in both cases, vegetation was remarkably healthy and even luxuriant for a lengthened period. A small plant of *Convolvulus arvensis* (having its roots in the soil, or in water containing ample carbonic acid and mineral ingredients) vegetated in an atmosphere of pure nitrogen for ten days—from June 22nd to July 2nd. I then let in carbonic acid (an equal volume), which in twenty-four hours was absorbed by the water to the extent of about one-half, so that the artificial atmosphere on the second day consisted of about 3 vols. of nitrogen and 1 vol. of carbonic acid. In this the vegetation became truly luxuriant from July 2nd to 15th, and would doubtless have continued very much longer had not the experiment been stopped to analyse the gas, and because the plant had reached the summit of the receptacle and was pressing against the glass.

To give the results of these observations in as few

words as possible, I may state that the plant absorbs carbonic acid by the roots, whilst it secretes oxygen by the leaves, so that after awhile the nitrogen atmosphere contains a certain quantity of oxygen, and in time it would, no doubt, approach to the composition of ordinary atmospheric air.

Now, if I endeavour to go back to the primitive ages of the globe, I find that there was probably a period at which the heat was so intense that no compounds could exist; the matter of the earth then existed in the state of free elements, or, according to my own theory,\* in the state of atoms, all identical. As the temperature decreased, compounds of all kinds were formed according to the laws of affinity, and finally there remained surrounding the solidified surface of the earth an atmosphere of nitrogen, a substance which is known to have little or no tendency to combine directly with other substances. That there was no free oxygen in this ancient atmosphere is evident from the presence of various oxidisable substances in the primitive rocks, as I have before remarked. It is *into this primitive atmosphere of nitrogen that plants have poured oxygen, year after year, for countless myriads of ages, until it has attained the composition which it has at the present day.*

There may have existed, as Koene admitted, more or less carbonic acid at certain remote periods in the history of the earth's atmosphere; but it is unlikely ever to have predominated, from the fact that it would have been absorbed by the waters, and from my experiments, which show that some of our modern plants having their roots in the soil, or in water containing carbonic acid and the necessary mineral elements, will live in an atmosphere of nitrogen.

I am therefore led to the conclusion that *the original atmosphere of our globe consisted of nitrogen alone; and that the oxygen of the atmosphere is the product of vegetable life* (which must necessarily have preceded animal life). The production of oxygen by *Protococcus pluvialis*, alluded to above, is a symbol of what took place in the primitive ages of the Earth. It will be seen by my former papers that carbonic acid must be looked upon as a volcanic product extensively diffused through the earth's strata. The primitive atmosphere of nitrogen would doubtless derive abundance of carbonic acid from volcanic action, which continued to be intense until after the coal period, and appears to have gradually diminished from that period to the present time, though it is still very active.

Putney, July 22, 1893.

ON POISONING BY BADLY-TINNED AND  
UNWHOLESOME FISH.

By Dr. A. B. GRIFFITHS, F.R.S. Edin., &amp;c.

THE poisonous ptomaines, formed from albumenoids during the decomposition of food, produce symptoms of poisoning, &c., which are said to be referable to the digestive and nervous systems. These symptoms manifest themselves at periods varying from a few hours to several days after eating the food. The symptoms produced by this class of ptomaines are the following, among others:—Unpleasant taste in the mouth, headache, vomiting, diarrhoea, salivation, dyspnoea, paralysis, and death. Several ptomaines render the heart's beats slow and weak, and in some cases of poisoning by unwholesome fish the symptoms resemble those of poisoning by atropine.

Poisoning by unwholesome foods too frequently escapes notice; nevertheless every analyst or medical man who is careful of his scientific dignity should possess a thorough knowledge of the properties of the ptomaines, which have now quite a literature of their own.

\* Thomas Phipson, of Birmingham, into whose family Dr. Priestley married, and who helped him in his political work.

\* Phipson, "Outlines of a New Atomic Theory," 4th ed., 1884.

Numerous deaths have occurred in England (see Griffiths in CHEMICAL NEWS, vol. lxii., p. 17; and the reports in *Daily Graphic*, Nov. 25th, 1892; *Daily News*, Nov. 22nd, 1892, and April 22nd, 1893), on the Continent, and in America, from eating unwholesome foods; and it has been shown that the poisonous properties of such foods are due to the action of microbes on the proteids contained in the foods. It may be stated that these poisonous properties are due to certain ptomaines or animal alkaloids. The ptomaines are produced during the putrefaction or decomposition of animal substances. By the direct action of microbes, the proteids are disintegrated, with the formation of ptomaines among other products. It will be seen, from this remark, that the ptomaines are not secreted or excreted by microbes, for they are the *residua* after microbial action. To explain the action of microbes on organic matter generally: let  $a_3b_4c_5d_3$  represent the composition of the medium in which certain microbes live, and let  $a_2b_2c_3d_1$  represent the food extracted from such a medium by the microbes for their nourishment; it therefore follows that  $a_1b_2c_2d_2$  will represent the residue or the products of the microbial action—be it fermentation, nitrification, the production of ptomaines, &c.

It should also be borne in mind that the idea of ptomaines *without* microbes is inconsistent with an impartial study of facts. It is true that a suitable filtration (*e. g.*, through porous porcelain) will separate a ptomaine from its microbe; but when this microbe is separated from the original liquid, and transferred successively to nourishing media, so as to purify it from every foreign element, it continues to produce its characteristic ptomaine (or ptomaines), which is produced at the expense of the culture fluid. There is no true ptomaine without microbes, any more than there is ergotine without *Claviceps purpurea*, vinegar without *Bacterium aceti*, or alcohol without certain species of the *Saccharomycetes*.

Such is our preliminary remarks concerning the ptomaines; we now proceed to describe a new ptomaine which we have extracted, from *putrid sardines*, by the following process:—

The putrid mass was boiled with water, filtered, and the filtrate precipitated with subacetate of lead. This precipitate was filtered off, a current of  $H_2S$  passed through the filtrate, and the plumbic sulphide separated by filtration. The filtrate was concentrated by evaporation, and then extracted with amylic alcohol. The amylic solution was repeatedly treated with water, then concentrated, acidulated with  $H_2SO_4$ , and repeatedly shaken with ether, which removes the oxy-aromatic acids. Freed from ether, it was evaporated to a quarter of its volume, and thus volatile fatty acids were driven off. The  $H_2SO_4$  was precipitated by baryta, and the precipitate removed by filtration. The excess of baryta was precipitated by a current of  $CO_2$ , and this was also removed by filtration. The fluid was heated for some time on a water-bath, cooled, and precipitated with  $HgCl_2$ . The precipitate was washed and decomposed by  $H_2S$ ; the mercuric sulphide was filtered off, and the filtrate concentrated. The hydrochloride of the ptomaine was subsequently deposited in the crystalline condition. It was dissolved in water, and then treated with pure calcium hydroxide, which liberated the base. The ptomaine was separated by chloroform, in which it is soluble; and it was finally purified by washing with alcohol and water.

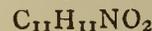
This new ptomaine is a white crystalline substance, soluble in water, and has a slight alkaline reaction. It is precipitated by hydrochloric acid in the form of a white crystalline hydrochloride. Platinic and auric chlorides precipitate this ptomaine, and the resulting platino-chloride and aurochloride are yellow crystalline compounds. This base produces with phosphomolybdic acid a greenish precipitate, with phosphotungstic acid a yellowish-white precipitate, and with picric acid a yellow one. It is also precipitated by silver nitrate and Nessler's reagent. Analyses of this base gave the following results:—

0.378 grm. of substance gave 0.9669 grm. of  $CO_2$  and 0.2034 grm. of  $H_2O$ .

0.2213 grm. of substance gave 14.1 c.c. of N.

	Found.		Calculated for $C_{11}H_{11}NO_2$ .
	I.	II.	
Carbon .. ..	69.77	—	69.84
Hydrogen .. ..	5.98	—	5.82
Nitrogen .. ..	—	7.45	7.40
Oxygen .. ..	—	—	16.94

The above figures correspond with the formula—



for this new ptomaine.

This base which has been named *sardinine*, is poisonous—producing vomiting, diarrhoea, and death; and there is little doubt that it is the cause of the poisoning which results from eating putrid sardines or sardines which have been badly tinned.

It may be useful to give a list of the ptomaines which have been extracted from the products of bacterial putrefaction of certain fishes, &c.:—

- (1.) Parvoline,  $C_9H_{13}N$ , from mackerel (Gautier and Etard).
- (2.) Hydrocollidine,  $C_8H_{13}N$ , from mackerel (Gautier and Etard).
- (3.) Scombrine,  $C_{17}H_{38}N_4$ , from mackerel (Gautier and Etard).
- (4.) Muscarine,  $C_5H_{13}NO_2$  (Brieger).
- \* (5.) Gadinine,  $C_7H_{16}NO_2$ , from cod (Brieger).
- (6.) Ethylenediamine,  $C_2H_8O_2$ , from cod (Brieger).
- (7.) Mytilotoxine,  $C_7H_{15}NO_2$ , from mussels (Brieger).
- (8.) Sardinine,  $C_{11}H_{11}NO_2$ , from sardines (Griffiths).
- (9.) Collidine,  $C_8H_{11}N$ , from cuttle-fish (De Coninck).
- (10.) Coridine,  $C_{10}H_{15}N$ , from cuttle-fish (De Coninck).

In addition to "fish-poisons," it may be mentioned, *en passant*, that Lewis (CHEMICAL NEWS, vol. lxvii., p. 52) believes that the twenty cases of poisoning in America, which resulted from eating tinned beef (in 1892), were due to neuridine ( $C_5H_{14}N_2$ ); and the poisoning which sometimes results from eating unwholesome cheese, ice-cream, &c., has been proved to be due to a ptomaine which is named tyrotoxicon ( $C_6H_5N_2$ ) by Vaughan.†

In conclusion, there is no doubt that the ptomaines play an important part in most cases of poisoning from eating unwholesome food, and it is of primary importance that analysts, medical men, and others, should make themselves thoroughly familiar with the properties of these curious products of putrefaction.

### ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.‡

By VICTOR SCHUMANN, of Leipzig.

The extension of the ultra-violet spectral region is in close connection with the invention of photography and the discovery of fluorescence. The main region of the ultra-violet light was opened up with the aid of fluorescence, but in its exploration photography has given brilliant evidence of its superiority. The fluorescence method of observation has since gradually lost ground, whilst the efficacy of sensitive plates in the ultra-violet region has increased.

\* Gadinine is non-poisonous.

† For further details concerning the ptomaines, see Griffiths's "Researches on Micro-Organisms" (Baillière), and "Manual of Bacteriology" (Heinemann); and the case of poisoning from eating ice-cream, reported in *Birmingham Daily Post*, Sept. 22, 1892.

‡ From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur.*, Class., vol. ciii., Part II., April, 1893).

The first observations in the ultra-violet region were undertaken by Edmond Becquerel (*Bibliothèque Universelle de Genève*, new series, vol. xxxix., pp. 341 to 367 [1842]), when he was studying the chemical action of the solar rays upon Daguerre plates. The solar spectra of Becquerel were formed, however, under the influence of the absorption of the glass, and they extended, therefore, only to Fraunhofer's P line.

Stokes, who recognised the greater transmissive power of quartz for light (*Phil. Trans.*, vol. cxlii., pp. 463 and 559 [1852]; vol. clii., pp. 599 to 619 [1862]), succeeded with prisms and lenses of quartz in following the ultra-violet of the solar spectrum to an extent which, measured from Fraunhofer's H line, was twice as long as the total visible spectrum. Still more surprising was his result with the electric light. The ultra-violet of his spark spectra extended to from six to eight times the length of the visible spectrum. The most refrangible rays of all substances were given by aluminium, the spectrum of which bounded the region of the smallest perceptible wave-lengths with a strongly luminous pair of lines of the wave-lengths 186.0  $\mu\mu$  and 185.2  $\mu\mu$ . More strongly deflected rays do not seem to have been ever recognised in this region by Stokes and his successors. On the same day (June 19th, 1862), when Stokes submitted to the Royal Society of London his treatise on the above subject, W. A. Miller gave in to the same Society his no less important memoir "On the Photographic Transparency of Various Bodies, &c." (*Phil. Trans.*, vol. clii., pp. 861—887 [1862]).

Both these memoirs pursued the same object—ascertaining of the ultra-violet spectra of electric origin, and the behaviour of these spectra with substances in all three states of aggregation. But whilst Stokes made his observations with the aid of fluorescence, Miller utilised the photo-chemical action of the rays and took photographs of his spectra. The method of fluorescence showed itself strikingly preferable to the photographic method in one point: Stokes arrived at the wave-length 185.2  $\mu\mu$ , whilst Miller did not get beyond the wave-length 202.4  $\mu\mu$ . Miller afterwards, induced by Stokes, repeatedly attempted to photograph the remaining rays, but always without the desired result (*Phil. Trans.*, vol. clii., p. 882: 52 aluminium). The fluorescence spectrum retained here and in the sequel an advance which extended to the considerable extent of 172.0  $\mu\mu$ .

This photographic ill success in the extreme ultra-violet excites hesitation if we see that L. Soret, Edouard Sarasin, and others, in their extensive researches, observed this part of the spectrum only by means of fluorescence. Hence it might seem as if photography was not suitable for the observation of the most refrangible light. Such an assumption is, however, completely refuted by the fact that Cornu made use of photography for determining the wave-lengths of the most refrangible rays of Mg, Cd, Zn, and Al (*Archives des Sci. Phys. et Nat.*, III. period, vol. ii., pp. 119—126 [1879]).

Cornu, driven to photography by the feeble light of his grating, adopted here the moist process, but, in contradistinction to Miller, he used the precaution of bathing the sensitised collodion plate in distilled water before its exposure to light. In this manner he obviated the most important photographic hindrance which the most refrangible rays encounter on a plate which has not been bathed, and secured at once a better photographic result.

A further difference between the experimental arrangements of Miller and Cornu deserves notice. The apparatus of these two investigators differed widely in their focal lengths. The focal distance of Miller's apparatus was by far the longer of the two. Hence the absorption of the rays in the air must have come into play to a different degree whilst the proof was taken. The experimental arrangement of Cornu was consequently preferable also in this respect.

The photographic result of Cornu for the smallest wave-lengths seemed to open out a favourable prospect

for the investigation of the ultra-violet region which had hitherto been neglected. Unfortunately the future did not answer this expectation. Experimental hindrances of an unknown kind have again estranged the region of the most refrangible rays of aluminium (198.8—185.2  $\mu\mu$ ) from photographic spectroscopy. The majority of all researches extends even at present to the neighbourhood of the most refrangible lines of cadmium (226.55—214.41  $\mu\mu$ ), and only occasionally the region of the most refrangible lines of zinc (214.41—198.8  $\mu\mu$ ) is taken into consideration. This phenomena is the more striking as since Cornu's investigations spectroscopy has obtained, in silver bromide gelatin dry plate, an auxiliary which throws into the shade, in every respect, all the results of the collodion plates formerly employed.

The gelatin plate has for a series of years conferred invaluable services upon spectral research. It is only since its introduction that photographic observation has made successful way in spectroscopy; with it the conviction has been secured that a study of the visible spectrum alone does not suffice for the comprehension of spectral processes, but that there is required as thorough a knowledge of the invisible spectral regions, especially the ultra-violet. In recent observations this necessity is taken into account wherever possible.

In view of the fruitfulness of the efforts in the ultra-violet regions which recent years have matured, it seemed to me desirable and highly remunerative to open up to photographic study the remaining ultra-violet, as far as the wave-length 185.2  $\mu\mu$ , by means of a more suitable process than those hitherto applied, and at the same time to consider the extension of this region of observation in the direction of greater deviation.

For several years I have been approaching the execution of this thought. My task resolved itself into two portions. The first was the photography of the spectral region between the wave-lengths 231.35 and 185.2  $\mu\mu$ ; the second was the opening up of the unknown region beyond 185.2  $\mu\mu$ .

The present report discusses the first part of this work, and at the same time the preliminaries for the second.

Its results, as also the representations of the apparatus used and of the spectra obtained, will form the contents of a brief subsequent second report.

Each of these portions has engaged a considerable time, and the second portion still awaits completion.

If I now venture upon publicity with the results already obtained, although years must probably elapse before the completion of my work, the step has been induced, on the one hand, by the requests of a number of eminent physicists to whom I have had the honour of submitting my chief results, and, on the other, by my own wish to bring the facts ascertained to the knowledge of the most extended circles.

(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 JUNE 30TH, 1893.

By WILLIAM CROOKES, F.R.S.,  
and  
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,  
Professor of Chemistry at the University of Oxford.

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

London, July 6th, 1893.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the

mains of the 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 June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

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

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

The quality of the water supply during June has been very good, and bears a close relationship to that of the supply during May. Towards the end of the month the long drought began to break, but the rainfall was too insignificant in quantity to make itself apparent in the composition of the waters. During June the average rainfall for Oxford, taking a mean of twenty-five years, is 2·21 inches, whereas the rainfall during the past month has only been 0·77 inch, showing a deficiency of 1·44 inch. Most of this fall took place during the latter part of the month.

In our report for May we drew attention to the steady and appreciable decrease in the proportions of common salt, oxidised nitrogen, and hardness of the Thames-derived waters. The following Table shows that the supposed deterioration in quality of the river water consequent on greatly deficient rainfall and high temperature has no foundation in fact, the increased activity of fluvial vegetation more than counteracting any slight excess of mineral matter which might theoretically be present.

1893.	Common salt per gallon.	Nitric acid per gallon.	Degrees of hardness per gallon.
March.. ..	2·167	0·931	16·80
April .. ..	2·181	0·888	15·11
May .. ..	2·196	0·611	14·66
June .. ..	2·132	0·601	14·74

The organic carbon and the oxygen required for oxidation were practically the same as in the two previous months, the difference showing an excess only in the third place of decimals.

The turbidity, or dull appearance, which has been recorded in five of the samples supplied by the Grand Junction Water Company was due to suspended clay particles, and is accounted for by temporary local disturbances in the mains resulting from the fixing of fire hydrants in accordance with the requirements of the London County Council. The turbidity was only local, samples from the works on these days being perfectly clear. With these exceptions, all the samples were well filtered, clear, and bright.

We are, Sir,  
Your obedient Servants,

WILLIAM CROOKES.  
WILLIAM ODLING.

## NOTICES OF BOOKS.

*The Newer Chemistry.* ("Theoretische Chemie vom Standpunkte der Avogadro'schen Regel und der Thermodynamik"). Von Dr. WALTHER NERNST, A. O. Professor an der Universität, Göttingen. Mit 26 Holzschnitten. Stuttgart: Verlag von Ferdinand Enke, 1893.

To a large number of chemists this excellent book will be open only in part. Unfortunately, too, this list will include many of the younger generation of chemists, for whom the book has a special significance. The title gives the reason. Of course, so far as the ordinary subject-matter of theoretical chemistry is dealt with, and expressed in everyday language, the book will find many readers, but such reading is not competent to bring out the real value of the work. It is not intended for elementary students. It has a particular purpose, and for the accomplishment of this purpose within allotted limits, much that is elementary must be assumed and passed over without special treatment, but nothing which could aid in bringing out the commanding position of thermodynamics and the kinetic theory of gases as foundation stones in the structure of chemistry has been omitted, and from this standpoint the book is consistent, complete, and fairly exhaustive.

As previously remarked, the real value of the work will not appear to the cursory, or even to the careful but non-mathematical, reader. In order to read it intelligently, an elementary knowledge of the higher mathematics will not suffice. It must not be inferred that the pages of Dr. Nernst's book bristle with integration signs; there is, on the contrary, a notable freedom from long and involved expressions, and there are abundant signs that it was the author's aim to avoid mathematical formulæ so far as possible; but, after all this is said, it is nevertheless true that unless the reader is familiar with the fundamental mathematical formulæ and equations of thermodynamics and physics generally—unless he has, withal, considerable freedom in mathematical thinking, his reading will be rather slow and painful. The style is quite concise, and the extent to which the higher analysis has been utilised has enabled a vast amount of material to be put within a comparatively small space. In this connection, some remarks of Ostwald, in the preface to his "Outlines of General Chemistry," as translated by Walker, may be quoted:—

"The task has been all the more difficult that the course of study still pursued by the average chemist has laid upon me the necessity of avoiding the employment of higher mathematics. When possible, I have applied graphic methods. When a clear proof could not be given in an elementary way, I have contented myself with simply stating the result. Of course one can, with the aid of more or less cumbersome mathematical apparatus, give an 'elementary' proof of almost anything, but experience has shown that such diffuse page-long calculations are of no real aid to the comprehension of the subject. Another reason that has led me to adopt the above mode of treatment is that the reader who has only an acquaintance with elementary mathematics may be brought to see the necessity of acquiring at least the rudiments of the higher analysis. Without such knowledge it is possible (as I have endeavoured to show in the following pages) to understand both the methods and the results of general chemistry; but for successful work in this field such knowledge is indispensable."

It would be well for every student to lay these words well to heart. The expenditure of time needed to gain the necessary mathematical training is not great, and there is no good reason why so fruitful and important a line of study should be so often omitted. The case is somewhat different with those who have to "brush up" mathematics grown rusty by disuse. In the face of all

Le Chatelier's Thermo-element for the Measurement of High Temperatures.—Emilio Damour.—An exposure of five seconds is sufficient for measuring the temperature of a space. H. M. Howe (*Mining Journal*) recommends Le Chatelier's instrument for industrial uses. L. Holborn and W. Wien have compared (*Annalen der Physik und Chemie*) the thermo-element with the air thermometer. The mean difference between separate experiments is 5°. A thermometer on the principle of the differential air thermometer has been described by H. L. Callendar, German patent No. 62,796.—*Zeitschrift für Analytische Chemie*, xxxii., Part 3.

that has been said the question *cui bono* will certainly be raised, and the claims of the methods and results of the so-called "Physical Chemistry" to particular attention will be, as they have been, more or less called in question. Whatever may be thought on this point, we certainly have to thank the modern chemistry for a host of ideas, which in their development have been wonderfully prolific; and the methods of thought it has brought in will, without doubt, exercise upon chemistry much such an effect, both in kind and degree, as did the introduction of the Cartesian philosophy upon the ancient geometry.

There is, for the present at least, little danger of chemistry becoming too speculative. The smoke of the battle between the unitary and dualistic systems has hardly cleared away, and we still have with us many of those who saw, and had active part in, that battle. It has left upon their minds an impression which will not soon be blotted out, but of which the younger generation have only a faint conception. They will not be likely to speculate too freely, or lose sight of the essentially inductive nature of the science; but the probability is that history will repeat itself. Man does not learn wisdom from the past. He prefers the hard teaching of experience, and the younger chemists will probably have to learn their own lesson from their own experience. Moreover, it is true that while the characteristic theories of "Physical Chemistry" are perfectly safe under their present exponents, the case may be quite different when they are more general subjects of investigation. The theories of one generation do not always prosper in the hands of the next. From this point of view it is very desirable that attention should often be called to the aspect of the new methods and results as they appear *in situ* in the structure of our chemical philosophy, and the work now under consideration does so in a very satisfactory manner.

The most conservative will find in it nothing which by its infusion into chemical philosophy will detract in the least from its completeness and consistency.

In conclusion, it is good news that Dr. Nernst's book is to be translated, for the German is a trifle peculiar, and it is certainly a fact that most students, in America at least, read German with very much less fluency than English, and the majority of German works of the calibre of the present one remain unread until they are translated.—JOSEPH TORREY, Cambridge, Mass., U.S.A.

*Lecture Notes on Theoretical Chemistry.* By FERDINAND G. WIECHMANN, Ph.D. New York: John Wiley and Sons, 1893. Pp. xiv.—225. 12mo. Ill.

THE author of this well-written volume, who holds the position of Instructor in Chemical Physics and Chemical Philosophy at the School of Mines, Columbia College, New York City, is already favourably known by his work on Sugar Analysis. In the present volume the author offers a general view over the wide domain of chemical theory, exhibiting very clearly the correlation of the many lines of research along which investigations of the questions of theoretical chemistry are conducted, as well as pointing out the practical bearings of its teachings on problems constantly occurring in the application of chemical knowledge.

The treatise does not, however, offer an exhaustive discussion of the subject. The scope is well shown by the headings of the chapters:—I. Introduction; II. Specific Gravity; III. Nomenclature and Notation; IV. Atoms, Atomic Mass, Valence; V. Chemical Formulæ; VI. Structure of Molecules; VII. Chemical Equations and Calculations; VIII. Volume and Weight Relations of Gases; IX. The Periodic Law; X. Solutions; XI. Energy, Chemical Affinity; XII. Thermal Relations, Thermo-chemistry; XIII. Photo-chemistry; XIV. Electro-chemistry.

In Chapter III. Dr. Wiechmann portrays briefly the development of the language of chemistry, with appro-

appropriate illustrations of the systems in use at different periods. He adopts the "Rules for Spelling and Pronouncing Chemical Terms" recommended by the committee of the American Association for the Advancement of Science. In Chapter VI. stereochemistry receives brief notice. In Chapter VII. three methods of writing chemical equations are clearly set forth. Stoichiometry is made prominent throughout, but the book is not loaded up with problems "in view of the fact that several excellent collections have been recently published." In Chapter XIV. Arrhenius's theory of electrolytic dissociation is described. In Chapter IX. Newlands receives credit for his Table.

Throughout the work the author pays due regard to the historical method of unfolding theories. He acknowledges his indebtedness to the works of Kopp, Ostwald, and Muir, and he appends an excellent bibliography of 193 titles. The book concludes with a very full index of subjects, as well as an index of names cited.

This little volume will be welcomed by all teachers who appreciate clearness and accuracy of statement, as well as modern methods of presentation. The book is fully abreast of the times.—H. C. B.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

*Revue Universelle des Mines et de la Metallurgie.*  
Series 3, Vol. xxii., Nos. 1 and 2.

**Determination of Sulphur in Fuel by the Eschka Process.**—Dr. Hundeshagen has reopened this subject in the *Chemiker Zeitung*. He concludes that with rare exceptions the Eschka process yields exact results with ordinary coals, but with coals rich in volatile sulphur compounds (and probably in nitrogen) the result may be too low. Certain lignites, if treated according to the Eschka process, yield an emission of ammonium sulphide sufficient to blacken instantly a lead-paper.

No. 3, June, 1893.

**Sterilisation of Drinking Water by the William Kuhn System.**—The author contends that water for a public supply should be absolutely sterilised. This can be effected by heat alone, the water being kept for twenty minutes at a temperature of 110°. The cost of the operation on the large scale does not exceed 0.035 franc per hectolitre. Such water, however, must not be allowed to remain in the reservoirs, &c., for longer than twenty-four hours.

*Bulletin de la Société Chimique de Paris.*  
Series 3, Vols. ix. and x., No. 13.

**Determination of Phosphoric Acid.**—M. A. Villiers and Fr. Borg.—This memoir will be inserted in full.

**Observations on the Determination of Manganese by means of Potassium Permanganate, and on the Manganese Permanganate of Antony Guyard.**—Alex. Gorgeu.—This paper will also be inserted in full.

**On the Native Manganese Oxides, Polianites, and Pyrolusites.**—A. Gorgeu.—The author here undertakes to determine the exact composition of the native manganese peroxide known as polianite, and pyrolusite.

**Absorbent Action of Cotton upon Dilute Solutions of Mercuric Chloride.**—Léo Vignon.—In these solutions cotton seems to dissociate mercuric chloride according to the equation  $\text{HgCl}_2 + \text{H}_2\text{O} = \text{HgO} + 2(\text{HCl})$ . The cotton

combines with the mercuric oxide in virtue of its acid function, whilst it simply absorbs hydrochloric acid without entering into combination.

**Determination of Mercury in Dilute Solutions of Mercuric Chloride.**—Léo Vignon.—We take, *e.g.*, 50 c.c. solution of sublimate at 1 part in 1000; we add 5 c.c. of pure hydrochloric acid at 22°, and 10 c.c. of a saturated clear solution of hydrogen sulphide. We obtain a yellow precipitate, which quickly becomes black, and filter on a filter which has been previously weighed to one-tenth of a m.grm. The precipitate is washed, dried, and weighed. It is useful to operate in comparison with a check filter, through which we have filtered a mixture of 50 c.c. of distilled water, 5 c.c. of hydrochloric acid, and 10 c.c. of H<sub>2</sub>S, which is washed like the foregoing. The weighing of this check-filter, of the same size and the same paper as the filter containing the mercury sulphide, furnishes a means for correction.

**Action of Cotton upon Sublimate Absorbed in Dilute Solutions.**—Léo Vignon.—The author concludes that bleached cotton, plunged into dilute solutions of sublimate, fixes mercuric oxide in excess over the hydrochloric acid. Cotton dried at the common temperature, then steeped in water, after some days gives up only a part of its mercury in the state of HgCl<sub>2</sub> and of hydrochloric acid. It retains mercuric oxide, HgO, and mercurous chloride, Hg<sub>2</sub>Cl<sub>2</sub>.

**Syntheses with Aluminium Chloride.**—P. Geniesse.—Already inserted.

**Cause of the Variation of the Rotatory Power in certain Solutions of Optically Active Substances with Time and Dilution, and on the Rotatory Power of Amorphous Substances.**—A. Béchamp.—This extensive memoir does not admit of useful abstraction.

ERRATUM.—P. 35, col. 1, line 5, for "D.Ph., Cantab.," read "D.P.H., Cantab."

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# THE CHEMICAL NEWS.

VOL. LXVII., No. 1758.

## THE DETERMINATION OF MANGANESE BY OXYDIMETRIC METHODS.

By ADOLPHE CARNOT.

WHEN the state of oxidation of manganese is exactly known we may find the proportion of the metal by determining the oxygen. The determination of the available oxygen may be effected quickly and satisfactorily either by a gasometric method founded on the mutual decomposition of manganese peroxide and of hydrogen peroxide, the liberation of oxygen double the quantity of that which is to be ascertained, or by one of the numerous oxydimetric methods which have been proposed. The best of these, in despatch and accuracy, seems to me that which employs standard solutions of oxalic acid and of permanganate.

But to be warranted in substituting the determination of available oxygen for that of manganese, we must be sure of the relative proportion of the two elements.

I. Ignition in contact with air, sufficiently prolonged and at a very high temperature, converts the different oxides into a compound which has almost exactly the formula  $Mn_3O_4$ . But different circumstances, especially the contact of reducing agents or the presence of powerful bases, such as the alkalis or the alkaline earths, may modify the composition. It must also be remarked that the determination of 3 equivalents of manganese has to be deduced from that of a single equivalent of oxygen, which interferes with the precision of the process.

II. The solution of manganese in nitric acid, followed by evaporation to dryness and the careful ignition of the residue until all the nitrous vapour disappears, yields a black oxide which is commonly considered as binoxide, but which has really a composition remote from  $MnO_2$ . We may approach accuracy by repeating the evaporation with nitric acid two or three times, and igniting below  $200^\circ$ ; but notwithstanding these precautions the degree of oxidation remains uncertain.

III. If we dissolve manganese in nitric acid, and introduce by small portions crushed potassium chlorate into the hot solution, we obtain a black residue which has the composition  $MnO_2$ . Other metals are generally dissolved, though the iron is not immediately eliminated.

The residue, which is insoluble in nitric acid alone, is easily dissolved with that acid along with hydrogen peroxide. By evaporation and repeated addition of concentrated nitric acid and potassium chlorate, we may arrive at a product not containing more than a minimum of iron, and in which the manganese is entirely present as  $MnO_2$ .

I have satisfied myself that after a good washing with water, cold at first and then boiling, the binoxide obtained, either by one precipitation or by two precipitations, may be accurately determined by the oxydimetric method.

IV. The results are still more certain by the method with hydrogen peroxide and ammonia, a method which I have summarily explained in 1888, and on which I have made since that date numerous series of experiments.

On pouring into the solution of manganese hydrogen peroxide, either in excess or only in a sufficient quantity, and then quickly supersaturating with ammonia and heating for some minutes to ebullition, we obtain a deep brown precipitate, in which the degree of oxidation of the manganese is very exactly expressed by the formula  $Mn_6O_{11}$  or  $5MnO_2, MnO$ .

The volumetric and gasometric determinations have

shown that 6 equivalents of manganese correspond very accurately to 5 equivalents of available oxygen.

The operation being extremely simple and rapid, the method has seemed to me to admit of frequent applications, and I have carefully studied the influence of the various circumstances which may occur.

I found that ammoniacal salts (nitrate, hydrochlorate, and especially acetate), in considerable quantities (from 10 to 20 grms.), interfere with the formation of the peroxide  $Mn_6O_{11}$ , but their influence may be counteracted by the use of a larger quantity of hydrogen peroxide.

If the precipitation of manganese is effected in presence of salts of copper, zinc, nickel, or cobalt, a small portion of these oxides, although soluble in ammonia and the ammoniacal salts, is retained by the manganese binoxide, with which they tend to form manganites comparable to the manganese manganite,  $5MnO_2, MnO$ . But we can cause them entirely to disappear, and obtain the pure manganese peroxide,  $Mn_6O_{11}$ , by re-dissolving the precipitate upon the filter in very dilute nitric acid and hydrogen peroxide, and precipitating again with ammonia. With large quantities of copper, nickel, or zinc, three precipitations are sufficient, but with cobalt five precipitations are required. We may then execute very accurately either the volumetric or the gravimetric determination of manganese.

Iron oxide, which accompanies manganese in its precipitation and interferes with its gravimetric determination, does not affect the accuracy of its volumetric determination unless it predominates. If there is more iron than manganese the determination is less satisfactory. It is, then, necessary to eliminate the main part of the iron by treatment with nitric acid and potassium chlorate (III). The insoluble residue, dissolved in nitric acid and hydrogen peroxide, and re-precipitated with ammonia, is then perfectly suitable for volumetric or gasometric determination.

This process succeeds well with ores of manganese and iron, cast metal, spiegel, and ferro-manganese.

V. We may also precipitate manganese as peroxide by the use of bromine and ammonia in the cold, taking care to leave the bromine to digest for a long time with the liquid almost neutral, or, for greater despatch, repeating the addition of bromine and ammonia twice. The manganese is deposited as an oxide, nearly black; but before proceeding to the oxydimetric determination it is necessary to submit the precipitate to a very prolonged washing with boiling water. This method is less to be recommended than the foregoing, which is more expeditious and more trustworthy.—*Comptes Rendus*, cxvi., p. 1375.

## THE SEPARATION OF COPPER FROM BISMUTH.

By ALEX. CLASSEN.

ED. SMITH and J. Salter report (*Zeits. für Anorganische Chem.*, No. 6) concerning experiments which they have made for separating copper and bismuth in solutions containing nitric acid, and refer to statements in my textbook on Electrolysis. I wish here to make known that the method itself, as also the quotations on the strength of current, the nitric acid, &c., for its execution are not due to me. The communications on the separation of these metals, at the passages indicated by Smith and Salter, have been transferred from the second edition of the book to the third edition without further remarks, though in two other passages of the book (pp. 80 and 186) it is expressly pointed out that in presence of bismuth portions pass into the copper precipitate. On p. 186 it is simultaneously mentioned how bismuth is to be separated from copper.

It has long been known that, in presence of bismuth, copper is not deposited pure, as has been confirmed by

the researches of W. Hampe and V. Klobulow. Three years ago I utilised the fact that bismuth can be deposited electrolytically from a solution containing free nitric acid for obtaining pure bismuth; and I pointed out that, along with metallic bismuth on the negative electrode, a coating of bismuth peroxide is obtained on the positive electrode, which, however, disappears towards the end of the decomposition, as Smith and Salter have recently confirmed. These chemists have further occupied themselves with experiments for separating bismuth from lead in a solution containing nitric acid, and they have found that the lead peroxide obtained is always bismuthiferous. I had previously made the same observation in connection with obtaining bismuth in a state of purity. In the work referred to it is stated:—"If the bismuth contains lead it is by degrees totally deposited as peroxide on the positive electrode along with bismuth peroxide. No separation of metallic lead takes place at the negative electrode provided there is a sufficiency of nitric acid and that feeble currents are employed.

As Smith and Salter project further experiments on the behaviour of different metals with the current in presence of nitric acid, and have already announced a separation of mercury from bismuth, I remark that as far back as 1880 I have shown (*Berichte*, xix., 323) that these metals cannot be separated in the manner mentioned. These facts are here especially pointed out with reference to the circumstance that the proposals for the separation of bismuth from lead and mercury have been already transferred to my book without criticism.—*Zeitschrift für Anorganische Chemie*, iv., p. 234.

### SOME NEW LABORATORY FITTINGS.\*

By G. A. GOYDER, F.C.S., Analyst and Assayer.

A MODIFIED form of sulphuretted hydrogen apparatus has been fitted up both in the assay and students' laboratory, and as they have been found to work very economically, and with less trouble than those previously in use, and with a minimum of smell, a description of them is appended.

#### Construction.

The construction of the apparatus may be readily seen from Fig. 1.

The stopper in A should fit loosely.

The tap A may be replaced by a pinchcock.

The valve B may be made by bending a 10 c.c. or 15 c.c. pipette, and it is joined to A by a piece of rather stout indiarubber tubing, the ends being tightly tied over the glass. This remark applies to all the indiarubber tube connections used. The lower end of B is drawn out, as at C, so that only a very thin stream of acid can run through it: B is fixed in the neck of B by means of a short indiarubber stopper.

B is most conveniently made from a Woolfe's bottle, with three necks at the top and one neck near the bottom (a bottle with two necks at the top only may, however, be used, by having an indiarubber stopper perforated with three holes, through which pass B F, and a syphon reaching to the bottom instead of the tap D. See 1.) A bottle 3 feet high by about 5 inches in diameter, as shown by the dotted line, would be much preferable to the one used, which is about 7 inches high by 5 inches diameter, but the former are not at present procurable.

The middle neck of B—E—is used for inserting the sulphide of iron, and should be easily accessible, and fitted with an indiarubber stopper tied down.

The third neck of B is fitted with a tube, as shown at H enlarged. This may be done by drawing out a glass tube to a capillary and sealing the end; the bulb H is then

blown out; the tube is then heated at G over the blow-pipe flame, while blowing into the other end of the tube until a hole is made, the edges of which are flattened down by the blowpipe; the sealed end is then cut off, leaving a small opening: F is fitted into the neck of B by means of an indiarubber cork pressed down about half an inch, and the cup thus formed filled with melted pitch. The same method is used for the other necks fitted with tubes, and in case of a breakage the stoppers can be removed after warming the neck carefully with a Bunsen flame.

The funnel P in E is kept closed by a glass rod tipped with indiarubber tubing.

The sulphuretted hydrogen branch-pipes for students are made by joining glass T-pieces, as seen enlarged at G. The down pipe T is drawn out to a thick capillary and cut off, and the size of the capillary adjusted by blowing through the other end of the tube, after fitting a glass tube to it with indiarubber tubing, until only a slow stream of air passes when blowing with moderate pressure.

The arrangement of the different bottles can of course be modified by varying the lengths of the connecting-tubes to suit the space available.

In setting up the apparatus care should be taken that fresh acid may be poured into A, fresh sulphide of iron put into B, more water poured into E, and spent acid drawn off through D, without disconnecting any of the parts or moving any of the bottles.

A is filled with dilute hydrochloric acid, one acid to one water.

B. As much mercury is put in B as will fill at least 4 inches of the upright tube.

B. Some small marbles are placed at the bottom of B to prevent D being choked by sulphide of iron, and the rest of the bottle is filled with sulphide of iron.

C contains 3 inches of mercury.

D is filled with cotton-wool.

E is filled with distilled water.

The bulb H in F is not essential.

Taps may be used instead of the clips at TT'.

#### Action.

The apparatus being set up as described, the tap N being closed, on opening tap A the acid flows gently into B through B, and H<sub>2</sub>S gas is generated. As soon as the pressure rises in B the mercury in B is driven back and stops the flow of acid. Should much acid have entered B the pressure may increase until the mercury is depressed to the bottom of I in C, when some gas escapes through K into the draught cupboard. On opening N the gas passes through G into F; thence through D into E, where it is slowly absorbed by the water, which soon becomes saturated. The beaker of solution X is then connected with T by the tube V, and the clip on W opened, when a slow and regular current of H<sub>2</sub>S passes until the clip is again replaced on W. Similar beakers may of course be attached to T', T'', &c.

H<sub>2</sub>S water may be drawn from E by R as required.

Fresh acid is poured into A as required.

The sulphide of iron in B should be replaced, before it gets low, through E, A being turned off meanwhile.

More water may be added to E through the funnel P, the tap N being turned off before taking out plug Q.

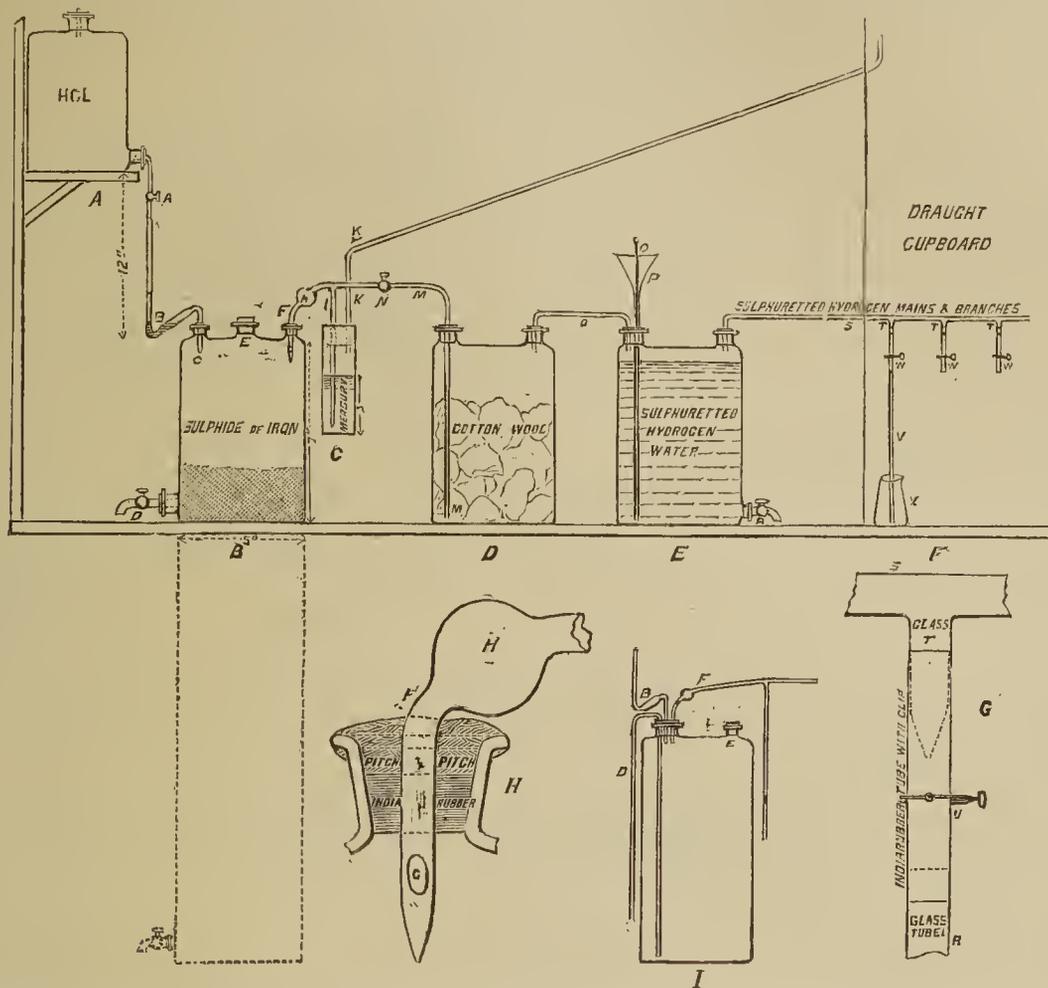
The tap A can be left open, except when putting sulphide of iron into B; and the tap N need only be closed when the apparatus is not required, as the large size of D and the water in E in a great measure prevent the blow off of H<sub>2</sub>S through K when a rapid supply of gas is suddenly stopped.

The mercury in the valve B remains quite clear and bright; that in the safety blow-off tube C has become a little blackened after six months' use, but its action is quite unimpaired.

The sulphuretted hydrogen water in E keeps quite clear and bright, and free from any trace of iron.

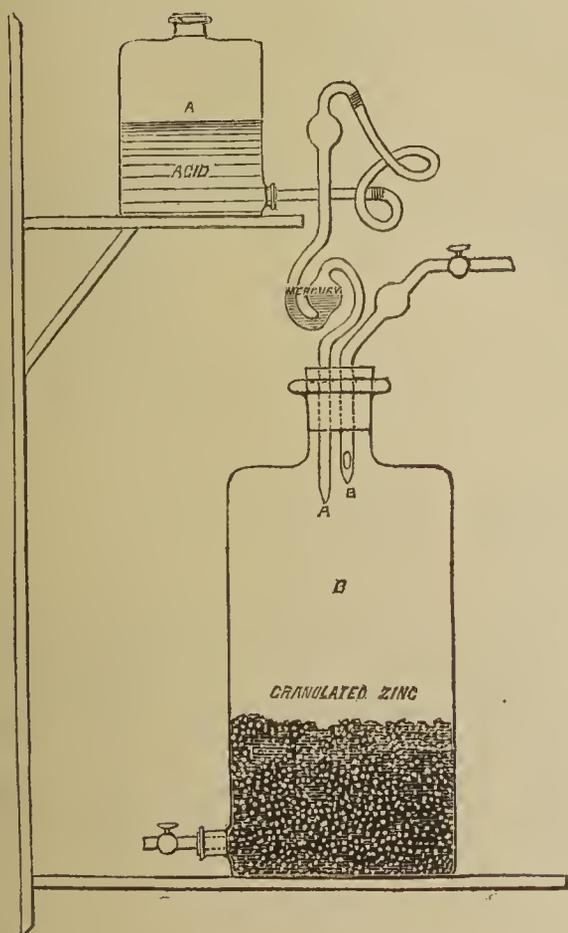
\* From the Annual Report of the "School of Mines and Industries of South Australia."

FIG. 1.



The tube F has proved very effectual in preventing the passage of any liquid with the gas, even when the evolution of gas is very rapid. A similar plan has been tried in distilling off the alkaline liquid from a Kjeldahl determination of nitrogen, the end of the tin condenser being

FIG. 2.



drawn out to about 3-16ths of an inch inside diameter, and a slot cut at G (as in H). There was, however, no bulb at H. In working this it was found that the tip at the bottom was always closed by a drop of water, and all the vapour passed through G into the condenser. The distillate from a strongly alkaline solution, kept rapidly boiling, in a test experiment was quite neutral.

A modified form of this apparatus has also been tried for generating hydrogen and carbonic acid gas when a constant supply was required for some time, and it was found that the supply could be regulated much more accurately than with the apparatus generally used. Fig. 2 illustrates this apparatus, which requires no further description except that it is well to have the bottle B long and narrow and A short and wide, and the tip of the tube A should be below the tip B. The bottle A can, of course, be raised or lowered as required, being connected to B by indiarubber tubing.

**Radiation of Different Refractory Substances Heated in the Electric Furnace.**—J. Violle.—It was important to know if there occurs in the arc, as Rosetti announced, a temperature notably higher than that of positive carbon. To decide this question I introduced into the arc a fine rod of carbon. This rod was rapidly worn away, becoming hollow on the side facing the cathode, and being coated with a powdery deposit opposite the anode. In a word, it behaves exactly like a metal wire in a galvanoplastic bath, according to the law of Grotthus. On applying to the examination of the cavity in the rod the methods which I had used for studying the extremity of the positive carbon I found that the lustre was the same on the rod as on the positive carbon. I operated on coke, lime, magnesia, zirconia, and chromic oxide, and found that all these different substances present in the furnace exactly the same brilliance and act equally upon the eye and the photographic plate. Thus in an enclosure all parts of which are at an equal temperature all these bodies are in an equilibrium of radiation according to Kirchhoff's law.—*Comptes Rendus*, cxvii., No. 1.

## NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.\*

By Lieut.-General C. A. McMAHON, F.G.S.

(Continued from p. 44).

No.	Name.	System.	Form.	Double refraction shows colours of.	Direction of major axis.	Other optical characters.
COBALT.						
21	$\text{CoSO}_4(\text{NH}_4)_2\text{SO}_4 + 6\text{H}_2\text{O}$	M	Large stumpy prisms.	Some as high as 6th, but generally 3rd order.	No. 21. With- in about $8^\circ$ of $e$ in the few cases in which the crystals are elongated.	No. 21. Absorption with single nicol strong.
CHROMIUM.						
22	$\text{CrSO}_4$	.. ..	Chromous sulphate.			
23	$\text{Cr}_2(\text{SO}_4)_3$	.. ..	Chromic sulphate.	—	Crystalline.	
24	$\text{Cr}_2(\text{SO}_4)_3 + 5\text{H}_2\text{O}$	.. ..	Chromic sulphate.	—	Non-crystalline.	
25	$\text{Cr}_2(\text{SO}_4)_3 + 15\text{H}_2\text{O}$	.. ..	Chromic sulphate.			Green in transmitted light.
26	$2\text{CrSO}_4(\text{OH})_4 + \text{Cr}_2(\text{OH})_6 + 5\text{H}_2\text{O}$	.. ..	—			
Double Salts.						
—	With sulphates of K, Na, and $(\text{NH}_4)$	—	See alums.	—	—	—
CÆSIUM.						
27	$\text{Cs}_2\text{SO}_4$	.. ..	R	Prisms with numerous faces.	2nd order. $R.L.$ to $e$ .	
28	$\text{CsHSO}_4$	.. ..	R			
Double Salts.						
29	$\text{Cs}_2\text{SO}_4\text{MgSO}_4 + 6\text{H}_2\text{O}$	.. ..	M	—	—	—
—	With sulphate of Al.	—	See alums.	—	—	—
IRON.						
30	$\text{FeSO}_4 + 4\text{H}_2\text{O}$	.. ..	Ferrous sulphate.	{ R M		
31	$\text{FeSO}_4 + 5\text{H}_2\text{O}$	.. ..	Ferrous sulphate.	Tr		
32	$\text{FeSO}_4 + 7\text{H}_2\text{O}$	.. ..	Melanterite or green vitriol.	M	When evaporated on slide generally in rhombs or tabular prisms.	7th order. Generally    to a line dividing the obtuse angle of rhomb into two unequal portions.
33	$\text{Fe}_2(\text{SO}_4)_3$	.. ..	Ferric sulphate.	—	In oval and rounded disks, often with radiating fibrous structure and in fibrous patches.	1st order,    to axis of elongation. Extinction coincides with axis of elongation. Decided absorption with single nicol.

## Remarks.

No. 21.—On heating changes from rose-red to violet: on cooling rose colour returns. Traces of a very oblique bisectrix, apparently positive.

No. 22.—Only known in solution.

No. 23.—A red salt formed by heating No. 24 to  $370^\circ$ . Insoluble in water, alcohol, or acids.

No. 24.—A green salt. Soluble in alcohol. Formed by boiling No. 25, or by heating it to  $100^\circ$ .

No. 25.—A violet salt. Insoluble in alcohol.

No. 26.—A basic salt.

Chromates and Dichromates, see K and Na.

No. 30.— $\text{FeSO}_4$  under ordinary conditions crystallises in the form of No. 32, but it takes the orthorhombic form if its supersaturated solution is touched with a crystal of zinc sulphate, and the triclinic form (No. 31) if a crystal of copper sulphate is placed in a concentrated solution. When a solution of  $\text{FeSO}_4$  containing free  $\text{H}_2\text{SO}_4$  is allowed to evaporate in a vacuum, No. 32 separates first, then No. 31, and lastly No. 30. When the ferrous sulphate is exposed to the air it is changed into a compound containing ferric sulphate and ferric hydroxide, or a basic ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3(\text{OH})_3$ .

No. 33.—Ferric sulphate readily forms basic salts, the composition of which is not positively known. It dissolves slowly in water, and is decomposed by heating into ferric oxide and sulphur trioxide. Columns 5 to 8 is the anhydrous salt dissolved in water and re-crystallised.

	No.	Name.	System.	Form.	Double refraction shows colours of.	Direction of major axis.	Other optical characters.
IRON.							
$\text{Fe}_2(\text{SO}_4)_3$ . . . .	34		R	Radiating needle-shaped prisms (see Remarks, Part 3).	Blue of 2nd order.	to <i>e</i> .	
$\text{Fe}_2(\text{SO}_4)_3 + 9\text{H}_2\text{O}$ . .	35	Coquimbite.	H	Prisms usually with terminal edges replaced.			
$\text{Fe}_2(\text{SO}_4)_4 + 12\text{H}_2\text{O}$ .	36	Ferrous fer-ric sulph.	M	Yellow crystals.			
$\text{FeS}_2\text{O}_7$ . . . . .	37	Ferrous di-sulph.	—	Green microscopic prisms.			
$\text{FeSO}_4(\text{OH})_4 + \text{Fe}(\text{OH})_6 + \text{H}_2\text{O}$	38	Vitriolochre.	—	Massive earthy stalactitic.			
$\text{Fe}_2(\text{SO}_4)_3 + \text{Fe}_2(\text{SO}_4)_2(\text{OH})_2 + 10\text{H}_2\text{O}$	39	Copiapite.	H?	In six-sided crystalline scales.	Red of 2nd order.	to <i>e</i> .	Basal sections give cross on bluish ground in <i>c.p.l.</i>
$2\text{Fe}_2(\text{SO}_4)_2(\text{OH})_2 + \text{Fe}_2\text{SO}_4(\text{OH})_4 + 24\text{H}_2\text{O}$	40	Fibroferrite.	M?	In delicate fibres.			
<i>Double Salts.</i>							
$\text{FeSO}_4\text{Na}_2\text{SO}_4 + 6\text{H}_2\text{O}$ (see Remarks, Part 3) . . . .	41		M	Globulites, spherulites, and radiating fibrous crystals.	2nd order.	About $45^\circ$ to longer axis of fibres.	Sometimes has a concentric as well as radiating structure, and resembles chalcedony.
$\text{FeSO}_4\text{K}_2\text{SO}_4 + 6\text{H}_2\text{O}$	42		M	Large tabular crystals.	7th order and higher.	Variable.	Absorption with single nicol, very strong.
$\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 + 6\text{H}_2\text{O}$	43		M	Large stout prisms variously terminated. Also in skeleton crystals.	5th order.	Within a few degrees of    to <i>e</i> .	Strong absorption with single nicol. Zonal structure. <i>In c.p.l.</i> either an optic axis or a more or less oblique bisectrix emerges.
With sulphate of K and $\text{NH}_4$ . . . . .							
POTASSIUM.							
$\text{K}_2\text{SO}_4$ . . . . .	44	Normal sulphate.	R	Flat prisms elongated in one direction; terminations various.	2nd order.	Generally   , sometimes <i>R.L.</i> to <i>e</i> .	Relief strong when mounted in balsam; when unmounted faces at angle to glass cover are black.
$\text{KHSO}_4$ . . . . .	45	Acid sulphate.	{ M R	(a) Six-sided tabular prisms. (b) Needle-shaped do., also fibrous. (c) Irregular-shaped tabular crystals.	6th order.	Low angle to <i>e</i> .	Absorption with single nicol. Mottled appearance under crossed nicols seldom extinguishing uniformity; unmounted deep black margin; strong relief; shagreened irregular surface marked with black lines. Penetration twins often seen.

Remarks.

- No. 34.—Is formed by adding No. 32 to boiling  $\text{H}_2\text{SO}_4$ .  
 No. 36.—The two sulphates of iron form various double salts, of which this (Roemerite) is one.  
 No. 37.—Is formed by adding iron sulphate to several times its volume of concentrated  $\text{H}_2\text{SO}_4$ . It decomposes on contact with water.  
 No. 40.—Pale yellow to white, pearly, or silky.  
 No. 44.—Soluble 1 in 10 in cold and in much smaller quantity of boiling water. Occurs in Apthitalite and Kainite. The difference in appearance of mounted and unmounted specimens is a striking feature, and one useful for identification.  
 No. 45.—Occurs native in the *grotto del solfo*, near Naples, in the form of silky needles. Dissolves readily in water: is decomposed by alcohol into No. 44 and  $\text{H}_2\text{SO}_4$ . When 45 is re-crystallised from aq. sol., No. 44 separates out first, then crystals of a salt having composition of  $\text{K}_2\text{SO}_4 + \text{KHSO}_4$ , and finally No. 45 crystallises out.

To be continued).

ON THE PHOTOGRAPHY OF THE  
LUMINOUS RAYS OF THE SHORTEST  
WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 47).

*Photography of the Spectral Region between the Wave-lengths 231.35 and 185.2  $\mu\mu$ .*

A. With ordinary apparatus permeable for the ultra-violet.

*The Photographic Spectral Apparatus, with particular reference to its Optical portion.*—The photography of this spectral region requires an apparatus of great permeability to light. Glass (G. G. Stokes, *Phil. Trans.*, 1852, cxlii., Art. 202), which keeps back most of the ultra-violet rays, is unfit for the prisms and lenses of such an instrument. Calcareous spar is not much better (L. Soret, *Archiv. des Sci. Phys. et Nat.*, lxi., 334 [1878]). Its availability for the ultra-violet ends where the above-named region begins. The only media which can be taken into consideration are quartz (L. Soret, *ibid.*, p. 332, and G. G. Stokes, "On the Change of Refrangibility of Light," *Phil. Trans.*, 1852, Art. 204) and white fluor-spar (W. A. Miller, "On the Phot. Trans. of Various Bodies," *Phil. Trans.*, clii., p. 865 [1862]; A. Cornu, *Archiv. des Sci. Phys. et Nat.*, III. periode, ii., p. 119).

Fluor-spar in its white variety—all other kinds of fluor-spar are coloured and less permeable for the ultra-violet—is more transmissive than quartz; but it has hitherto been applied only in isolated cases on account of its rarity and as it frequently contains defects in crystallisation which imperil the clearness of the image (H. Deslandres, "Spectres des Bandes Ultra-violet des Metalloids avec une faible dispersion," p. 32. Paris: 1888).

In the photography of the ultra-violet region, quartz presents upon the whole greater advantages than any other medium. It yields spectra of faultless definition, and its lower transmissibility—just mentioned—is, according to present experience, not so important as seriously to impair the photographs.

*The Quartz Prism.*—Not every quartz prism is fit for spectral photography. Every prism whose refractive edge runs parallel with the optical axis is unsuitable. The reason lies in the partial superposition of the ordinary and extraordinary ray, and in the circumstance that the photographic result on the extinction of one or other of the two spectra, which is certainly practicable with a Nicol prism, is destroyed by the non-transmissive character of the calc-spar.

The relations are more favourable with a quartz prism, the refractive edge of which is cut at right angles to the optical axis in such a manner that the latter forms equal angles with the refractive planes. If the rays traverse the quartz in the direction of its optical axis they no longer experience the ordinary double refraction, but they undergo circular polarisation, and in so palpable a degree that, *e. g.*, in a prism of 60°, every line of the spectrum is split up into two very nearly adjacent but clearly resolved components. It is plain that such a spectral image must be uncertain even if the lines are mutually isolated, but must be completely obscure in the case of crowded lines. This scission of the lines may indeed be avoided if a system of lines is cancelled by a quarter-wave plate with a Nicol inserted in the emerging ray. But the plate, as it consists of mica (W. A. Miller, *Phil. Trans.*, clii., p. 865 [1862]), is so impervious that it absorbs almost all rays beyond the wave-length 325  $\mu\mu$ , and, without considering the inconvenience in photographing occasioned by the impervious nature of the Nicol, it renders any photographic result in the ultra-violet at once impossible.

The only expedient to preserve the image from the disturbing effect of linear and circular polarisation, without interfering with brightness, consists in the use of a double prism (A. Cornu, *Comptes Rendus*, 1885) composed of a lævo- and a dextro-rotatory quartz, each of an equal refractive angle (30°). In preparing such prisms care must be taken that the optical axes of the semi-prisms are placed vertically to their common plane of contact. To avoid the loss of light the semi-prisms may be joined together with glycerin or distilled water; but this is not necessary. Double prisms of this kind, whether single or when several are connected in a circle, give spectra of a faultless definition.

*The Quartz Lens.*—The lenses for the collimator and the camera are best of a plano-convex form. They may either be of a like or of an antagonistic rotatory power. It is, however, essential that the geometric axis has the same direction as the optical axis of the crystal, or, as the opticians call it, are cut at right angles to the axis. Quartz lenses consisting only of one part never double the image. Therefore double biconvex lenses, composed like the double prism just mentioned, of lævo- and dextro-rotatory plano-convex quartz lenses, afford no advantage in spectral photography.

The focal distance of the lenses must be equal, and not exceed 1 metre. If larger, it may easily happen that the aperture of the apparatus is too small. Although lenses of sufficient diameter can be procured without too great difficulty, the aperture of the prism still remains. But quartz prisms with a rather large aperture rank among rarities. Insufficient apertures easily occasion the formation of inflection fringes, which appear on both sides of the brighter lines of the spectrum, and may easily prove serious in interpreting the spectrum.

On the other hand, the focal distance must not be reduced too far, not below  $\frac{3}{4}$  metre, as the spectrum is otherwise too short. An increase of dispersion by the application of several prisms is not to be recommended. With a combination of several double prisms the spectrum appears clearly defined only for a short extent. The greater the number of prisms the shorter is the clearly defined extent. The simultaneous photography of extensive spectral regions should therefore be effected at the outside with a few, but preferably with a single double prism. This applies especially to a general photograph of the ultra-violet region.

It will be understood that the selection of crystals from which prisms and lenses have to be cut has to be effected with great care. Distortions, which are not rare in quartz crystals, make every crystal unfit for use.

As great attention must be given to the nature of the refractive planes, curvatures which, on account of their moderate size, have in glass prisms no effect on the spectrum, may greatly interfere with the effect of a quartz prism.

Quartz prisms with faulty planes always give an impure image of lines, though less when used singly than when several are associated in a circle. Such a circle is capable of bringing the spectrum into complete confusion.

Excellent prisms and lenses of quartz are made by the optician Bernhard Halle, of Steglitz, near Berlin. As a proof of the excellence of his work, the fact may serve that a circle of nine double prisms supplied to me by Herrn Halle, in which the rays have to traverse thirty-six refractive planes, gives in an extent of  $3\frac{1}{2}$  m.m. all the eighty-five lines which H. C. Vogel's Atlas of the Solar Spectrum shows between the lines H and K.

The moderate sensitiveness of the spectrum to certain defects of the lenses is remarkable. This applies to the centring and the direction of the optical axis of the crystals. I have been able to use continuously, without disadvantage, a pair of quartz lenses which showed unusual deviations for resolving dense groups of lines.

This circumstance deserves attention the more as the

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

spectrum is very sensitive to all kinds of faults in the quartz.

The adjustment of the prism and the lenses is effected in the same manner as in the spectral apparatus.

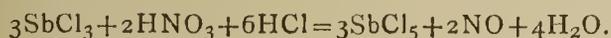
(To be continued).

ON THE IODOMETRIC DETERMINATION OF THE NITRATES.\*

By HIPPOLYTE GRUENER.

(Concluded from p. 42).

*The Decomposition of Nitrates by Antimonious Chloride.*—The failure mentioned above, in attempting to use arsenious oxide to register the action of nitric acid, led to the trial of antimonious chloride as a substitute, inasmuch as this substance is easily oxidisable and less volatile than arsenious chloride in presence of hydrochloric acid. This latter fact is of great importance in the decomposition of a nitrate. The point to be tested was whether the complete decomposition of nitrates by the action of antimonious chloride in hydrochloric acid solution, and the absorption of the nascent oxygen to form antimonious chloride would be secured, so that the antimonious chloride left at the end as compared with the amount taken should give the measure of the nitrate used, according to the equation:—



Antimony chloride was dissolved in strong hydrochloric acid, and the solution standardised by diluting convenient portions, adding tartaric acid, nearly neutralising with 25 per cent solution of sodium hydrate, treating with excess of hydrogen sodium carbonate and titrating with decinormal solution of iodine in presence of starch, the blue colour being taken as the end reaction.

Known portions of this solution boiled with potassium nitrate for a considerable length of time, then diluted, neutralised, and titrated (all a simple quick process), showed oxidation to the extent of about 90 per cent of the nitrate present. The evidence pointed to the conclusion that the nitrate was broken up, but that the residue failed to register the amount of decomposition. The products of decomposition when passed in a current of carbon dioxide into potassium iodide set free iodine, but had no oxidising effect upon an alkaline solution of arsenious oxide. The conclusion was drawn that nitrosyl chloride was probably given off, which breaking up on contact with water into hydrochloric and nitrous acids exerts no effect upon arsenious oxide in alkaline solution. To see if the nitrosyl chloride was set free in exact measure of the nitric acid lost the following experiments were made.

Into a diminutive retort—made from a pipette shaped like a Liebig's drier, and connected by a sliding joint covered by rubber into a Kjeldahl tube used as a receiver, and so placed that carbon dioxide passing through the apparatus should enter from below—lifting the air before it—was introduced the nitrate, dry, washed down with a few drops of recently boiled water, or, if more liquid was required, with hydrochloric acid, lest the liquid become too dilute. From a burette a definite amount of antimonious chloride solution, somewhat in excess of the nitrate taken, was introduced. The receiver was charged with 0.25 gm. potassium iodide diluted with recently boiled water and was joined to a trap filled with water. After carbon dioxide was passed through the apparatus, for about ten minutes, the solution was warmed on a high boiling bath (103°—107°) to ensure the safety of the retort, to keep the antimony pentachloride from breaking up, to retain the bulk of the acid in the retort, and to prevent mechanical loss. This method of procedure was found

entirely satisfactory. After fifteen minutes digestion the receiver and trap were washed out and at once titrated with sodium thiosulphate. The residue in the retort was treated exactly as was the antimonious chloride when it was standardised. The solution here must be kept dilute, lest at the great heat caused by neutralising strong solutions there be action upon the pentachloride on the part of the small amount of tartaric acid now present. The difference between the trichloride left in the retort and the iodine found in the receiver is the measure of trichloride left unoxidised by the nitrate, and by difference we have the measure of the nitrate present. The results are given in Series I. and II. In experiments 1 to 8 the receivers were washed with ordinary distilled water; after that, with water recently boiled.

SERIES I.

	KNO <sub>3</sub> taken. Grm.	KNO <sub>3</sub> correspond- ing to I found in receiver. Grm.	Entire KNO <sub>3</sub> found. Grm.	Error in KNO <sub>3</sub> . Grm.	Error in HNO <sub>3</sub> . Grm.
1	0.0222	0.0020	0.0233	0.0011 +	0.0007 +
2	0.0336	0.0026	0.0333	0.0003 -	0.0002 -
3	0.0470	0.0045	0.0471	0.0001 +	0.0001 +
4	0.0553	0.0057	0.0554	0.0001 +	0.0001 +
5	0.0664	0.0076	0.0679	0.0015 +	0.0009 +
6	0.0759	0.0082	0.0752	0.0007 -	0.0004 -
7	0.0837	0.0103	0.0841	0.0004 +	0.0002 +
8	0.0934	0.0113	0.0955	0.0021 +	0.0013 +
9	0.1034	0.0134	0.1036	0.0002 +	0.0001 +
10	0.0262	0.0024	0.0259	0.0003 -	0.0002 -
11	0.0127	0.0007	0.0130	0.0003 +	0.0002 +
12	0.0065	0.0003	0.0067	0.0002 +	0.0001 +
13	0.0026	0.0001	0.0023	0.0003 -	0.0002 -
14	0.1232	0.0098	0.1227	0.0005 -	0.0003 -
15	0.1540	0.0146	0.1540	0.0000	0.0000
16	0.1878	0.0210	0.1865	0.0013 -	0.0008 -

Three more experiments were performed to see if the titration of the iodine set free in the receiver could be accomplished as well in alkaline solution by means of arsenious oxide. For this purpose the solutions from the receivers were poured into a strong solution of sodium bicarbonate, care being taken to prevent loss during effervescence.

SERIES II.

17	0.0530	0.0052	0.0533	0.0003 +	0.0002 +
18	0.0547	0.0065	0.0549	0.0002 +	0.0001 +
19	0.0541	0.0063	0.0537	0.0004 -	0.0002 -

The results run from extremes of 0.0021 gm. + to 0.0013 gm. -, with a mean error of 0.00016 gm. +, which tends to emphasize the well-known fact that it is impossible to remove every trace of air from reagents and generator. The operation is quick, taking in all three-quarters of an hour, and requiring very little watching. The experiments given are all that were performed with the apparatus as described, it not having been found necessary to reject a single determination for mechanical mishances.

Neither of the processes described presents in general advantages equal to those of the manganous chloride method to which reference has been made, but under special conditions they may be found useful.

In concluding, I would express my thanks to Professor Gooch for valuable advice and assistance given during the course of the investigation.

*On the Mercuric Salicylates.*—H. Lajoux and A. Grandval.—The authors have distinguished and examined the normal salicylates and the basic salicylate. The former is a white precipitate, decomposable by heat, and insoluble in water. The basic salicylate is a white powder insoluble in water, alcohol, ether, and chloroform.—*Comptes Rendus*, cxvii., No. 1.

\* American Journal of Science, xlvii., July, 1893.—Contributions from the Kent Chemical Laboratory of Yale College.

## THE SPECIFIC HEATS OF THE METALS.\*

By JOS. W. RICHARDS, Ph.D.,  
Instructor in Metallurgy, &c., in Lehigh University.

For the purpose of showing clearly the field to be covered, I will refer at once to five heads under which the subject will be considered:—

1. Definitions. The range of the subject.
2. Methods.
3. Historical Treatment. The investigators; work done by each.
4. Discussion of the results. Tables, diagrams, formulæ.
5. Theoretical Treatment. Discussion from the chemical and mechanical standpoints.

## I.

The specific heat of a body is the ratio between the amount of heat necessary to increase its temperature  $1^{\circ}$ , and the amount necessary to increase the temperature of an equal weight of water  $1^{\circ}$ .

Being a *ratio*, it is, of course, independent of the weights of the substance and water taken, or of the kind of thermometric scale employed, but in order to introduce regularity into these comparisons the weights taken are a kilogram, or a pound, and the degree either Centigrade or Fahrenheit. Throughout this lecture I shall use the metric unit of weight and the Centigrade scale.

Since the observations on so many substances are to be compared with water as a standard, it will be well to examine our standard carefully, to see if it is invariable. We find that *pure* water is absolutely the same substance at all times, so that no variation can arise from there being two kinds of water; but, examination reveals the fact that the amount of heat required to raise the temperature of a kilo. of water  $1^{\circ}$  is a different amount at different temperatures. For instance, it takes more heat to heat a kilo. of water from  $90^{\circ}$  to  $91^{\circ}$  than from  $1^{\circ}$  to  $2^{\circ}$ . Scientists have investigated this matter for fifty years, and it is only quite recently that reliable figures have been obtained showing just to what extent, quantitatively, the specific heat of water varies with the temperature. The French scientist Regnault had found a gradual increase from the freezing-point up, and for this reason the water unit was chosen as the amount of heat required to raise a kilo. of water from  $0^{\circ}$  to  $1^{\circ}$ ; but since these observations of Regnault have been proven incorrect, the general conclusion now is that the water unit should be considered at from  $15^{\circ}$  to  $16^{\circ}$ , at which point the specific heat of water appears to reach a minimum value.

I have just explained how the specific heat of water varies with the temperature at which it is taken. This is also true of all other bodies, so that a complete investigation of the specific heat of any substance would mean the determination of that property at all attainable temperatures, from the lowest to the highest. In the course of such an investigation the substance would in many cases pass from solid to liquid and then to gas, and it would be found to possess different specific heats in these different states. Furthermore, in passing from solid to liquid, or liquid to gas, it would be observed that a large amount of heat is absorbed without any increase of temperature at all. At these points we say that heat is rendered latent in the body. The complete calorific investigation of a body should therefore include the fixing of the temperatures at which such sudden absorptions of heat occur, and the amounts of heat rendered latent.

A new name has thus attached itself to this branch of experimental physics; we now speak of undertaking the "calorific investigation of a substance" in place of the mere determination of its specific heat at ordinary temperatures.

\* A Lecture delivered before the Franklin Institute, Jan. 30, 1893.

As we shall see more clearly further on, while this subject is properly a branch of physics, yet it treads very close to the foundation ground of chemistry, throwing a side light on many of the conceptions of that science, and tending in many ways to give us chemical theories on a pure mechanical basis.

## II.

Referring to the experimental methods employed in these investigations, we may class them under two heads:—

1. The method of cooling.
2. Calorimetric methods.

The first method may be briefly described as follows:—The substance is made hot, and then placed in a close vessel kept at a constant temperature by a stream of water, and the rate at which it cools carefully observed. A delicate thermometer embedded in the substance is read every five or ten seconds, and the curve of cooling carefully plotted. Since the conditions are such that the amount of heat radiated per second depends only on the temperature of the substance, it follows that the rate at which it will cool will depend directly on the amount of heat stored up in the body, or its calorific capacity. Thus, different substances can be investigated and compared, but it will be readily seen that the method gives only comparative results, and in order to get absolute values, we must take some one substance whose specific heat has been otherwise determined as a standard, and then the values for the other substances can be calculated.

This method was first used by J. T. Mayer, in 1808, and afterwards greatly improved by Dulong and Petit, but the results obtained by it are not considered as accurate as those given by some other methods, and it is not now used to any extent. The complicated formulæ for cooling, which must be used, and the great care required to obtain good results, have also helped to bring the method into disuse.

Under the second head, calorimetric methods, we include all those methods in which the heat capacity of a body is directly measured. This may be accomplished in three ways:—

1. The method of mixtures.
2. The ice calorimeter.
3. The steam calorimeter.

The method of mixtures consists simply in heating up the substance to an accurately-determined temperature, then to immerse it suddenly into a known weight of water, or any fluid whose specific heat is accurately known. From the temperature of the mixture, and the known specific heat of the liquid, the unknown specific heat, or rather the amount of heat given out by the substance under investigation in falling from the high temperature to the temperature of the mixture, becomes known. Of course, in determining the true temperature of the mixture it is necessary to make corrections for heat absorbed by the vessel in which the mixture takes place, &c., but this line would lead to a discussion of calorimetric methods which would be outside the scope of this lecture. But, aside from this difficulty, there are other defects in this method. One of these is the accurate determination of the temperature of the substance as it was dropped into the calorimeter. Even supposing that its temperature while in the air-bath or furnace is accurately determined (a difficult matter for high temperatures) yet, there is a certain fall in temperature during the transfer into the calorimeter, an amount which increases very rapidly with high temperatures. Another defect sometimes mentioned is loss of heat by vaporisation of the water, but this is so small as to be in most cases negligible. The most serious of these defects, the first, has been remedied by the use of the "double method of mixtures," which consists in using two calorimeters and a platinum ball along with the substance being investigated. If the substance and the

platinum ball are placed in the furnace together, then removed together and dropped simultaneously into the two calorimeters, the amounts of heat given out by each in cooling from the same temperature can be measured, for it can fairly be assumed that the platinum ball is at exactly the same temperature as the other substance at the moment of immersion. But the specific heat of platinum has been investigated with the greatest care, and so from the amount of heat it has given out to the calorimeter we can calculate its temperature at the moment of immersion. In this way the most serious defect of the method of mixtures has been overcome, especially when working at high temperatures. Your lecturer has done considerable work by this double method, with very satisfactory results.

The ice calorimeter measures the heat given out by the substance in cooling to zero by the weight of ice which it melts. Knowing just how much heat is absorbed by one grm. of ice in becoming water, it is necessary only to weigh the amount of water formed to get the heat given up. This calorimeter was first devised and used by Lavoisier and Laplace, and has been greatly improved by Bunsen. As a measurer of heat its principal defect was that all the water produced could not be collected and weighed. Bunsen's improvements largely overcame this error. The other defects incident to its use were principally the loss of heat during transfer to the calorimeter, which can be overcome by the "double method" already explained. All determinations made in this calorimeter depend on the value of the latent heat of water, which is, however, known to a high degree of accuracy.

The steam calorimeter measures the amount of heat absorbed by a body in being heated up to 100° by the amount of steam which it condenses in doing so. For this purpose, the substance at an accurately known temperature is suddenly plunged into a current of dry steam. The weight of water finally collecting on it is determined, and the heat absorbed by the body is the product of this into the latent heat of steam. Like the ice calorimeter, all determinations made in this way depend on this constant, the latent heat. More serious errors, however, are caused by the condensed water falling off the body, and by some of it being carried away mechanically by the steam. Also, since the latent heat of steam is very large, a small error in weighing the water condensed will make a large error in the result. No very exact figures can be expected from this method of investigation.

Before closing this description of methods I might here remark that the latent heat of fusion, a very interesting phenomenon when speaking of the metals, can be determined in several ways. Assuming the melting-point known, we can calculate from the observed variation of the specific heat in the molten state how much heat the *molten* substance would contain at the melting-point; we can in a similar way calculate how much heat the *solid* metal contains at that temperature; the difference between these two quantities will be the latent heat of fusion. Or, we may determine the first quantity directly by taking a large quantity of molten metal and letting it cool gradually to the setting-point. When part is already set, the part which is still fluid and whose temperature is exactly the melting-point is poured out directly into a calorimeter, and the amount of heat in it thus measured directly. The second quantity may also be determined directly by taking a bath of molten metal, letting part set, and then plunging a little spiral of wire of the same metal into the still-fluid part. The heating up of the wire chills a certain quantity of metal into the solid state at this temperature, and the little lump thus formed is dropped into a calorimeter. Or, the latent heat of fusion can be determined by the method of cooling; for while the metal is setting, its temperature remains constant, and from the time which it takes to set, compared with the rate at which the liquid and solid metal cools before and after the setting, the amount of heat evolved during setting can be computed. We need for this, how-

ever, to know the value of the specific heat of the metal somewhere in the neighbourhood of its setting-point.

### III.

Historically considered, we may begin by saying that about 1750 it was universally supposed that there was little or no difference in the heat capacity of different kinds of substances, and it was further supposed that solids were converted into liquids by the addition of an insignificant amount of heat when they had once been raised to the melting-point.

Dr. Black, of Edinburgh, was the first to announce correct ideas on these subjects. In his chemical lectures at Glasgow, between 1760 and 1765, he pointed out the great differences in the heat capacities of different substances, and made experiments in his lectures demonstrating the great amount of heat absorbed during the fusion of ice and the vaporisation of water. He determined the latent heat of water to be 140° F. units, equal to 77.8° C. units. A very able assistant of his, Dr. Irvine, made further investigations between 1765 and 1770, and determined the latent heat of fusion of tin, which he called 500°. By this he meant that the heat given out by tin in setting would be sufficient to raise the temperature of 500 times its weight of solid tin 1°, or an equal weight of solid tin 500°. These being Fahrenheit degrees would be equal to 277.7° C. These we might call tin units, and to convert into the ordinary water units we should have to divide by the ratio of the specific heat of water to the specific heat of solid tin at its melting-point. The figure thus reached is not far from that obtained by later observers.

Dr. Crawford was another colleague of Dr. Black, and published in his "Treatise on Heat" the results of many experiments on specific heats. It was said of him, thirty years later, "To this ingenious experimenter we owe some of the most remarkable facts respecting specific heat yet known." He investigated the specific heats of antimony, copper, iron, lead, mercury, tin, and zinc.

Dr. Black called this newly-investigated property of bodies "*capacity for heat*," but before the publication of his and his colleague's results, which was delayed by Dr. Black's great modesty, Professor Wilcke, of Stockholm, who had been working out similar ideas, published the results of some experiments and attached the name "*specific heat*" to this property. Professor Wilcke worked by the method of mixtures, and published values for antimony, bismuth, copper, iron, lead, silver, tin, and zinc.

Dr. Kirwan, in England, made similar experiments, with values for the specific heats of antimony, gold, iron, lead, mercury, and tin.

Lavoisier and Laplace made experiments with their ice calorimeter, the only one of the metals which they seem to have investigated being mercury. We owe to Lavoisier the expression "*latent heat of fusion*," and we find in his writings a wonderfully clear conception of what specific heat really includes, how it increases with temperature and to a different amount in different substances. So clear were his views that an enthusiastic Frenchman exclaims, in 1886, "All work on specific heats since his time has been done on the lines laid down by Lavoisier."

J. T. Mayer, Leslie, and Dalton worked by the method of cooling, but only the latter gives results for the metals, and these appear to be very rough approximations. The method was afterwards greatly improved by Dulong and Petit. Count Rumford and Avogadro can also be included in the list of experimenters in this line, but their results, especially those of Avogadro, were little trustworthy.

Dr. Wm. Irvine, son of Dr. Black's one-time assistant, repeated and extended some of his father's experiments. He determined the latent heat of fusion of bismuth, lead, tin, and zinc.

Rudberg, in 1830, determined the latent heat of fusion of lead and tin by the method of cooling.

Erman made similar experiments in 1830, but the discordance of his results show that his apparatus was not properly constructed or managed.

F. E. Neuman determined in 1831 the specific heats of antimony, bismuth, and zinc, by the method of cooling. De la Rive and Marcet investigated cadmium, cobalt, and molybdenum by the same method.

Dulong and Petit were the first investigators to make any systematic study of the variation of specific heat with the temperature. They determined the specific heat of antimony, copper, iron, mercury, platinum, silver, and zinc, at various temperatures up to 350° C. Their method was that of mixtures. They also determined the specific heats of antimony, bismuth, copper, gold, iron, lead, platinum, silver, tin, and zinc, at ordinary temperatures, by the method of cooling. These scientists were the first to remark that the specific heats of the elements are inversely proportional to their atomic weights—a law which, while not rigidly exact, yet is so nearly true that the slight deviations from it may fairly be ascribed to other causes yet to be investigated. In fact, it will be seen further on, in discussing the theory of specific heat, that this law may be directly deduced from the modern mechanical theory of heat.

Bède in 1855, Byström in 1860, and Naccari in 1877, have made series of experiments in exactly the same manner as Dulong and Petit's first set by the method of mixtures, at temperatures between 100° and 300°. Bède examined antimony, bismuth, copper, iron, lead, tin, and zinc; Byström, iron, platinum, and silver; Naccari, aluminum, antimony, cadmium, copper, iron, lead, nickel, silver, and zinc.

In 1836 Pouillet made a very careful study of platinum, using an air thermometer for recording temperatures and extending his determinations up to 1200° C. He worked with great care, and his results would have been excellent had it not been that a defect in his air thermometer introduced an error of 30° or 40° in his determinations of very high temperatures, and thereby vitiated his results.

A classical set of experiments was made by Regnault by the method of mixtures. Commencing with 1840, he worked for several years in this field, giving us values which are usually regarded as standards. However, whenever he used metals not quite pure for his experiments, he gave figures which have since been revised. He used a steam bath for his upper temperature, so that his figures are really the mean specific heats between 10° or 15° and 98° or 99°, or the true specific heats in the neighbourhood of 55° to 60°. He investigated twenty-seven of the metals, as follows:—Aluminum, antimony, bismuth, cadmium, cobalt, copper, gold, iron, iridium, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, osmium, palladium, platinum, potassium, rhodium, silver, sodium, thallium, tin, tungsten, and zinc.

Dr. Kopp was a laborious investigator of specific heats. He determined those of many metals and a host of chemical compounds. He used the method of mixtures, but he seems to have worked with unusually small weights of the substances, and from this cause or some others inherent in his apparatus his results on the same substance often varied among themselves 5 per cent, and occasionally even 10 per cent. In all such cases he figures up the average value of all his determinations. Regnault's results for one substance seldom varied over 1 per cent from each other, so that, wherever Kopp's values vary from Regnault's, the latter's deserve the preference. Kopp obtained the mean specific heats between 10° or 20° and 60° or 70°, or the true specific heat at about 35° to 40°. He investigated aluminum, antimony, bismuth, chromium, copper, cadmium, lead, magnesium, platinum, silver, tin, and zinc.

Prof. Bunsen used his modification of the ice calori-

meter for determining the mean specific heats of antimony, calcium, cadmium, indium, ruthenium, silver, tin, and zinc, between 0° and 100°, or the true specific heats at about 50° to 55°.

Prof. Mallet determined the specific heat of chemically pure aluminum (used in investigating its atomic weight) between 0° and 100° with Bunsen's ice calorimeter.

Person used Regnault's apparatus and the method of mixtures to determine the specific heats of bismuth, cadmium, lead, tin, and zinc, in the solid and liquid states, from which data he calculated their latent heat of fusion. He also determined the latent heat of fusion of cadmium, silver, and mercury, by the method of cooling.

Dr. W. F. Hillebrand, in 1876, determined the specific heats of cerium, lanthanum, and didymium, by the Bunsen ice calorimeter.

T. S. Humpidge determined the specific heat of beryllium in 1885.

L. Pebal and H. Jahn investigated antimony between -76° and +33°.

Zimmerman and Bluncke both determined the specific heat of uranium.

Nilson and Pettersson investigated germanium and titanium.

Milthaler investigated mercury at different temperatures and derived a formula for the variation of its specific heat with the temperature. Naccari went over the same ground for temperatures between 0° and 250°.

Kunt and Warburg investigated the specific heat of mercury vapour. E. Reynolds determined the specific heat of beryllium, and Mixer and Dana that of zirconium.

Weinhold investigated platinum at high temperatures, using the air pyrometer, but his results are discordant, showing imperfections in his method, so that his results did not supersede those of Pouillet.

More recently J. Violle made a study of platinum up to 1200° C., using the method of mixtures, an air pyrometer, and every refinement possible to ensure accuracy. His determinations are the best we have for this metal, and serve as the basis for calculating the temperature of the ball at the moment of immersion when working by the double method. Violle used platinum in this way for determining the specific heats of gold, iridium, and palladium up to 1200°. He also found the latent heat of fusion of platinum and palladium by determining the amounts of heat in the molten and just-set metal.

Le Verrier (Conservateur des Arts et Metiers) has recently investigated aluminum, copper, lead, silver, tin, and zinc, by the method of mixtures, using the recently-devised Le Chatelier pyrometer to determine temperatures, which it is stated can be done at the very moment of the immersion of the metal in the water of the calorimeter. He finds sharp variations in the specific heats of most of these metals, which no other investigator has seen any indications of, so that his results are very much doubted. Careful and very concordant experiments made by your lecturer on copper, by the double method, have failed to show any indications of variations at points indicated by Le Verrier, so that we must put on Le Verrier the burden of proving his results by repeating his experiments and giving all their details; in short, he must prove his position by further proofs before his results will be seriously considered as true.

Pionchon has done perhaps the most accurate work of recent years in his studies of cobalt, iron, nickel, silver, and tin (1886), and aluminum (1892). He worked by the double method of mixtures, using Violle's formula for calculating the temperature of the platinum. His results are very concordant except in the case of aluminum below 300°, where a variation of 5 per cent between his formula and the experimental results would be possible. Otherwise, he has given complete curves for the specific heats of aluminum, cobalt, iron, nickel, and silver, to 1200°, and tin to 1000°, and determined the latent heats of fusion of aluminum, silver, and tin.

(To be continued.)

NOTICES OF BOOKS.

*Alkali, &c., Works' Regulation Act, 1881.* Twenty-ninth Annual Report on Alkali, &c., Works. By the CHIEF INSPECTOR. Proceedings during the Year 1892 presented to the Local Government Board and to the Secretary for Scotland. London: Her Majesty's Stationery Office.

THE present report presents few features of an encouraging character. Thirteen additional classes of works have been brought within the purview of the Act, and progress has been made in preventing the discharge of noxious gases. But the light thrown upon the position of our chemical manufactures reveals in some respects a decline. The number of alkali works was in 1890 117, in 1891 113, and last year only 100. Other works included under the provisions of the Act have increased during the same three years from 791 to 810. In some cases a numerical standard is laid down in the Alkali Act limiting the amount of offensive gases which may be allowed to escape. In other cases there is no numerical standard, but it is enacted that "the owner of every work shall use the best practicable means for preventing the discharge into the atmosphere of all noxious gases and of all offensive gases evolved in such work." It may be asked whether this obligation may not be interpreted in too arbitrary a manner?

The total salt consumed in the Leblanc alkali process has progressively declined in the years 1890, 1891, and 1892 from 598,684 tons to 479,869 tons! Even if we take both the Leblanc and the ammonia process together, we find in the same three years a decline from 855,029 to 824,490 tons. It is, however, of interest to note that two new and extensive works on the Leblanc process have been built during the year 1892, *i.e.*, at Irvine and at Felling-on-Tyne. The manufacturers engaged in the ammonia process are meantime continually striving to produce chlorine (for bleaching-powder and chlorate) in connection with that process. Their success would practically involve the closing of the Leblanc works.

A new process is being attempted at Bristol apparently with a fair prospect of success. Mr. Gossage reduces salt-cake with coal without the co-operation of lime in an ordinary black-ash revolver, and after lixiviation he treats the sodium sulphide liquor with carbonic acid from a lime kiln. He makes no tank-waste, but recovers all the sulphur as hydrogen sulphide expelled from the sulphide by the carbonic acid.

At two works an attempt is being made to obtain chlorine by the action of nitric acid upon hydrochloric acid.

The production of sulphate of ammonia has increased from 134,257 tons in 1890 to 149,826 tons in 1892, but the proportion obtained from the shale works has slightly diminished.

There have been during the year 1892 five prosecutions under the Act; all, save one, for non-registration of works.

It is remarked that the enormous chimneys formerly built in the hope of getting rid of the hydrochloric acid gas are now useless, since this gas is the main source of profit. Some of these chimneys have been destroyed; but the loftiest of all, that of St. Rollox, Glasgow, 453 feet in height from the foundation, "still stands as a monument of expensive brickwork."

The principal works most recently brought under the provisions of the Act are those in which sulphuretted hydrogen is or may be given off, and those where hydrochloric acid is made or volatilised.

It is very satisfactory to learn that the escape of sulphuretted hydrogen at first encountered in the recovery of sulphur from tank-waste, by the process of Mr. Alex. M. Chance, of Oldbury, is now overcome, and the presence of this offensive gas is no longer perceived.

The manufacture of arsenious acid has occasioned some difficulty; in one instance the air of the chimney was found to contain 7.40 gr. arsenious acid per cubic foot. The use of wet condensers was found inadmissible; not only was there a waste of arsenic, but the condensing water poisoned the streams. Dry condensers are now used with much better results.

Means are being taken for improving certain manufacturing processes which are indirectly injurious to the health of the workpeople. The Chief Inspector remarks that the most difficult point here is "protecting the workman against himself." The average yearly death rate among the men employed in the alkali manufacture in the Widnes district is 8.51 per 1000, a figure which certainly gives very slender foundations for the sensational articles which have appeared in a certain portion of the press.

The question of coal-smoke, though it does not come within the scope of the Alkali Acts, is being continually forced upon the notice of the inspectors; many people charge upon any chemical works within fifty miles the injury occasioned by the acid evolved by the combustion of coal. The inspectors think that for this evil no practicable remedy has been proposed. It seems to us, however, that the only way of attacking the smoke question is to obtain from every ton of coal consumed its maximum duty, and thus limit the total amount of the nuisance. If we remember that at the lowest estimate three-fourths of the heat generated in our household fires is wasted, we must own that a great reduction both of black smoke and of sulphurous acid is possible. In addition, a reduction of the coal burnt in London to one-fourth its present amount would "draw the fangs" both of the coal merchants' and of the colliers' unions. This, however, is not a question upon which the CHEMICAL NEWS can enlarge.

The air of the underground railways also calls for notice. Mr. Fletcher suggests that each tunnel should be divided longitudinally by a partition of sheet iron running down the middle.

It seems to us that the Alkali Acts are still being worked judiciously, so as to combine the greatest possible protection to the public health and the least practicable interference with the important industrial interests concerned.

*Manual of Bacteriology.* For Practitioners and Students. With especial Reference to Practical Methods. By Dr. S. L. SCHENCK, Professor Extraordinary in the University of Vienna. Translated from the German (by the Author's permission), with an Appendix, by W. R. DAWSON, M.D. Univ. Dublin, late University Travelling Prizeman in Medicine. With 100 Illustrations, partly coloured. London and New York: Longmans, Green, and Co. 8vo., pp. 310. 1893.

DESPITE its increasing importance and the number of minds which have been attracted to it, the study of bacteriology is becoming dangerous. It can scarcely be carried out with thoroughness and success without occasional experiments on living animals. Hence the bestiarists, whose watchfulness is worthy of a better cause, are rising in arms, and denouncing, not alone the authors, but the publishers of such works. The Society for Promoting Christian Knowledge a short time ago brought out an excellent work from the pen of Dr. Percy Frankland entitled "Our Secret Friends and Foes." For this offence the Lord Chief Justice threatens that unless the book is withdrawn he shall at once withdraw himself from the Society. It is a consolation to know that should this threat be effective there are other works—such as the one before us—which cannot thus be suppressed.

Prof. Schenck's work treats firstly of the general morphology and *biology* of micro-organisms. We submit that physiology would be the more fitting term. In this country biology is the entire science of living beings, including morphology, physiology, embryology, and

taxonomy. On the Continent it is used in a less definite manner.

The author next takes into consideration preliminary processes, apparatus, and reagents, nutrient materials and methods of cultivation, the examination of microbia under the microscope, the bacteriological analysis of air, of water, of soils, and of putrescent solids; microbia in foods; the examination of pus, of the organs and cavities of the body and their contents, of the digestive tract, of fæces and urine, of the respiratory system, and of the blood.

An Appendix added by the translator examines vaccination against Asiatic cholera, parasitic protozoa, the action of light on microbia, with some recent methods and formulæ.

This book must be warmly recommended, not merely to students, but to practitioners, medical and chemical. It is impossible for the analyst to arrive at satisfactory results in the examination of waters, air, and soils without the aid of bacteriological methods.

*Kelly's Directory of Chemists and Druggists.* This Book includes Manufacturing Chemists, Wholesale Druggists, Drysalts, Patent Medicine Vendors and the Trades connected therewith in England, Scotland, Wales, and most of the Principal Towns in Ireland. Seventh Edition. London: Kelly and Co., Limited.

THIS very useful work of reference might be no little improved if its classifications were altered. At present it is too comprehensive, or perhaps rather too promiscuous. We scarcely see how the hospitals, herbalists, chiropodists, dentists, and veterinary surgeons can be classed as "connected therewith." It would seem to us that the above callings should come within the scope of a medical directory. Photographers, on the other hand, should, we submit, be transferred to an art directory, where they might appropriately figure along with painters, sculptors, carvers, and engravers.

A useful feature here is that under every town its early closing day, or half-holiday, if one exists, is duly mentioned. This little detail may save commercial travellers no little time and trouble.

Under the heading "Medical Booksellers," there figure the Philanthropic Reform Publishing Offices, an establishment which seems somewhat mysterious. We fear that a publisher who should proceed on philanthropic lines would have the opportunity of doing a large but ruinous business.

## 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. cxvii., No. 1, July 3, 1893.

**Auto-conduction, a Novel Method of Electrifying Living Beings; Measurement of Electric Fields of Great Frequency.**—A. d'Arsonval.—This paper requires the two accompanying cuts.

**On Chromopyrosulphuric Acid.**—A. Recoura.—The author has recently combined 1 mol. of chromium sulphate respectively with 1, 2, and 3 mols. of sulphuric acid, obtaining thus chromosulphuric, chromodisulphuric, and chromotrisulphuric acids. He has since combined chromium sulphate with 4 and with 5 mols. of sulphuric acid, obtaining novel compounds, with properties entirely different from those of the three above-mentioned acids. The compound with five mols. of sulphuric acid

he has named chromopyrosulphuric acid. Its constitution is expressed by the formula  $(S_2O_7H)_4Cr_2(OH)_2$ . Its solution precipitates all the solutions of metallic salts, even those of potassium, sodium, and ammonium. The precipitate is flocculent and of a greenish white. All these precipitates are quite insoluble.

**Constitution of Colouring-matters of the Rosaniline Group.**—M. Prud'homme and C. Rabaut.—The authors support the view of Rosenstiehl that these colouring-matters are not salts of amines, but ethers of amidic triphenylcarbinol.

**On Cinchonibine.**—E. Jungfleisch and E. Léger.—It appears that cinchonibine is capable of being split up into cinchonifine and apocinchonine. The saline compounds of cinchonibine do not exist. Cinchonibine should disappear from the list of the true isomers of cinchonine. It appears to be a combination of two of these isomers.

**The Metallic Combinations of Gallanilide.**—P. Cazeneuve.—There is here an account of the calcium, barium, zinc, lead, mercury, and copper compounds, the two latter not being regular salts.

**On the Carbohydrates of Helianthus Tuberosus.**—Ch. Tanret.—The tubers, if examined a short time before their complete development, contain saccharose, inuline, pseudo-inuline, inulene, helianthene, and synanthrine. At full maturity there appears a small quantity of levulose and glucose.

**Essential Oil of Spike (*Lavandula spica*).**—G. Bouchardat.—The oil of spike consists chiefly of linalol, the camphor of the Laurineæ, eucalyptol, with a little borneol, terpinol, geraniol, a turpentine, a copahuvène, and traces of undetermined products.

**Heat of Combustion of Coal-gas in relation with its Luminous Power.**—M. Aquilon.—The author thinks that gas may be valued by the calorimetric bomb in preference to the photometer.

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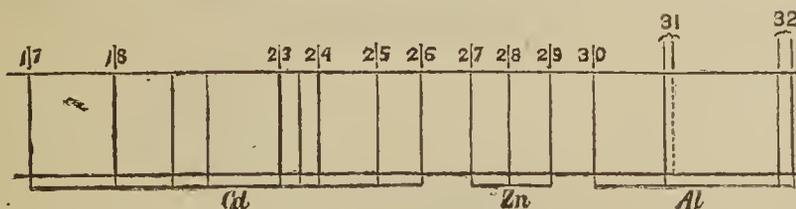
ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 57).

THE slit-tube of the photographic spectral-apparatus is of the ordinary construction. Only the photographic part of the apparatus differs from well-known instruments, and this only as regards the holder of the dark slide, by which I understand that part of the camera which serves for the reception of the dark slide.

The slide-holder is much more capable of being turned than in the ordinary camera, for the following reason:— Quartz lenses, as their focal lengths decrease considerably with the wave-length, require frequently, in photographing the spectrum, a very unusually inclined position of the photographic plate to the axis of the camera lens. If, e.g., the focal length of the sodium line D ( $589 \mu\mu$ ) is 1000, the focal length for the most refrangible line of aluminium No. 32 ( $185 \mu\mu$ ) is only  $806.2$  (E. Sarasin, *Archives des Sci. Phys. et Naturelles*, lxi., p. 109, 1878). This oblique position is not constant; it varies with the dispersion and with the proportion of the focal lengths of the collimator and the camera. If the focal length of both is equal (the usual case) the angle between axis and plate, measured on the more refrangible side of both, varies from  $22^\circ$  in a single prism ( $60^\circ$ ) to about  $90^\circ$  for twelve double prisms (two circles of prisms placed the one behind the other). But the angle is not constant, even for one and the same prism-body. It varies here with the selection of the rays for which the prism is adjusted



as at the minimum of deflection, also requirements made for the resolution of single parts of the photograph. Under these circumstances it varies in a single double prism from  $28^\circ$  to  $22^\circ$ . According to a circuit of the angle above named the plate with the dark slide and the slide-holder must be capable of rotation on one of the middle lines of its sensitive side, and have such a position that this medium line forms a parallel to the refractive edge of the prism cutting the optical axis of the camera lens.

The Source of Light.

The purpose of the photograph demands a source of light rich in energetic rays of the shortest wave-lengths.

Only the light of electric discharges fulfils this condition. Hence I had merely the choice between the arc light and the light of sparks. As the latter promised the better result, all my photographs have been produced with spark-light. For its production there was used a Ruhmkorff inductorium arranged for a maximum spark-length of 25 c.m. The primary current was furnished by six Grove elements. A Leyden jar, of 500 square c.m. of external coating, was inserted in the track of the secondary current. In some cases an additional jar was introduced, and even occasionally two more.

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

For the region of wave-lengths  $198.8 \mu\mu$  to  $185.2 \mu\mu$  only aluminium electrodes are available according to the observations of Stokes (*Phil. Trans.*, clii. p. 606, fig. 1, 1862), and Cornu (*Archiv. des Sci. Phys. et Naturelles*, III. periode, t. ii., p. 125, 1879), and merely for the wave-lengths  $230.0 \mu\mu$  to  $198.0 \mu\mu$ , which I could not leave unnoticed, I used electrodes of zinc and cadmium. Zinc and cadmium deserve to be preferred to other metals, on account of the uniform distribution and relatively powerful action of their most refrangible rays.

The Photographic Procedure.

I used dry gelatin plates of my own preparation. Commercial plates are less suitable for the photography of spectra. When it is important to support as far as possible the optical power of the photographic spectral apparatus, where the sharpness of the image is a main condition, and also where a strong contrast in the intensity of the images of the lines is needed (photometry), the commercial plate is inadequate. It does not work intensely enough to assist spectroscopy to the extent of the modern dry plate.

The gelatin plate of my own preparation gives an intense and finely granular image on a ground clear as glass. The emulsion is relatively rich in silver iodide, containing, to 100 parts by weight of silver bromide, 4 to 5 parts of silver iodide. Its preparation is effected exclusively on Eder's method, with silver-oxide ammonia (J. M. Eder, *Ausf. Hand. d. Photographie*, Part III., pp. 208—211, 4th ed., Halle, 1890), which I have used for more than ten years.

For developing the plates I use the soda-pyrogallic developer, and for fixation sodium thiosulphate.

The Photographic Proof.

Before proceeding to treat of photographic proofs it may be remarked that I have long occupied myself in a complete manner with the photography of the ultra-violet region. My chief object was then the development of the graphic portion of the proofs, the most refrangible rays being overlooked. Only now and then, in

a transitory manner, I have attempted to photograph the most refrangible lines of aluminium, but without success.

More favourable than with aluminium were the conditions of the most refractive lines of zinc, which precede the above-named aluminium lines in the series of the most striking rays of the ultra-violet. But though I did not here operate unsuccessfully, the image which I obtained was always pale and indecisive.

The most refrangible lines of cadmium, which are still less deflected than most refrangible zinc lines, appeared regularly after a short exposure to light. But in intensity they were decidedly inferior to the neighbouring lines of smaller wave-length of the same spectrum.

In general the wave-length of the cadmium line No. 24 ( $226.55$ ) formed the limit of my earlier photographs of the ultra-violet.

The above-mentioned most refrangible lines of cadmium, zinc, and aluminium have been marked by Mascart and Soret with numbers, and generally in spectroscopy, where the wave-lengths are not necessary, this system has come into use. I shall use it in what follows. Here follows a list of these lines with the Mascart-Soret characterisation, the wave-lengths as determined by Cornu (*Archives des Sci. Phys. et Nat.*, III. Periode, t. ii., pp. 121—126, 1879), and a design (fig. 1) taken from my own photographs.

(To be continued).

## NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.\*

By Lieut.-General C. A. McMAHON, F.G.S.

(Continued from p. 55).

	No.	Name.	System.	Form.	Double refraction shows colours of.	Direction of major axis.	Other optical characters.
POTASSIUM.							
$K_2S_2O_7$ .. ..	46	Disulphate.	—	In long slender needles.			
<i>Double Salts.</i>							
With sulph. of Al, Cr, Mn, Fe, &c..	—	—	—	See alums.			
With sulph. of Be	—	—	—	See Be.			
" " Fe	—	—	—	See Fe.			
" " Mg	—	—	—	See Mg.			
" " Mn	—	—	—	See Mn.			
LITHIUM.							
$Li_2SO_4$ .. ..	47		R				
$Li_2SO_4 + H_2O$ ..	48		M				
$Li_2SO_4 + 3H_2O$ ..	49		{ H R	(a) Six-sided prisms, elongated in one direction; some tabular, some radiated. (b) Stars of radiating blades.	White of 7th order.	R.L. to e.	Some of the crystals show a negative bisectrix in <i>c.p.l.</i> , almost all of (a) show traces of one.
$LiKSO_4$ .. ..	50		H	Prisms with pyramidal terminations. Sometimes basal plane truncates the pyramid.	Sometimes so low as to look like an isotropic mineral, sometimes pink of 2nd order.	to c.	Relief good. Margins dark and sharp. Absorption with single nicol.
$LiNaSO_4$ .. ..	51		H	Spherulitic.	3rd order.	Various.	Relief good. Sharp dark margins. Slight absorption.
$LiNH_4SO_4$ .. ..	52		H	Large six-sided mica-ceous-looking plates.	Generally very low, sometimes as high as blue of 2nd order.	R.L. to e.	(n) Cannot be far from that of Canada balsam.
$LiRbSO_4$ .. ..	53		H	(a) Hexagonal tabular crystals. (b) Rectangular four-sided plates. (c) Fibrous or stalk-like.	Very feeble.	R.L. to e.	Outline well defined.
MAGNESIUM.							
$MgSO_4$ .. ..	54	—	—				
$MgSO_4 + H_2O$ ..	55	Kieserite.	M	In prisms, or in granular masses.			
$MgSO_4 + 6H_2O$ ..	56	—	M				

*Remarks.*

No. 46.—Is obtained by heating No. 44 in  $H_2SO_4$  until the mass fuses quietly. Decomposes on contact with water.

No. 48.— $LiHSO_4$  is also known.

No. 51.—Some of the spherulites have a radial structure, some have not, and others show a fixed dark cross when revolved between crossed nicols. In the former the cross is very irregular owing to overlapping. Sometimes opaque centres. In *c.p.l.* the spherulites show traces of lemniscates.

No. 53.—The hexagonal tables differ from those of  $RbSO_4$ . Latter are transparent, sharply outlined, and much twinned. 53 are often only translucent, never in my specimens clear or glassy.

No. 54.—When this salt is dissolved in  $H_2SO_4$  the solution on standing deposits  $MgSO_4 + H_2SO_4$  in six-sided tables, which soon absorb moisture from the air and decompose.

No. 55.—This salt is as difficult of solution in water as gypsum.

\* *Mineralogical Magazine*, vol. x., No. 46, p. 79.

	No.	Name.	System.	Form.	Double refraction shows colours of.	Direction of major axis.	Other optical characters.
MAGNESIUM.							
MgSO <sub>4</sub> +7H <sub>2</sub> O ..	57	Epsom salt.	R	(a) Needle - shaped prisms in radiating groups. (b) Stout prisms.	(a) 2nd order. (b) Sometimes as high as 7th order.	(a) R.L. to <i>e</i> . (b) Sometimes R.L. to <i>e</i> , sometimes    to <i>e</i> .	Absorption with single nicol.
MgSO <sub>4</sub> Na <sub>2</sub> SO <sub>4</sub> +6H <sub>2</sub> O (I have followed Roscoe and Schorlemmer; Fock gives 4H <sub>2</sub> O for this salt).	58	Blödite.	M	(a) Crystals like primrose leaves radiating from a centre. (b) Elongated irregular shaped prisms radiating from a centre. (c) Spherulitic radiating groups.	(a) 1st order. (b) 7th order. (c) Blue of 2nd order.	(a) About 45° from axis of quartz wedge. (b) High angle to <i>e</i> . (c) About R.L. to Q.W.	Absorption with single nicol.
MgSO <sub>4</sub> K <sub>2</sub> SO <sub>4</sub> +6H <sub>2</sub> O	59		M	Large irregular crystals.	7th order, sometimes higher.	—	Absorption here and there. Internal structure often not homogeneous, giving dusty appearance.
MgSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> +6H <sub>2</sub> O	60		M	(a) Prisms with complex terminations elongated in one direction. (b) Stumpy prisms, not elongated.	(a) 3rd order. (b) 7th order.	(a) Within 8° or 9° of    to <i>e</i> .	Strong absorption with single nicol zonal structure. (a) Extinction 5° to 8° from ( <i>e</i> ). In <i>c.p.l.</i> an optical axis emerges from ( <i>a</i> ).
MgSO <sub>4</sub> Cs <sub>2</sub> SO <sub>4</sub> +6H <sub>2</sub> O	61		M	Large tabular crystals; shapes varied and irregular, rarely well formed prisms.	Sometimes as high as 6th order.	—	Absorption with single nicol.
MgSO <sub>4</sub> Rb <sub>2</sub> SO <sub>4</sub> +6H <sub>2</sub> O	62		M	Generally in rhombs, sometimes with two corners truncated.	5th order.	High angle to <i>e</i> when crystal is elongated.	Absorption with single nicol.
MANGANESE.							
MnSO <sub>4</sub> +H <sub>2</sub> O ..	63		M				
MnSO <sub>4</sub> +4H <sub>2</sub> O ..	64		{ R M				
MnSO <sub>4</sub> +5H <sub>2</sub> O ..	65			A platy mass of felted blade-like crystals, sometimes radiated, sometimes like the shafts and barbs of a bird's wing.	7th order.	High angle to <i>e</i> .	Strong absorption with single nicol. Some crystals show a negative bisectrix.
MnSO <sub>4</sub> +7H <sub>2</sub> O ..	66		{ R M				

Remarks.

No. 57.—At the ordinary temperature 100 parts of water dissolve 125 of salt. Epsom salt on heating melts in its water of crystallisation, and loses six molecules of water at 150°. The last molecule is not driven off until 200° is reached. The prisms are usually six-sided, with complex to rounded terminations. 57 (b) commonly contain liquid cavities with bubbles; also endo-prisms. There is conclusive evidence that the latter are not negative crystals.

No. 60.—Liquid cavities with bubbles very common. Often arranged in zones.

No. 61.—Liquid cavities with bubbles rather numerous.

No. 62.—If the concentrated solution of manganous sulphate is allowed to evaporate below 6°, rhombic crystals of No. 66. are deposited. Between 7° and 20° (viz., at the ordinary temperature) crystals of No. 65 are formed. Between 20° and 30° No. 64 is deposited (Roscoe calls them "quadratic"); at the same time a crystalline crust containing 3H<sub>2</sub>O is formed.

When the hydrates are heated to 200°, or their concentrated solution is boiled, the anhydrous salt MnSO<sub>4</sub> is deposited in a reddish yellow powder. It decomposes at a bright red heat. Manganous sulph. is insoluble in absolute alcohol, but it removes a portion of the water from the hydrates.

(To be continued).

A NEW METHOD FOR THE PRODUCTION  
OF PURE PHOSPHORIC ACID.

By H. N. WARREN, Research Analyst.

A SOLUBLE phosphate, preferably sodium phosphate, is introduced into a solution of copper sulphate; and the insoluble copper phosphate thus produced, after washing, is dissolved in solution of phosphoric acid: the solution thus obtained is brought into suitable tanks, into which is placed, in order to retain the strength of solution, a further quantity of copper phosphate enclosed in porous bags. The solution is next electrolysed with medium voltage, using platinum electrodes; a pure and very dense copper is then thrown down. This, if regulated in accordance with the intensity of the current, may be obtained as a crystalline precipitate. The liquid phosphoric acid being electrolysed, with additional quantity of copper phosphate, until the required density is obtained, a large quantity of pharmaceutical acid of 1.75 sp. gr. may thus be obtained in a short space of time.

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## REMARK ON RED PHOSPHORUS.

By W. MUTHMANN.

HERR RATGERS has recently contributed a memoir to the *Zeitschrift für Anorganische Chemie* (iii., 399) in which he shows that the red modification of phosphorus is not amorphous, but crystalline, and that consequently the name "amorphous phosphorus" should be abandoned in favour of "red phosphorus." This latter name is already in use, and is *e. g.* exclusively employed by Rammelsberg in his "Lehrbuch der Krystallographischen Chemie," and by Michaelis in Graham Otto's "Lehrbuch."

Meanwhile I should remark that red phosphorus can be easily obtained also in an amorphous state, and that the red phosphorus of commerce is often a mixture of the amorphous and the crystalline products. If we heat ordinary phosphorus in a sealed glass tube for twenty-four hours to 230°, in an atmosphere of carbonic acid, the resulting product is chiefly amorphous, and contains crystalline parts only here and there.

In my experiment I had placed the tube vertically in the air-bath, and I observed that in its upper part there was deposited an exclusively amorphous product in the form of a crust adhering to the glass, and occasionally also in the form of drops. This red phosphorus can likewise be distinguished externally from the crystalline form. It has a lighter (orange-red) colour, whilst the crystalline kind has a violet surface colour; it is also very brittle, and can be easily ground to a very fine powder,

For examination in polarised light a specimen of the powder was extracted five times with carbon disulphide in order to remove colourless phosphorus, placed on an object glass, moistened with  $\alpha$ -bromnaphthaline (index of refraction for Na light 1.658), and rubbed up with a covering-glass. The several particles transmitted light with a fine orange-red or yellowish-red colour; they proved perfectly isotropic; the fracture was distinctly conchoidal. Hence the substance displays all the properties of an amorphous substance.

It was otherwise different with the portion of the phosphorus remaining in the lower part of the tube. It had a darker colour than the sublimed portion, and, after levigation and extraction with carbon disulphide, it had exactly the properties which Retgers observed in the commercial product. It was therefore a finely crystalline aggregate.

The portion formed in the upper part of the tube, being produced by sublimation, was beyond doubt purer than the residue just described. It seems hence that the crystal-

lisable property of red phosphorus is increased by the impurities generally present, consisting chiefly of traces of arsenic.

As for the red phosphorus of commerce it is, as Retgers correctly remarks, almost always finely crystalline; but in one of three samples which came under my examination I found particles of an orange colour and a conchoidal fracture, which on microscopic examination proved to be amorphous.

Moreover the above results are not novel, since MM. Troost and Hautefeuille (*Comptes Rendus*, lxxviii., p. 748) have some time ago reached the same conclusions. They observed that red phosphorus has a darker colour as the specific gravity is higher. The lower the heat of combustion the higher was the temperature at which it was prepared. On heating very pure ordinary phosphorus to 265° for 650 hours, the above-named authors obtained a splendid red mass of a vitreous fracture and a sp. gr. of 2.148. This is evidently the same amorphous substance which was formed in my experiment from the sublimed phosphorus.

Troost and Hautefeuille also obtained red phosphorus in distinct ruby-coloured crystals, of sp. gr. 2.34, by heating ordinary phosphorus to 580°.—*Zeitschrift für Anorganische Chemie*, iv., p. 303.

DETERMINATION OF THE  
HYDROCYANIC, HYDROSULPHOCYANIC, AND  
HYDROCHLORIC ACIDS.

By P. L. JUMEAU.

THE scanty information which we possess on the determination of the sulphocyanides and cyanides in presence of chlorides has induced us to study this question.

*Determination of Hydrosulphocyanic Acid in presence of  
Chlorides and Cyanides.*

We cannot attempt to determine hydrosulphocyanic acid directly with silver nitrate in presence of cyanides or chlorides, the acids CHNS, HCl, and HCy being equally precipitable by this reagent, and their precipitates behaving identically with reagents, as they are entirely soluble in ammonia and completely insoluble in dilute nitric acid.

It has been proposed to determine it by oxidising a known weight of the substance in solution by potassium permanganate, and precipitating the sulphuric acid produced with barium chloride and weighing the barium sulphate. The proportion of sulphocyanide or of hydrosulphocyanic acid is deduced from the weight, 100 parts  $\text{SO}_4\text{Ba} = 50.643 \text{ CNSH}$ .

When the solution contains sulphates along with sulphocyanides it is necessary first to determine the pre-existing sulphuric acid by precipitating a known volume of the liquid with  $\text{BaCl}_2$ . A second precipitation is then effected in an equal volume of the liquid after oxidation, and the excess of  $\text{SO}_4\text{Ba}$  found in the second experiment enables us to calculate the hydrosulphocyanic acid.

We thought that the same end might be reached by the result of standard solutions. We prepare a liquid containing about 10 grms.  $\text{NH}_4\text{CNS}$  per litre, and determine volumetrically its exact value with silver nitrate in an acid medium ( $\text{NO}_3\text{H}$ ) in presence of a ferric salt, or by weighing the silver sulphocyanide: 100 parts  $\text{CNSAg}$  correspond to 45.783 ammonium sulphocyanide or 35.542 hydrosulphocyanic acid.

On the other hand, we dissolve about 8 grms. permanganate in a litre of water. We take 5 c.c. of the standard solution of ammonium sulphocyanide, and dilute with water to make up nearly 100 c.c.; we add 10 c.c. pure  $\text{SO}_4\text{H}_2$ , and then, drop by drop, the permanganate solution contained in a burette. The perman-

ganate is immediately decolourised. There is formed hydrocyanic acid, which is partly set free at the same time as the sulphur is converted into sulphuric acid. As soon as a drop of permanganate is in excess the mixture takes a bright rose tint, which remains for a long time. We note the number of c.c. added; then it is easy to calculate how much permanganate corresponds to the sulphocyanide or the sulphocyanic acid.

When once its standard is known the permanganate liquor may serve for a great number of determinations. It is sufficient to dissolve 1 grm. or more of the substance to be examined, according to its supposed proportion of CNSH, make up the volume of the solution to 100 c.c., add 10 c.c.  $\text{SO}_4\text{H}_2$ , and then the permanganate drop by drop until a permanent rose tint appears.

#### *Hydrosulphocyanic and Sulphuric Acids.*

If for the 10 c.c.  $\text{SO}_4\text{H}_2$  we substitute HCl we may, when the determination is completed, verify the number found by weight; it is sufficient to expel by heat the chief part of the acid, dilute with water, and precipitate the sulphuric acid produced as barium sulphate. The results should agree perfectly; if not, the substance in question must contain sulphates as well as sulphocyanides.

#### *Hydrocyanic or Hydrochloric and Hydrosulphocyanic Acid.*

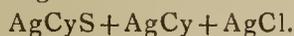
When it is required to determine at once the acids CNSH and HCy in the absence of chlorides, or CNSH and HCy in the absence of cyanides, we make a first determination of the two acids by precipitating them together with silver nitrate, and note the weight of the precipitate. On the other hand we determine, in another portion of the solution, the CNSH as above directed, and transform the result into silver cyanide: 100 parts CNSH = 281.35 NCyS; the figure found, subtracted from the first result, gives the weight of the silver cyanide or chloride, as the case may be, and consequently the proportion of HCy or HCl.

We may also take merely one portion of the solution under analysis, precipitating the two acids together by silver nitrate, weighing the precipitate, re-dissolving it in ammonia with the aid of heat, diluting with water to prevent the formation of salts of argent-ammonium, and precipitating the silver with an excess of HCl. The silver chloride is filtered off, washed, and the CNSH is determined in the filtrate and washings by means of permanganate as above directed (but without the addition of  $\text{SO}_4\text{H}_2$ ).

We thus find rapidly and accurately the weight of the silver sulphocyanide and the other acid by difference. When the titration of CNSH is completed we may precipitate the sulphuric acid produced, and verify by weight the figure obtained.

#### *Hydrosulphocyanic, Hydrocyanic, and Hydrochloric Acids.*

If it is required to determine the three acids in a mixture, we begin by separating them from the other acids and bases which may accompany them by precipitating all three by silver nitrate in a liquid acidified with nitric acid, and weigh the mixture—



We re-dissolve the precipitate in ammonia, and determine the hydrosulphonic acid as already directed—at first volumetrically by HCl in an acid medium, and then by weighing the  $\text{SO}_4\text{Ba}$ : 100 parts of barium sulphate correspond to 71.244 silver sulphocyanide.

*AgCy.*—After a preliminary research has indicated the presence of a larger or smaller quantity of cyanides\* we precipitate a considerable volume of the substance in question, and precipitate with silver nitrate, so that the

precipitate  $\text{AgCNS} + \text{AgCy} + \text{AgCl}$  may contain a noteworthy quantity of silver cyanide.

Of this precipitate we take at most 1 grm., and determine in it the nitrogen.

Contrary to the opinion of certain authors the cyanides yield the totality of their nitrogen by the Kjeldahl process, modified as follows:—The weighed precipitate is placed in a platinum capsule of 10 c.m. in width and 5 c.m. in depth. We cover it with 15 c.c. of Nordhausen sulphuric acid, add 0.750 Hg, place upon the capsule a funnel which fits its sides, and heat nearly to the point of ebullition of the acid. The solution is effected rapidly; we still keep up a little heat, wash the funnel when cool externally and internally, and transfer the liquid into a like flask. The capsule is carefully washed, and the entire volume made up to about 300 c.c.

The flask is closed with a caoutchouc stopper having two perforations. The one receives a tube funnel passing to the bottom of the flask; the other aperture admits the end of an ascending worm, or more simply a tube, upon which two bulbs have been blown at slight distances, and which is then twice bent at right angles. The free extremity plunges into 10 c.c. of dilute standard sulphuric acid.

We pour in through the funnel tube 85 c.c. of soda-lye of sp. gr. 1.31, then 5 c.c. of a saturated solution of sodium sulphide, and connect the tube with a hydrogen apparatus.

By operating thus we escape any loss of ammonia on the saturation of the acid by the soda. It is merely requisite to distil in order to drive the ammonia into the standard acid (causing the current of hydrogen to pass which regulates the ebullition and sweeps out the apparatus), and to titrate the distillate.

From the figure found it is proper to deduct the ammonia introduced by the reagents. To this end we perform a second distillation with equal volumes of the reagents employed: 15 c.c. Nordhausen sulphuric acid, 300 c.c. water, saturated as above with 85 c.c. soda-lye and 5 c.c. sodium sulphide. This correction must never be neglected.

When the correction has been made the remainder represents the nitrogen of the silver cyanide and of the sulphocyanide. The weight of the latter being already known, we can calculate its proportion of nitrogen: 100 parts  $\text{AgCNS} = 8.4337 \text{ N}$ . On deducting from the nitrogen determined the nitrogen of the sulphocyanide, the remainder is the nitrogen of the silver cyanide, and on multiplying it by 10.4477 we have the proportion of the latter.

*AgCl.*—On deducting from the weight of the precipitate analysed  $\text{AgCy} + \text{AgCNS}$  as already obtained, the difference gives AgCl.

If we wish to determine the chlorine directly instead of finding it by difference, we first determine in the solution of the substance CNSH, as already directed in a liquid acidified with  $\text{SO}_4\text{H}_2$ ; we then expel the hydrocyanic acid produced by the reaction, and the hydrocyanic acid of the cyanides, by ebullition in presence of zinc, and in the residue we precipitate chlorine with silver nitrate. By this process we may determine the three acids. It is sufficient to precipitate another portion of the solution in question with silver nitrate. On deducting from the total weight the acids CNSH and HCl calculated as salts of silver, the difference will be AgCy.—*Bull. de la Soc. Chim. de Paris*, vols. ix.—x., p. 346.

On the Saturation of the Nitrogen of Nicotin, and on an Acetylnicotine.—A. Etard.—Nicotin is active by means of carbon. This activity persists in the hydrides, and disappears in isodipyridine. It yields both a dihydride and a hexahydride. On pyrogenation there is an almost exclusive formation of  $\beta$ -propylpyridine. Nicotin combines with acetic anhydride by simple addition,  $\text{C}_{10}\text{H}_{14}\text{N}_2(\text{C}_2\text{H}_3\text{O})_2\text{O}$ .—*Comptes Rendus*, cxvii., No. 3.

\* If we search for cyanides by the formation of Prussian blue, it must be observed that the precipitation is incomplete in presence of sulphocyanides. Small quantities are not detected by this method.

THE DETERMINATION OF PHOSPHORUS IN  
VEGETABLE SOILS.

By ADOLPHE CARNOT.

THE detection of phosphorus in vegetable soils may be simplified by means analogous to those which the author has already indicated for the determination of phosphorus in steels (*Comptes Rendus*, Jan. 16th, 1893). In the first place the method of destroying the carboniferous compound by means of concentrated nitric acid and chromic acid, though very suitable for steels, does not suffice for vegetable soils, especially if humus is present in important quantity. A preliminary roasting is then required for eliminating the chief part of the organic substances.

Secondly, the use of sulphuric acid may occasion great difficulties with soils on account of the formation of a larger or smaller quantity of sparingly soluble calcium sulphate. But I have found that we may here dispense with the isolation of silica by employing subsequently, as in the case of steels, the method of double precipitation of the phospho-molybdate, a method to be recommended on other grounds, especially because it enables us to obtain a final precipitate of a quite definite composition. I have ascertained, in fact, that the determination of phosphoric acid is not altered by more than half a hundredth if we introduce sodium silicate into the nitric liquid before the addition of the nitro-molybdate.

The detection of phosphoric acid in vegetable soils may be performed in the following manner:—

We take 10 grms. of the soil sifted and dried at 100°. If it contains much organic matter it is destroyed as well as possible by roasting at a very moderate temperature, which would be useless for soils poor in humus or for specimens of sub-soil.

We first pour into the capsule a little water to steep the soil and then nitric acid in small quantities until no further effervescence is produced. When this point has been reached we add further 10 c.c. of the same acid and allow it to remain for two hours on the water-bath or the sand-bath at about 100°, stirring from time to time with a platinum spatula or a glass rod, and adding, if needful, a little acid to hinder the substance from drying up.

It is then taken up with hot water, filtered, and the insoluble residue is washed. The liquid is then concentrated, and when its volume is reduced to about 50 c.c. we add 5 c.c. of concentrated nitric acid and about  $\frac{1}{2}$  gm. of chromic acid in crystals. Then placing a small funnel over the vessel to cause the condensed vapours to fall back, we heat it to ebullition for half an hour to complete the destruction of the organic matter.

We add to the liquid 5 grms. of ammonium nitrate in order to facilitate the precipitation of the phosphoric acid, and then 50 c.c. of the nitric solution of ammonium molybdate. The solution is prepared by dissolving in water 150 grms. of crystalline ammonium molybdate, diluting to 1 litre, then pouring into it one litre of nitric acid of specific gravity 1.20, leaving the whole for three or four days at the temperature of 60°, separating the clear liquid and using only the clear liquid.

It is heated to about 100° for an hour on the water-bath or the sand-bath. In this time the precipitation is completely effected by reason of the large proportion of the molybdic solution and the ammonium nitrate.

After having allowed the precipitate to subside the clear liquid is decanted off, there is put in the beaker a little water acidified with  $\frac{1}{2}$  of its volume of the molybdic solution. It is shaken up, allowed to subside, and again decanted twice, causing the liquid to pass through a small flat filter which retains the particles of precipitate carried away in washing.

The precipitate is then treated in the flask and on the filter with 30 c.c. of ammonia mixed with an equal volume of hot water. The washing is completed with 50 c.c. of hot water rendered slightly ammoniacal, and the

entire liquid is received in a small flask and suffered to cool.

We pour into it dilute nitric acid until the ammoniacal liquid is neutralised, taking care to proceed slowly and to cool the flask, if necessary, to prevent the temperature from rising above 40°. When the yellow precipitate of phospho-molybdate is no longer re-dissolved on agitating the liquid, that is to say when the ammoniacal liquid has been neutralised, we add further 3 c.c. of pure nitric acid mixed with 4 to 5 c.c. of water and as much molybdic solution. It is left at rest for two hours at 40°, then the precipitate and the liquid are poured upon a tared filter. We complete the washing with a little water acidified with 1 per cent of nitric acid, then with a little water, using the filter pump. It is dried in the stove at 100° and weighed at once.

The weight found if multiplied by the coefficient 0.0373 gives the proportion of phosphoric acid contained in the 10 grms. of soil submitted to analysis.—*Bull. de la Soc. Chim. de Paris*.

## A CRYSTALLINE CHROMIUM TUNGSTATE.

By EDGAR F. SMITH and HERMAN L. DIECK.

POTASSIUM bichromate was brought together with an equivalent amount of pure tungstic oxide. Heat was applied to the mixture; fusion followed and the mass was held in this condition until the evolution of gas bubbles ceased. The temperature was never higher than necessary to maintain a liquid condition of the mixture. After cooling, the fused mass was treated with water until the latter ceased to dissolve anything. Sodium hydroxide and ammonium hydroxide were next employed for washing purposes, and these finally displaced by pure distilled water. The well-washed substance was carefully dried at 100°. It showed a dark brown colour, and when examined under the microscope revealed the presence of acicular, brown-coloured crystals of orthorhombic outline: associated with these were green-coloured crystals, which were apparently of the same crystallographic system. This mixture was exposed to the action of aqua regia for an hour; it was then filtered, washed, and dried. A re-examination of the brown residue showed that the green crystals had been removed and that the brown-coloured body alone remained. It had been unaffected by the acid. Two weighed portions of the mixed crystals were treated with aqua regia, the acid solutions evaporated, the residues dissolved in water, and the aqueous solutions treated with ammonium hydroxide. Chromium hydroxide was precipitated. In the one case the ignited oxide equalled 2.89 per cent and in the other 2.92 per cent of the original mixture. A sufficient quantity of pure brown crystals was prepared for analysis. We first endeavoured to effect their decomposition by fusion with sodium carbonate and sulphur. Several attempts demonstrated that this course offered little chance of a satisfactory analysis. Digestion with hydrofluoric acid gave a poor result; the acid failed to completely decompose the material. Portions of the substance were next ignited in a current of hydrogen, the residue then oxidised with aqua regia, evaporated to dryness, and treated with ammonium hydroxide. Considerable tungsten was removed in this manner, but much remained with the chromium, from which it seemed almost impossible to free it. The mixture of tungstic and chromium oxides was ignited a second time in hydrogen and again treated with aqua regia. This operation was repeated until no more tungsten could be extracted. Combining the separate portions of tungstic oxide, their total quantity gave 88.37 per cent  $WO_3$ . The chromium oxide, previously associated with this amount of tungstic oxide, equalled after careful purification 11.75 per cent. This method of analysis having proved tedious and time-

consuming, we determined to try fluxing the brown coloured material with a mixture of pure sodium carbonate and potassium nitrate, as we had previously satisfied ourselves that it did not contain the alkali metals. The fusion was taken up with water, acidulated with hydrochloric acid, and evaporated to dryness. Tungstic acid separated; the residue was moistened with acid and again evaporated. It was then digested with acid and left pure tungsten trioxide, which was filtered, washed, and weighed. It equalled 88.08 per cent. The chromium oxide in the filtrate, after precipitation and purification, equalled 12.10 per cent. Upon repeating this course with new portions of the substance we obtained results that agreed with those just given, so that we feel satisfied that they represent the true composition of the brown crystals. Taking the mean of the percentages of the two analyses given above as a basis of calculation we deduce as the most probable ratio,  $1\text{Cr}_2\text{O}_3, 5\text{WO}_3$  or  $\text{Cr}_2\text{O}_3, 5\text{WO}_3$ . The theoretical requirements of this formula are:

						Per cent.
$\text{WO}_3$	..	..	..	..	..	88.40
$\text{Cr}_2\text{O}_3$	..	..	..	..	..	11.59
						Per cent found.
$\text{WO}_3$	..	..	..	..	88.37	88.08
$\text{Cr}_2\text{O}_3$	..	..	..	..	11.75	12.10

Tungstates of chromium that exist ("Fremy's Encyclopedie Chimique," iii., 166) are hydrous and have been prepared by double decomposition in the wet way. The salt we describe is, so far as we can ascertain, the first of its class.—*Fourn. Amer. Chem. Soc.*, xv., No. 3.

#### THE SPECIFIC HEATS OF THE METALS.\*

By JOS. W. RICHARDS, Ph.D.,  
Instructor in Metallurgy, &c., in Lehigh University.

(Continued from p. 60).

An exactly similar set of experiments was made by your lecturer on aluminum, up to  $600^\circ$ , with a determination of its latent heat of fusion. In connection with Prof. B. W. Frazier, of our University, a similar set of experiments is now in progress with copper, the result of which will give the curve for its specific heat to the melting point, its latent heat of fusion, and the specific heat of molten copper. The approximate values so far found are given in discussing copper. The calorimeters and apparatus used by Professor Frazier and myself are shown in the accompanying cuts. Fig. 1 shows a section of the calorimeter. The outer box is walnut, the calorimeter proper is of thin brass, tightly covered, packed in with cotton. The stirrer is of wire mesh, fitting closely to the walls, and provided with a glass rod for a handle. (Wooden rods warped and worked stiffly.) The thermometers are standard Baudin, graduated to  $0.02^\circ$  and easily read with a lens to  $0.0025^\circ$ . The calorimeter is charged with about 300 grms. of water, and using a platinum ball of 52 grms., the rise in temperature is approximately  $0.5^\circ$  for every  $100^\circ$  fall of the platinum ball. The corrections for losses of heat to the calorimeter during the experiment are made by a system worked out by us, which gives most satisfactory results, but which cannot be described in the limits of this lecture. Suffice it to say, that the probable errors in the calorimeters themselves are within 0.1 per cent.

Fig. 2 shows the apparatus for containing the metals in the furnace. It is a piece of fire-brick, cut as indicated, and with two smooth French annealing cups fastened into the holes. In operation, the platinum is put in one side, the other metal in the other, and the crucibles covered by porcelain lids connected by a stout platinum wire. The whole is then heated several hours at the

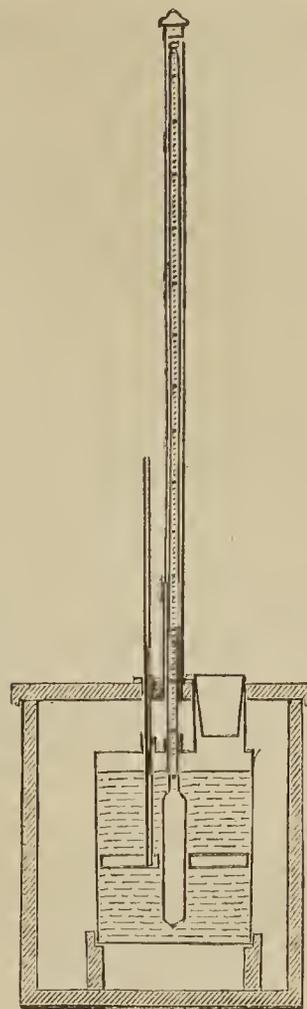


FIG. 1.

desired temperature. Everything being ready, the two calorimeters are brought into the furnace room, opened to receive the balls, the brick withdrawn from the furnace, the lids lifted off by the platinum wire, and then by inclining the brick between  $45^\circ$  and  $90^\circ$  to one side one ball

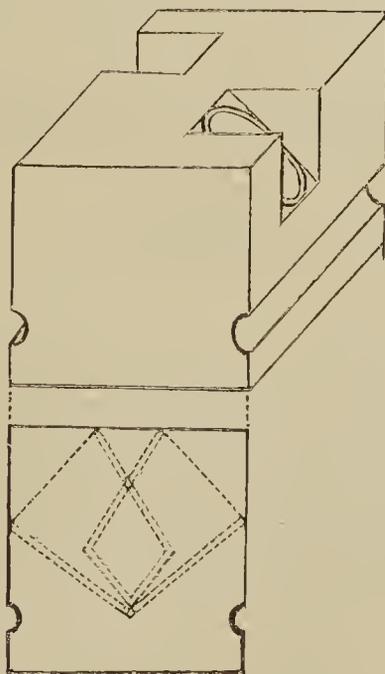


FIG. 2.

is dropped into its calorimeter, and by inclining the brick to the other side the other is dropped into its. The stoppers are replaced, the calorimeters carried to their room and readings taken for five minutes. In order to correct all possible errors, a full experiment consists of

\* A Lecture delivered before the Franklin Institute, Jan. 30, 1893.

two separate ones made as nearly as possible at the same temperature, but with every condition which could affect the result reversed; these are:

1. The position in the furnace.
2. The position in the brick.
3. The order of dropping out of the brick.
4. The calorimeter into which it is dropped.

With these precautions, we have not rested satisfied until we have attained to a maximum difference between corresponding experiments of less than one per cent, and a deviation from the mean of less than 0.5 per cent.

#### IV.

In general we may say that the only factor we really find out in investigating specific heats by the method of mixtures is the amount of heat given out by the substance in cooling through a certain range of temperature. The lower temperature is that of the calorimeter, which usually varies between 15° and 25°, while the upper temperature varies at will. If the results obtained for any one substance are plotted on a diagram, taking the range of temperatures as abscissæ and the heat given out as ordinates, it is at once found for most metals that a straight line will not pass through the points. The heat given out increases in greater proportion than the temperature, giving a curve which is convex towards the axis of abscissæ, gradually getting steeper and steeper. The formula for such a curve must then be of this nature:—

$$Q = \alpha t + \beta t^2 \quad (1)$$

in which  $Q$  represents the quantity of heat given out to zero, and  $t$  any temperature. If a curve of this nature does not rise sufficiently fast at high temperatures, a third term can be added, making it—

$$Q = \alpha t + \beta t^2 + \gamma t^3$$

It has been found that formulæ of this kind will fit within the errors of experiment almost all the observations on specific heats so far made, and in most cases the formula of two terms answers perfectly. The third term seems to be needed only when the curve is approaching the melting point or a critical point of the substance, when part of the heat necessary for a change of state seems to be absorbed before the point itself is actually reached. At temperatures distant from these points only two terms are needed in the formula.

Suppose, now, that a series of experiments have been made with a metal, and it is wished from the data obtained to construct the formula reckoned to zero. For a body cooling from  $t_2$  or  $t_1$  to zero the formula gives—

$$\begin{aligned} Q_1 &= \alpha t_1 + \beta t_1^2 \\ Q_2 &= \alpha t_2 + \beta t_2^2 \end{aligned}$$

therefore, for a body cooling from  $t_1$  to  $t_2$ , the amount of heat given out must be—

$$(Q_1 - Q_2) = \alpha(t_1 - t_2) + \beta(t_1^2 - t_2^2) \quad (2)$$

Having measured the quantity of heat given out in the different experiments between various high and low temperatures, the values of  $(Q_1 - Q_2)$ ,  $t_1$  and  $t_2$  can be substituted in equation (2), and thus each experiment gives us some relation between  $\alpha$  and  $\beta$ ; therefore any two experiments will give us two equations from which the value of these unknown coefficients may be derived. Two other experiments might give slightly different values for  $\alpha$  and  $\beta$ , and thus several slightly varying values could be obtained and their average taken as the true values. A much neater and more accurate way, however, is to substitute the data obtained in each experiment in equation (2), thus obtaining as many equations of condition as there are experiments made, and from these calculating the most probable values of  $\alpha$  and  $\beta$  by the method of least squares. The formula thus derived will give a curve which will pass through the mean of all the observations made.

If we divide the heat given out by a substance falling

from  $t$  to zero by the range of temperature  $t$ , we get the mean value of the specific heat between those temperatures; therefore—

$$S_m = \frac{Q}{t} = \frac{\alpha t + \beta t^2}{t} = \alpha + \beta t. \quad (3)$$

Or, if the substance does not fall to zero, but from  $t_1$  to  $t_2$ ,—

$$S_m = \frac{Q_1 - Q_2}{t_1 - t_2} = \frac{\alpha(t_1 - t_2) + \beta(t_1^2 - t_2^2)}{t_1 - t_2} = \alpha + \beta(t_1 + t_2). \quad (4)$$

If we evaluate equation (2) for two temperatures within 1° of each other, we obtain the heat given out for a fall of 1°; that is, the actual or true specific heat at that temperature. A much more elegant method, however, is to take the first differential coefficient of the equation representing the heat given out in falling to zero [equation (1)], and we thus obtain the equation for the ratio of the heat given out to the fall in temperature which is the true specific heat.

Therefore, taking—

$$Q = \alpha t + \beta t^2 + \gamma t^3,$$

we have—

$$S = \frac{dQ}{dt} = \alpha + 2\beta t + 3\gamma t^2.$$

Or, leaving out the third term as before,—

$$S = \alpha + 2\beta t. \quad (5)$$

This formula is very similar to equation (3) for the mean specific heat, both of them being the formulæ of straight lines, starting when  $t=0^\circ$  at the value  $\alpha$ , which is therefore the true specific heat of the body at zero. The formula for the true specific heat can thus be easily deduced from that for the amount of heat; and it is this quantity which has an intimate dependence on the properties of the substance at any given temperature. For this reason the diagrams which follow show the variations of the true specific heat with the temperature.

(There were here thrown upon the screen a number of diagrams, with running comments by the lecturer. It has been thought advisable in printing the lecture to incorporate these diagrams into an Appendix, in which is discussed the specific heat of each of the metals separately at a length which would have been impossible, and indeed undesirable, during the delivery of the lecture.)

#### V.

The heat or energy absorbed by a substance for 1° rise of temperature is divided up in the body into several parts. One fraction of it does external work, if the substance is free to expand. The amount of this for solids and liquids is so small as to be negligible, but for gases it amounts to as much as two-fifths of the whole specific heat. As far as the metals are concerned, we can neglect it. A second fraction of the energy absorbed goes to increasing the energy of atomic motion within the molecule. For solids and liquids, where the molecule is complex, this will amount to a considerable portion of the whole; for gases it is a much smaller fraction. The third and last part of the energy absorbed may be considered as going to increase the energy of vibration of the molecules as a whole—that is, increasing the temperature of the substance; for, on the mechanical theory of heat, the temperature of a body is measured by the energy of vibration of its molecules as a whole. We can therefore put—

$$Q = \text{molecular energy} + \text{atomic energy} + \text{external work.}$$

Leaving out of the discussion the last term, we may say that the proportion which the first two terms bear to each other or to the whole has not been solved for solid and liquid bodies, but has been worked out very satisfactorily for gases, especially by Clausius and Naumann.

The most striking law which has been discovered re-

garding specific heats is the law of Dulong and Petit, which affirms that they vary inversely as the atomic weights of the elements. The metals behave very well in this respect, the products of their atomic weights and specific heats being all nearly the same. But, in order to attain this uniformity, the metals must be compared at ordinary temperatures, since the specific heats vary so greatly. Iron, for instance, gives the usual product, about 6.3, if the specific heat at 50° is taken; but if its specific heat at 900° were taken this product would be just about double. But the fact remains that there are slight variations in the products (atomic heats) at ordinary temperatures, and much speculation has been indulged in regarding their causes. In some instances a great variation has been due to incorrect determinations of the specific heat, or from the specimen used not being perfectly pure. Manganese, for instance, has never been obtained perfectly free from silicon or carbon, either of which increases its specific heat; while aluminum has generally been used containing iron, which decreases its specific heat. Determinations with the chemically pure metal would give in both cases atomic heats nearer the average. Yet, allowing for this source of error, there are still variations to be explained, and the only reasons we can assign are that the metals are in different states of aggregation, requiring different amounts of work to overcome the interior cohesion of the particles or to elongate the metal. It is possible, therefore, that the differing densities, hardness, and strength of the metals are the various disturbing influences which prevent their atomic heats from being exactly alike at ordinary temperatures.

Some investigators have tried to bring these facts into the calculation and take strict account of them. P. Joubin, for instance, states that for any metal the product of the specific heat and specific gravity (which would be the specific heat of unit volume) is proportional to the product of the modulus of elasticity into the [linear?] coefficient of expansion by heat. H. Fritz states that the product of the atomic heat, the specific heat of unit volume, and the cube root of the atomic volume, is equal to the cube root of the absolute temperature of the melting-point into the specific heat of unit volume divided by 1.28; that is,—

$$(\text{At. ht.}) \times (\text{sp. ht. unit vol.}) \times (\text{at. vol.})^{\frac{1}{3}} \\ = \text{M.P.} \left( \frac{\text{sp. ht. unit vol.}}{1.28} \right)^{\frac{1}{3}}$$

Fritz claims to have verified this formula for forty-eight of the elements; but I cannot offer any remarks, not having seen the original paper.

Weibe holds that the amount of heat necessary to raise an element from the absolute zero to its melting-point (taking atomic weights) is inversely apportioned to its coefficient of cubical expansion. This rule holds good for some of the elements, especially for those crystallising in the isometric system, but there are many exceptions to it, so that it is not a satisfactory solution of the problem of reconciling the differences in the atomic heats.

A rule of somewhat similar nature has been discovered by the writer, applying to the latent heats of fusion. I have found that the latent heat of fusion of the metals is frequently a simple fraction of the heat required to raise the metal from the absolute zero to its melting-point. It is in many cases simply one-third. Let us illustrate by several examples, referring to the previous discussions for the data:—

	Calories.
<i>Tin.</i> —	
Bede's formulæ would give for the heat from absolute zero to melting-point .. .. .	27.6
One-half of this would be .. .. .	13.8
Observed by Person .. .. .	{ 13.73
Observed by Richards .. .. .	{ 14.56

	Calories.
<i>Silver.</i> —	
Pionchon gives from M. P. to 0° .. .. .	60.32
Formula suggested gives (0° to 273°) .. .. .	14.45
<hr/>	
Total heat to absolute zero .. .. .	74.77
One-third of this .. .. .	24.92
Observed by Pionchon .. .. .	24.72
<i>Platinum.</i> —	
Gives in cooling to 0° (Violle) .. .. .	75.21
From 0° to -273° (Violle's formula) .. .. .	8.19
<hr/>	
Total to absolute zero .. .. .	83.40
One-third of this .. .. .	27.80
Observed by Pionchon .. .. .	27.18
<i>Cadmium.</i> —	
Naccari's formula gives the mean specific heat to absolute zero 0.05, from which the total heat would be .. .. .	29.70
One-half of this .. .. .	14.85
Obtained by Person .. .. .	13.66
<i>Zinc.</i> —	
Le Verrier gives as the heat to 0° .. .. .	46.9
Formula (Bède's) gives from 0° to 273° .. .. .	24.3
<hr/>	
Total heat to absolute zero .. .. .	71.2
One-third of this is .. .. .	23.7
Obtained by Person (corrected) .. .. .	22.6
<i>Bismuth.</i> —	
Taking Bède's formula, and correcting it so that it passes through Regnault's value, we get the equation—	
$Q = 0.0308 t + 0.00002 t^2,$	
which gives for -273 to +266.8 .. .. .	16.57
One-half of this would be .. .. .	8.28
Obtained by Person (corrected) .. .. .	8.88
<i>Copper.</i> —	
The formula worked out by the writer gives	
from -273° to 1054 .. .. .	143.0
One-third of this is .. .. .	47.7
Observed .. .. .	43.3
<i>Palladium.</i> —	
Gives out to 0° (Violle) .. .. .	109.8
From -273° to 0° (Violle's formula) .. .. .	15.1
<hr/>	
Total to absolute zero .. .. .	124.9
One-third of this is .. .. .	41.6
Obtained by Violle .. .. .	36.3
(Violle remarks that this was an experiment of unusual difficulty, and that the result is approximate.)	
<i>Mercury.</i> —	
Taking Regnault's value for the specific heat of solid mercury, we have for the total heat from absolute zero to -40° .. .. .	
One-third of this .. .. .	7.46
Observed by Person .. .. .	2.49
Observed by Person .. .. .	2.84
<i>Alloys.</i> —	
The rule applies probably to alloys also; for instance, d'Arcet's Fusible Alloy. Its specific heat at 30° is 0.062 (Spring). The mean between 96° and -273° is very probably smaller than this, but how much we cannot say, probably 10 per cent. However, the above value would give for the heat from absolute zero .. .. .	
One-third of this is .. .. .	22.88
Observed by Person .. .. .	7.63
Observed by Person .. .. .	5.96

With metals having a small latent heat of fusion the inaccuracies of the formulæ for the specific heat may introduce relatively large errors. After all, there are too many deviations and variations to enable us to claim any strict rule regarding these coincidences. All that I wish to do is to call attention to the fact that for bismuth,

cadmium, and tin, the latent heat of fusion is very nearly one-half the total heat in the solid metal at its melting-point, while for silver, platinum, zinc, copper, palladium, mercury, and d'Arcet's alloy it is close to one-third. The latent heat of fusion of silver may be assumed as probably the most accurate known, as also the curve of its specific heat, and in this very case the proximity of the ratio to one-third is the closest.

I might close by venturing a prediction. The best results we have for *gold* would indicate about forty-two calories as the amount of heat contained in the solid metal at the melting-point. If the ratio in this case is one-third, as its similarity to silver, copper, and platinum might indicate, its latent heat of fusion would be about fourteen calories. It has not yet been determined, to my knowledge.

(To be continued.)

## NOTICES OF BOOKS.

*The Law of Cremation.* An Outline of the Laws relating to Cremation, Ancient and Modern; together with the Rules and Regulations of various Cremation Societies at Home and Abroad. By AUBREY RICHARDSON, Solicitor. London: Reeves and Turner. 1893.

IN this age of great cities the disposal of the dead must continually become a more pressing question. The work before us is, therefore, calculated to be very widely useful. It lays before us the essential features of the cremation controversy, showing the benefits to be derived by the use of fire in place of interment, and it shows the one sole difficulty to be avoided. This difficulty, it need scarcely be said, relates to the detection of poisons. At present if after death and burial suspicion should arise that some person has not come by his death fairly, the body can be exhumed and submitted to chemical and microscopical examination. After cremation, this is in most respects out of the question. But the author very justly says that "exhumation is at best a clumsy attempt to rectify culpable want of care before burial." If a body has been in the earth for, say, three or four weeks, the chance of identifying any poison found in the remains will be very much lessened. Some of the organic poisons may have escaped or undergone decomposition. Ptomaines may have been generated in the tissues, and may greatly complicate the issue. It may be pleaded—as has actually occurred in Germany—that arsenic present in the soil of the cemetery has been absorbed by the corpse. To meet this plea it became necessary to institute analyses of the wood of the coffin and of the soil both within the grave and at different distances on either hand. Surely it would be better for every corpse to undergo a due examination by a qualified medical man, who would be authorised to hand it over to the coroner if the circumstances demand.

Hence we feel justified in asserting that the general adoption of cremation, instead of promoting, would check, secret murders.

The sanitary advantages of cremation as compared with burial are most striking, especially in cases of epidemics. Accordingly, in Brazil and La Plata during visitations of yellow fever, the cremation of the dead is obligatory.

In this country cremation is legal, though unfortunately a man cannot leave any binding directions for his remains to be destroyed by fire. In that respect we are in a worse position than are our neighbours in several European countries and in the United States of America.

If the opponents of cremation have not many valid arguments at their disposal, they have at any rate a catch-word which is a great thing in a country governed by catch-words. They love to talk about "Christian burial," insinuating that any other way of disposing of

the dead is un-Christian, or even anti-Christian. If such objectors will consult the work before us, they will find that interment might rather be termed Islamite than Christian.

One of the most formidable opponents of cremation is so-called "funeral reform"; burial, not in stout coffins, but in light wicker cases. This slight modification is asserted to change the character of putrefaction. Chemists will at once repudiate this contention. But the general public may be reminded that, according to the observations of Pasteur, some oxen shot by way of stamping out the cattle plague and buried—of course, without coffins—to the depth of three yards were able to impart the disease to some sheep afterwards penned over their grave. Hence it does not seem as if decomposition could be rendered less virulent by a different mode of interment.

Mr. Richardson's work may be strongly recommended to sanitary reformers, and especially to municipal authorities. It is calculated to generate a healthier tone of thought on the cremation question.

*Ozone: its Commercial Production; its Applications.* By EMILE ANDREOLI. London: H. Alabaster, Gatehouse, and Co.

IF, as the author informs us, "no book has been published on ozone, its production and its commercial applications," it has been the subject of no little ink-shed in the form of memoirs and discussions. As regards its nature, we have about arrived at an agreement; but on its properties and its applications there is still much variety of opinion, as we find here shown in a series of paragraphs and extracts from the scientific journals and transactions extending from 1840 to the present day. Schönbein, the discoverer of ozone, seems to hold different views at different times; asserting on one occasion, in a letter to Faraday, that ozone is a compound of oxygen and hydrogen, and afterwards attacking Williamson for saying that hydrogen is one of the components of ozone!

There is mention here made of Fehling's most injudicious proposal to call ozone "electrical gas"—a step the more to be condemned as other gases may be obtained by electrical action, and as ozone itself may be produced without such action.

In speaking of the possible applications of ozone, in connection with the researches of Fröhlich, the author asks "why has not ozone been tried for disinfecting rags?" The question is here whether ozone will disinfect rags better and more cheaply than it can be done by high temperatures? It may seem hypercritical to remark that in this connection Signor Andreoli speaks of the "phylloxera microbe." Now the phylloxera is no microbe, but an insect. It is possible that ozone might kill this pest if it could be passed into the soil in sufficient quantity; but what about the working cost?

In like manner we may raise a question about the purification of sewage by means of ozone, as here suggested. To decompose the ammonia present in such waters into its constituents would be a doubtful policy. We want the ammonia as plant food.

On p. 68 we read:—"No one can state that ozone destroys *all* germs and bacteria. This is an Utopia." But we do not want all microbia destroyed; many of them are harmless, many more useful and even necessary. If we can destroy the morbid micro-organisms we shall have effected all that we need desire in this direction.

The remarks on the possible industrial applications of ozone are suggestive, and ought to draw the attention of inventors, many of whom are engaged with devising new forms of mischief, which they might well abandon in favour of the possibilities held forth in this little work.

The bibliography at the conclusion will be found very useful.

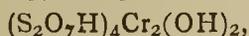
CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 2, July 10, 1893.

**Nomination.**—M. Bichat was elected a correspondent of the Academy for the Section of Physics.

**Pyrosulphochromic Hydrate.**—A. Recoura.—If into a solution of chromopyrosulphuric acid,—



there is poured a concentrated acid—hydrochloric, nitric, or sulphuric—there is produced a greenish white precipitate, which is the hydrate in question,  $(S_2O_7)_2Cr_2(OH)_2$ . This precipitate is soluble in pure water, yielding an opalescent yellowish green solution, which has the property of precipitating all metallic solutions.

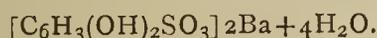
**The Compounds of Selenious Acid with the Molybdates, and on Molybdoselenious Acid.**—E. Péchard.—The author has formerly shown that sulphurous acid may combine with the alkaline molybdates to form molybdosulphites. Selenious acid forms analogous compounds which are more stable. The author has described the ammonium, potassium, sodium, and barium salts. Molybdoselenious acid is obtained by decomposing the barium salt with the equivalent quantity of sulphuric acid. The clear yellowish filtrate forms, on concentration, a syrupy mass which does not crystallise.

**Arsenic and Antimony Iodosulphides.**—L. Ouvrard.—The author has obtained the compounds  $As_2S_5I$ ,  $AsSI_2$ , and  $AsS_2I$ . With antimony the author obtained  $SbS_2I$ , a vermilion-red compound formed of entangled leaflets. Another compound,  $SbS_2I_3$  is soluble in dry carbon disulphide, and readily decomposed with moist air.

**The Dissociation of Calcium Plumbate.**—H. Le Chatelier.—Some time ago Kassner proposed to use this compound in place of barium peroxide for obtaining oxygen. If heated, it gives off a part of its oxygen; the reaction being  $PbO_2 \cdot 2CaO = PbO + 2CaO + O$ . The dissociation takes place at a higher temperature than that of barium peroxide. The heat for the latter substance is  $700^\circ$ , whilst that for calcium plumbate is  $900^\circ$ . This is a great inconvenience, on account of the increased consumption of fuel and the more rapid corrosion of the iron retorts. On the other hand, the plumbate has a great advantage over baryta, by absorbing oxygen more rapidly and more completely, and it does not require the air to be previously dried and freed from carbonic acid.

**On Benzoylcinchonine.**—E. Léger.—This compound, which was first obtained by Schützenberger, is found in prismatic crystals, inodorous and colourless. It is insoluble in water, but very soluble in alcohol and in ether saturated with water. It constitutes the true benzoic ether of cinchonine considered as a phenol. It acts upon polarised light, and is slightly laevorotatory.

**Action of Sulphuric Acid upon Pyrocatechin and on Homopyrocatechin.**—H. Cousin.—The barium salt of pyrocatechin has the formula—



That of homopyrocatechin is—



**Process for the Direct Combination of Ethylenic and Aromatic Carbides.**—A. Brochet.—Several syntheses have been of late effected by the direct union of the methyl groups of the methylbenzenes with cinnamene in presence of sulphuric acid. The author generalises this action, and thinks that the carbides of the ethylenic series must combine with benzene and its derivatives. With

amylenes the yields are less good than with normal hexylene. Toluene behaves in the same manner as benzene.

**Attempt at the Diagnosis of the Isomeric Amidobenzoic Acids, and of some other Aromatic Compounds.**—Oechsner de Coninck.—We may distinguish the amidobenzoic and nitrobenzoic isomers and the diphenols by preparing their alcoholic or ethereal solutions and exposing them to the solar rays or to diffused light. The diagnosis is possible, not only by the different colourations which appear, but by the greater or less stability of the tints produced on exposure to light, and the very different times in which they appear.

**On Geraniol.**—Ph. Barlier.—The linalol of the essence of spike lavender is nothing less than the instable stereoisomeric modification of geraniol, playing with it the same part as does licareol with licarhodol.

**Influence of the Acidity of Worts on the Composition of the Phlegms.**—L. Lindot.—The phlegms obtained from acidulous worts contain more higher alcohols than those from worts not acidulated, but they contain less bases, volatile acids, and ether, and must hence be regarded as of a better quality.

**The Greater Assimilability of the Nitric Nitrogen of Nitrates recently formed.**—P. Pichard.—The preference accorded to sodium nitrate as compared with potassium nitrate as a chemical manure is justified, not merely by its price, but by a greater efficacy resulting from its transformation into sulphate in a soil well supplied with potash. The practice of spreading soda and saltpetre in small repeated doses serves not merely to avoid loss from its being washed away, but to furnish the plants with potassium nitrate of recent formation.

**Honeydew of the Lime Tree.**—M. Maquenne.—This exudation is similar to the manna of the larch studied by Berthelot, and to that of *Alhagi camelorum*. Its presence is due to a parasite.

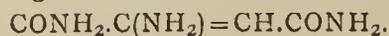
Vol. cxvii., No. 3, July 17, 1893.

**On the Simplicity of Samarium.**—Eug. Demarçay.—Lecoq de Boisbaudran has recently entrusted to me four solutions obtained from a fractionation of samarium, in order that I should examine their spectrum of absorption in the violet region. These fractions comprise:—1. The tailings of the fractionation by ammonia. 2. The middle portion of this fractionation. 3. The head of the fractionation by oxalic acid from the head of the fractionation by ammonia. 4. The tailings of the same fractionation by oxalic acid. I may summarise these observations very simply by saying that these four portions gave essentially the spectrum of samarium with a trace of neodymium in No. 1, and a trace of the earths of erbia (?) in No. 3 and especially No. 4. The spectrum of samarium did not present the slightest variation in these four portions. This led me to re-examine the products in which I thought I had detected signs of the variation of the spectrum of samarium, and which led me to assume the presence of two distinct substances in this element. This view has since been put forward anew by several chemists. According to this new examination, it does not seem to me justified. These variations have, in fact, been observed in solutions rich in didymium. If we examine the spectrum of a rather concentrated nitric solution of neodymium, we observe along with the strong ray ( $\lambda = 427.5$ ) a weak band, very vague, and spread out ( $\lambda = 418$ ) about, which almost coincides with one of the strong bands of samarium even in the absence of all the bands of this element. On contracting the slit of the spectroscope, this band always remained simple and vague. On the other hand, if we examine the acid nitrate of samarium with the same narrow slit we perceive that the band of Lecoq, Soret, &c., is composed of two relatively narrow rays ( $\lambda 415$  and  $419$ ). The middle of the band of the salts of neodymium coincides almost with the more refrangible margin of the less refrangible ray. It is thus easily

understood that with a broad slit and solutions rich in didymium this double band has a variable aspect. I have also observed in the spectrum of the four portions—though in a manner too uncertain to know if their intensity varied—three small bands rather more refrangible than H. Pure neodymium does not show these rays. I conclude that hitherto there is no room to suspect the simplicity of samarium on grounds drawn from the variability of the absorption-spectrum of these solutions.

**On the Cyclic Condensations of Carbon.**—Gustave Rousseau.—This paper will be inserted in full.

**On Aminobutenediamide and Butanonediamide.**—R. Thomas Mamert.—To the former of these bodies the author assigns the formula—



He has examined its behaviour with potassa and with copper sulphate. Butanonediamide forms white crystals which melt and are decomposed at 180°. It is moderately soluble in water, and the solution gives with ferric chloride a characteristic ruby-red colour.

**Rotatory Powers of the Derivatives of Quineic Acid.**—S. G. Cerkez.—This paper consists chiefly of tables. It appears that the introduction of hydrocarbon radicles and metals diminishes the rotatory power of quineic acid. The other organic bases, except diethylamine, do not combine with quineic acid in an alcoholic solution.

**Derivatives and Constitution of the Rhodinol of the Essence of Roses.**—Ph. Barbier.—If rhodinol is submitted in a closed vessel to the action of acetic anhydride at 180° there is merely formed rhodinolacetic ether,  $\text{C}_{10}\text{H}_{17}\text{OC}_2\text{H}_3\text{O}$ , a colourless mobile liquid of an agreeable odour, boiling at 131° under a pressure of 15 m.m. Its specific gravity at 0° is 0.9214. If saponified by alcoholic potassa this ether is re-converted to rhodinol without any change of properties.

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

**Volumetric Determination of Iron by Stannous Chloride.**—L. L. de Koninck.—The objection to the volumetric determination of iron by means of stannous chloride has been the difficulty of detecting the end of the reaction. The remedy generally employed has been the addition to the solution of a little cobalt chloride. The green tint thus produced passes to a decided blue as soon as the last trace of the ferric chloride is reduced. K. W. Mahon proposes another indicator composed of a solution of mercuric chloride containing 34 grms. of this salt per litre. There is further added a trace of platinum chloride containing 0.05 gm. of platinum. For a determination he employs 15 c.c. of this solution.

## MISCELLANEOUS.

**Thermometers for Low Temperatures.**—The International Meteorological Commission having intimated its desire that the International Bureau of Weights and Measures should supply the National Meteorological Institutes with first-class standard thermometers descending to about -70°, these instruments were put under study in 1889. After many experiments the results proved very satisfactory. M. P. Chappuis, of the International Bureau, gave a report of these experiments at a recent meeting of the Swiss Society of Natural Sciences. In the first place, the thermometric liquid had to be chosen. Alcohol, hitherto employed almost exclusively, has great inconveniences; from the outset, therefore, toluene was studied, together with alcohol. Toluene is of greater

fluidity, and has a much higher boiling-point (111° about), which enables determination of the average degree, by employing the graduation of the mercury thermometer, 0° and 100°. Some thermometers, with a tube of about 0.6 m.m. in diameter, were filled with mercury and carefully measured, then emptied and filled with alcohol or toluene; they were then compared with the hydrogen thermometer in a bath of alcohol, which was cooled by the expansion of carbonic acid in the annular space. The flow of gas, passing by a tube, was regulated by means of a point-cock with regulator; thus the temperature was kept very constant in the interval of -40° to -75°; between 0° and 40° chloride of methyl was employed instead of carbonic acid. Before these comparisons, care was taken to fix the points 0° and 100° very exactly in the toluene thermometers, and 0° and 30° for the alcohol thermometers; for these two kinds of thermometers the indications were referred to the average degree of these two respective intervals. The thermometers were made in such a way that at the highest temperature of graduation the space below the liquid was sufficient for the pressure to remain within rather low limits. Comparisons of many instruments, carefully examined, showed that thermometers filled with toluene, pure and well dried, agree with each other to nearly  $\frac{1}{100}$  of a degree, as far as -70°. Various samples of alcohol, considered pure, gave very great differences; for example, between alcohol purified in the laboratory of the École Normale, under the management of M. Joly, and a sample of pure alcohol from the firm of Billault, a difference of 1° was found at -70°. The following Table gives the readings of toluene and alcohol thermometers for different temperatures of the hydrogen thermometer:—

Hydrogen.	Toluene. Graduated from 0° to 100°.	Pure alcohol. Graduated from 0° to 30°.
+100	100	30
+50	26.9	0
0	0	0
-10	-8.54	-9.31
-20	-16.90	-18.45
-30	-25.10	-27.44
-40	-33.15	-36.30
-50	-41.08	-45.05
-60	-48.90	-53.71
-70	-56.63	-62.31

We find that the toluene, like alcohol, contracts less and less as the temperature falls. The above table might lead one to suppose that there is less difference between the alcohol and hydrogen thermometers than in the case of toluene; this difference is due simply to the fact that the points selected for its graduation are much nearer. Other liquids are being tried, but as yet toluene seems the best. Considering the increasing importance of researches at low temperatures, physicists will be glad to be able to attain, easily, an accurateness of  $\frac{1}{10}$  of a degree.  
—*La Nature.*

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1760.

THE CHEMICAL HISTORY OF THE  
ATMOSPHERE.

By Dr. T. L. PHIPSON, F.C.S., &c.

I DESIRE to lay before my readers, in a set of brief propositions, the chemical history of the atmosphere from its origin to our own day, as the result of observation and experiment, including the consequences of the theory deduced from the observations I have already published in the CHEMICAL NEWS during March, June, and July, 1893.

I. In the origin the matter of the Earth was in a gaseous or nebulous state, but a gas placed in such conditions of heat that no compounds could exist. Our world was then all atmosphere, if I may be allowed to use such an expression; but a superheated gas in which the atoms were all free, and *identical in nature*.\* The first result of loss of heat was the formation of atomic systems, similar to those systems which are recognised by astronomy; in other words, the formation of *elements* (groups of atoms) which combined according to the laws of affinity.

In time a solid crust covering the internal molten mass was thus formed, water was condensed upon the irregular volcanic surface, and an atmosphere surrounded the globe.

II. The primitive atmosphere was composed of nitrogen, the substance which has the least tendency to combine directly with others. Into this atmosphere volcanic action evolved large quantities of carbonic acid and water, as is still the case, on a smaller scale, at the present time.

There was no free oxygen in this primitive atmosphere, because we find combustible substances in the primitive rocks (sulphides, graphite, protoxides, &c.). It was in this primitive atmosphere of nitrogen, with more or less carbonic acid and vapour, that the first organised beings (plants) made their appearance. My experiments have shown that many plants of our own day can vegetate in an atmosphere of this kind, in which animal life is quite impossible.

III. Plants even of the lowest orders, such as the *Protococcus*, in vegetating evolve oxygen copiously, apparently more copiously (weight for weight) than the higher plants; and this oxygen, derived by plants from the carbonic acid supplied by volcanic action and abundantly diffused in the earth and its primitive atmosphere, has been poured into the air for an incalculable series of ages, through periods of such vast duration that the mind of man can form no conception of them, until it has acquired the chemical composition we find at the present time.

IV. The oxygen of the atmosphere has thus gone on increasing in quantity from the earliest ages of the Earth's history until the present time; and when it had attained to a certain amount, animal life became possible, and duly appeared. At the same time carbonic acid has diminished, since the strata of the Earth reveal immense deposits of carbon (coal, lignite, peat, &c.) which was originally present in the air as carbonic acid.

V. When the oxygen thus derived from plant-life was present in the air in much smaller proportions than we now find it, the lowest animals in the scale, whose respiratory functions required less oxygen, could exist.

As the oxygen became more abundant animal life of a higher order became possible, and we find that the development of the nervous system—the highest character-

istic of animal life—has coincided with the increase of oxygen in the air.

VI. It is possible that the increase of oxygen and diminution of carbonic acid still continues at the present time, but so slowly that it is perhaps impossible to put the change in evidence by chemical analyses, even supposing the latter to be made at intervals of more than a century. Nevertheless the latest and most careful determinations of carbonic acid in the air have shown a decided decrease in the last fifty years (0.05 to 0.03).

Putney, August, 1893.

THE FORMATION OF HYDROCYANIC ACID  
BY THE ACTION OF NITRIC ACID  
UPON SUGAR, &c.

By F. B. BURLS, R. E. EVANS, and C. H. DESCH.

IN the course of a preparation of oxalic acid from cane-sugar, by the usual method of oxidation by nitric acid, one of the writers (F. B. B.) noticed the formation of hydrocyanic acid, a fact which we believe has not been previously remarked. The experiments which we shall describe show that this compound is formed in perceptible quantities during the reaction.

The proportions employed in the preparation were 3 parts of crystallised cane-sugar, 2 parts nitric acid, and 1 part water. Hydrocyanic acid was first detected by its smell, just after the first violence of the reaction had subsided and the evolution of nitrous fumes had slackened. The flask containing the mixture was therefore attached to a condenser, and the products distilled. The distillate smelt distinctly of prussic acid, whose presence was confirmed by the usual test.

In subsequent repetitions of this experiment it was found that when the formation of HCN ceased, owing to the nitric acid being exhausted (which is readily seen by the darkening of the solution in the distilling flask), the addition of more acid caused the evolution to recommence, and in this way a considerable quantity of HCN could be obtained. The process was also tried continuously, the nitric acid being allowed to drop slowly into the sugar solution from a tap-funnel, this method giving very good results.

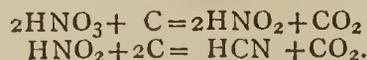
The sugar was also replaced by caramel, the formation of HCN being again evident, though the quantity produced was smaller than before.

This being the case, it was thought advisable to ascertain whether carbon itself, when acted upon by dilute HNO<sub>3</sub>, gave hydrocyanic acid among the products. Finely-divided charcoal was therefore heated with dilute nitric acid (1 to 4) in a closed bottle in the water-bath for some hours. On releasing the pressure a large quantity of carbon dioxide escaped. The liquid on distillation showed the presence of HCN.

We may here mention that the prussian blue test does not answer when a little HNO<sub>3</sub> distils over with the HCN.

The same result was obtained when cane-sugar was acted upon by nitrous acid, being first digested with KNO<sub>2</sub>, sulphuric acid being then added and the liquid distilled.

It thus appears that hydrocyanic acid is a normal product of the reducing action of carbon and certain carbon compounds upon nitric or nitrous acids. The exact course of the reaction is perhaps not very obvious, though in the case of carbon it may readily be expressed by an equation—



According to this the HCN is really produced by the action of the nitrous acid.

Analytical Laboratory, Stratford-on-Avon.

\* Phipson, "Outlines of a New Atomic Theory." London, 1886.

STUDY OF CERTAIN NOVEL PHENOMENA  
OF FUSION AND VOLATILISATION  
PRODUCED BY MEANS OF THE HEAT OF  
THE ELECTRIC ARC.\*

By HENRI MOISSAN.

IN the investigation which we now present, we insist especially upon the volatilisation of metals and metallic oxides.

When it is required to condense the vapours of bodies which are volatilisable with difficulty at high temperatures we use a metal tube cooled internally by a current of water. We employed a U-tube of copper of 15 m.m. in diameter, traversed by a current of water having a pressure of about 10 atmospheres. The curved part of the U-tube was introduced into the electric furnace at 2 c.m. from the arc above the crucible which contained the substance to be volatilised. Further, a sheet of asbestos pasteboard placed at the aperture which gave passage to the cold tube rendered it possible to condense the metallic vapours which issued from the furnace in abundance.

As an instance of the use of the cold tube, we cite the action of heat upon two stable mineral compounds, magnesium pyrophosphate and silicate.

Magnesium pyrophosphate was exposed for five minutes in the electric furnace to the action of an arc of 300 ampères and 65 volts. After a few moments there was an abundant escape of vapours. The cold tube placed in the apparatus at the outset was traversed before the experiment by a current of water at 15.4°. At the end of the experiment, whilst the furnace was still in full activity, the temperature of the water was only 17.5°. The vapours produced in the furnace were condensed with the greatest ease on the cold tube. When it was withdrawn from the furnace it was found covered in part with ordinary phosphorus, which took fire on friction and became slowly oxidised in the air, yielding a syrupy deposit which readily reduced silver nitrate. Besides this phosphorus we found evidence of the presence of magnesia on the tube.

In another experiment we heated asbestos (magnesium silicate containing a little iron) in a coke crucible for six minutes. The current measured 300 ampères and 75 volts. After the experiment there remained in the crucible merely a very small quantity of melted silicate and a ferruginous globule with a brilliant fracture, containing 1.6 of magnesium and 0.7 of silicon.

The cold tube was covered with a grey powder, containing a large excess of silica, magnesia, and very small quantities of carbon and silicon. We found in it spherules of transparent silica, which scratched glass, and gave distinctly the reaction of silica with a bead of phosphorus salt.

These two preliminary experiments, selected from among many others, demonstrate that the most stable salts are dissociated at the temperature of the arc, and that it is possible to collect the products of their decomposition and to study them with convenience.

*Volatilisation of Metals.*

*Copper.*—A fragment of copper of 103 grms. is placed in the coke crucible of the electric furnace. It is heated for five minutes with a current of 350 ampères and 70 volts. After a minute or two brilliant flames of 0.04 to 0.05 metre in length issue forcibly by the apertures which give passage to the electrodes on each side of the furnace. These flames were surmounted by clouds of a yellow smoke due to the formation of copper oxide from the combustion of the metallic vapour.

After five minutes the current was stopped, and the regulus remaining in the crucible weighed only 77 grms. Hence 26 grms. of copper had been volatilised.

All around the crucible, in the horizontal part between the furnace and the cover, there was found a large halo of globules of melted copper, coming from the distillation of the metal. The yellow vapour collected gave copper oxide to cold dilute hydrochloric acid, and left as a residue small spheres of metallic copper, blackened on their surface and soluble in nitric acid.

Abundance of metallic copper was found upon the cold tube.

*Silver.*—It has long been known that silver is volatile at a high temperature. In the electric furnace silver may be brought to full ebullition. It distils then more readily than silica or zirconia. Melted globules, an amorphous grey dust, and absorbent fragments may be collected in abundance.

*Platinum.*—If heated in the electric furnace, platinum melts in a few instants and is quickly volatilised. Metallic platinum may be collected in small brilliant globules and in dust on the cooler parts of the electrodes.

*Aluminium.*—Heated for six minutes in a current of 250 ampères and 70 volts there is obtained on the cold tube a grey powder, slightly agglomerated, which on agitation in water allows small spherules of aluminium to settle to the bottom of the beaker. These spherules have a metallic aspect; they are attacked by hydrochloric and sulphuric acids, with an escape of hydrogen. In the vapours issuing from the furnace small spheres covered with aluminium may also be collected upon asbestos pasteboard.

*Tin.*—Duration of the experiment, eight minutes; intensity of the current, 380 ampères and 80 volts. When the furnace is in full activity copious white fumes escape near the electrodes. There is found on the tube a small quantity of tin oxide, soluble in dilute hydrochloric acid, small brilliant globules, and grey substance of a fibrous aspect forming a decided felt. The fibrous portion and the metallic spheres yield with hydrochloric acid a very distinct development of hydrogen. They consist of metallic tin. It is also easy to collect on the outer part of the furnace small globules of metallic tin mixed with oxide.

*Gold.*—Duration of experiment, six minutes; current, 360 ampères, 70 volts. In the crucible were placed 100 grms. of gold; after the experiment there remained only 95 grms. During the experiment there escaped abundant fumes of a greenish yellow colour. The cold tube was covered with a powder of a deep colour with purple reflections. Under the microscope, with a low power, there were distinctly recognised small regular spheres of melted gold of a fine yellow colour. These spherules dissolved rapidly in aqua regia, and showed all the characters of salts of gold.

On the asbestos pasteboard, upon which the vapours of the furnace had been condensed, we recognised at the point which had been most heated numerous very minute globules of metallic gold. Around this part, which has a very distinct yellow colour, there is found a red halo and beyond that a fine dark purple.

*Manganese.*—This metal, to the volatilisation of which M. Jordan has recently called attention, has yielded very interesting results. We here describe merely a single experiment, which seems quite characteristic. Duration of heating, ten minutes; current, 380 ampères and 80 volts. There were placed in the crucible 400 grms. manganese. Very abundant fumes escaped, and at last there remained merely an ingot of metallic carbide weighing a few grms.

If in the preparation of manganese in the electric furnace the heat is too much prolonged, no metal is found in the crucible.

*Iron.*—Duration of heating, seven minutes; current, 350 ampères, 70 volts. There was collected on the cold tube a grey powder presenting some brilliant surfaces, very slender and warty, malleable enough to double up under the blade of a knife, mixed with a grey dust having the appearance of iron reduced by hydrogen. This dust

\* From the *Comptes Rendus*.

becomes brilliant under the burnishing-steel, and the entire specimen dissolves in dilute hydrochloric acid with an escape of hydrogen. Upon the asbestos pasteboard upon which the metallic vapours are condensed there are collected small globes of magnetic oxide, and globules of the same compound of a black colour and a wrinkled surface.

*Uranium.*—Duration of the experiment, nine minutes; current, 350 ampères, 75 volts. We can collect upon the cold tube small metallic spheres, solid and abundant, mixed with a grey powder easily soluble in acids, with an escape of hydrogen. The solution presents all the characters of salts of uranium. Upon the asbestos pasteboard we find abundant yellow spheres which, if crushed in an agate mortar, lose a crust of oxide, become grey, and take a metallic aspect.

These spherules of distilled uranium contain no carbon and are not attracted by the magnet.

(To be continued.)

### ON THE DETERMINATION OF VANADIC ACID.\*

THE original method of Berzelius, modified by A. Ditte, will be found in *Comptes Rendus* (civ., p. 982). The determination of vanadic acid in presence of alkaline and ammoniacal salts has been studied by A. Carnot (*Ibid.*, civ., pp. 1803 and 1850).

O. Manasse (*Liebig's Annalen*, 240, 23) uses the following methods for the analysis of the alkaline earths:—The barium salts are fused with 3 to 4 parts of sodium carbonate or sodium-potassium carbonate; the melt is treated with hot water, and the undissolved barium carbonate is filtered off. The latter was always impure, and contained as a mean 1.5 per cent of vanadic acid, which could not be completely removed even by a repeated fusion. The impure barium carbonate is therefore dissolved in hydrochloric acid, and the baryta re-precipitated as sulphate by sulphuric acid; the sulphate on examination was found free from vanadic acid.

A series of determinations was also effected by opening up with acid potassium sulphate. The substance was melted with from 5 to 6 parts of potassium disulphate, allowed to remain for a considerable time over a small flame, and the melt when cold was rinsed out of the crucible with water and a little sulphuric acid. The barium sulphate thus obtained passed very readily through the filter, but was in many cases fairly pure, as the vanadic acid present was often only 0.3 to 0.5 per cent. If, after the ignition of the barium sulphate, the presence of vanadic acid is detected on moistening with acid, the barium sulphate is dissolved in concentrated sulphuric acid, and the solution is poured into water. By means of this treatment the barium precipitate is certainly obtained perfectly free from vanadic acid; but the operation requires a long time, as the barium sulphate does not subside perfectly until after the lapse of from one to two days.

The strontium vanadates, sparingly soluble in water, are likewise decomposed by fusion with an alkaline carbonate. As the strontium carbonate thus obtained still contains vanadic acid, it is dissolved in hydrochloric acid, the solution supersaturated with ammonia, and precipitated with ammonium or potassium carbonate. The strontium carbonate thus obtained is free from vanadic acid. The separation of strontium as sulphate is less to be recommended since, in consequence of the requisite addition of alcohol, the filtrate cannot serve for the volumetric determination of the vanadic acid with permanganate.

Boiling the pulverised salts with a concentrated solu-

tion of potassium carbonate in excess gives also good results. The strontium carbonate is then further treated as above directed.

For the determination of the vanadic acid the filtrates from the strontium carbonate are mixed, supersaturated with sulphuric acid, reduced, and titrated with permanganate.

The double salts readily soluble in warm water, such as the strontium potassium vanadates, are simply dissolved by being covered with hot water, and the vanadic acid is precipitated with lead acetate. The lead vanadate is dissolved in nitric acid on the filter, the solution is evaporated with sulphuric acid until sulphuric vapours escape, diluted, the lead sulphate filtered off, and the vanadic acid determined volumetrically in the filtrate.

It is advisable to precipitate the lead vanadate from the hot solution, and to stir the liquid strongly at once. The precipitate then coagulates completely in a few minutes, whilst the supernatant liquid remains as clear as water. The lead vanadate can thus be at once easily filtered and washed with cold water. But if this precipitate is allowed to stand for some time it gradually becomes light yellow, pulverulent, and passes through the filter. After the precipitation of the lead with hydrogen sulphide, strontium and potassium are determined in the filtrate from the lead vanadate: in case of potassium sulphate traces of vanadic acid are still detected.

For the determination of vanadic acid in calcium salts the aqueous solution is simply supersaturated with sulphuric acid, and the vanadic acid is directly determined.

The latter process is applied also in the analysis of the magnesium salts. The acid magnesium vanadates are not readily soluble in cold water, but the addition of a few drops of sulphuric acid effects immediate solution.

As already intimated, the determination of vanadic acid is effected by Manasse volumetrically by means of permanganate. This method depends on the reduction of the acid solution of the vanadates to vanadium tetroxide (by means of sulphurous acid or sulphuretted hydrogen), and followed by oxidation of the tetroxide to vanadic acid by means of permanganate.

The first criticisms on this reduction were made by C. Czudnowicz (*Zeit. Anal. Chemie*, iii. 379). Subsequently H. E. Roscoe ("Researches on Vanadium," 1879) and C. Rammelsberg (*Berlin Acad. der Wissen.*, 1880) have made thorough investigations on this subject.

According to the author, when sulphurous acid was used for reduction the average result was too high, 100.18 per cent. With sulphuretted hydrogen, followed by a strong current of carbonic acid, the average result was 99.9 per cent. The author prefers the sulphurous acid method, as the colour reaction is more easily distinguished than when sulphuretted hydrogen is used, as in this case the solution always contains a little suspended sulphur.

(To be continued.)

**The Ascent of Saline Solutions in Filter-Paper.**—E. Fischer and E. Schmidmer (*Liebig's Annalen*).—Of any two salts the one which has the greater diffusion-speed ascends the more rapidly in paper; the process of diffusion can be observed in this manner as by the use of membranes. The process has the advantage of being applicable for all liquids which moisten paper.

**Attackability of Platinum and its Iridium Alloys by Sulphuric Acid.**—Heraeus (*Zeitschrift Angewandte Chemie*).—As unit he takes the loss of weight which his chemically pure platinum underwent. In an experiment made at the Gressheim works the loss on absolutely pure platinum was 100, that on pure platinum with 5 per cent iridium 73, on pure platinum with 10 per cent iridium 58, on a technically pure platinum made by Heraeus 90, on platinum from an English boiler 103, and on fine gold 10. Hence Heraeus now uses retorts of platinum coated with gold, which are said to be very serviceable.

\* *Zeitschrift für Analytische Chemie.*

## NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.\*

By Lieut.-General C. A. McMAHON, F.G.S.

(Continued from p. 65).

No.	Name.	System.	Form.	Double refraction shows colours of.	Direction of major axis.	Other optical characters.
MANGANESE.						
67	$\text{MnSO}_4\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$	?				
68	$\text{MnSO}_4\text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$	Tr				
69	$\text{MnSO}_4\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$	Tr				
70	$\text{MnSO}_4\text{Na}_2\text{SO}_4 + 4\text{H}_2\text{O}$	M	(a) Almond-shaped granules. (b) Spherulitic radiating groups. (c) Short prisms of cubic aspect.	(a) (b) Pink of 2nd order.	(a) R.L. to <i>e</i> . (b) R.L. to axis of Q.W. (c) Uncertain.	
71	$\text{MnSO}_4\text{K}_2\text{SO}_4 + 4\text{H}_2\text{O}$	M	In (a) spherulites and (b) confused matted masses.	Blue of 2nd order.	(a)    to axis of Q.W.	
72	$\text{MnSO}_4(\text{NH}_4)_2\text{SO}_4 + 6\text{H}_2\text{O}$	M	Large stumpy prisms of complex shape.	3rd order.	—	Strong absorption with single Nicol. Refraction probably near that of balsam. Small crystals cannot be seen without polarised light.
73	$\text{MnSO}_4\text{K}_2\text{SO}_4 + 6\text{H}_2\text{O}$	M				
	$\text{Mn}_2(\text{SO}_4)_3$ , with sulph. of K and $\text{NH}_4$	See alums.				
SODIUM.						
74	$\text{Na}_2\text{SO}_4$ .. ..	R	Salt cake.			
75	$\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$ ..	R				
76	$\text{Na}_2\text{SO}_4 + 3\text{H}_2\text{O}$ ..	{ H R				
77	$\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ ..	M	Glauber's salt.	Short stumpy prisms, showing many faces. Extremely feeble: from grey of 1st order to blue of 2nd order.	Low angle to <i>e</i> .	Crystals bordered by broad dark lines. Refraction probably high.
78	$\text{NaHSO}_4$ . . . .	Tr†	(a) Long blade-like prisms. (b) In granules or stumpy prisms with many faces.	Sometimes as high as 6th or 7th order.	Varies greatly.	Twinning not uncommon. In (a) the twins form penetration twins, taking the form of a cross. Outlines sharp.
	$\text{Na}_2\text{SO}_4$ with $\text{Al}_2(\text{SO}_4)_3$ and $\text{Cr}_2(\text{SO}_4)_3$	See alums.				

## Remarks.

Nos. 70 to 73.—The salts described under these Nos. are those obtained by evaporating a mixture of  $\text{MnSO}_4$  with  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $(\text{NH}_4)_2\text{SO}_4$ . I know of no test applicable to microscopic specimens on glass slides for determining whether the resulting double salts contain two, four, or five molecules of water.

No. 72.—Some crystals have well-marked zonal lines. Others are so full of minute liquid and air bubbles as to present a dark dusty appearance under low powers. Many of the crystals show an optic axis in *c.p.l.*

No. 77.—Glauber's salt (mirabilite) effloresces on exposure to the air. It forms from aqueous solution between  $12^\circ$  and  $33^\circ$ . Between  $33^\circ$  and  $40^\circ$  the anhydrous salt (74) is deposited. Solubility in water is greatest at  $33^\circ$ , after that it declines. Between  $12^\circ$  a salt with seven molecules of water forms. The anhydrous salt also forms if Glauber's salt is allowed to remain exposed to the air. The anhydrous salt occurs native in thenardite and in solution in sea-water, and in some springs.

\* Mineralogical Magazine, vol. x., No. 46, p. 79.

† I have followed Roscoe and Schorlemmer. Fock does not notice  $\text{NaHSO}_4$ , but gives  $\text{NaHSO}_4 + \text{H}_2\text{O}$  as a monoclinic salt.

	No.	Name.	System.	Form.	Double refraction shows colours of.	Direction of major axis.	Other optical characters.
<b>SODIUM.</b>							
$\text{Na}_2\text{SO}_4\text{CaSO}_4$	..	<i>See Ca.</i>					
$\text{Na}_2\text{SO}_4\text{MgSO}_4 + 6\text{H}_2\text{O}$		<i>See Mg.</i>					
$\text{Na}_2\text{SO}_4\text{MnSO}_4 + 2\text{H}_2\text{O}$		<i>See Mn.</i>					
$\text{Na}_2\text{SO}_4\text{MnSO}_4 + 4\text{H}_2\text{O}$		<i>See Mn.</i>					
$\text{NaLiSO}_4$	.. ..	<i>See Li.</i>					
<b>AMMONIA.</b>							
$(\text{NH}_4)_2\text{SO}_4$	.. .. 79	Mascagnite.	R	Long flat prisms. Laths with rectangular tops common.	Some as high as 6th order.	<i>R.L.</i> to <i>e</i> .	
$(\text{NH}_4)\text{HSO}_4$	.. .. 80		R	Stumpy prisms; complex shapes, six-sided outlines not uncommon. Twinning common.	Very high, probably near calcite.	<i>R.L.</i> to <i>e</i> when elongated.    to twinning plane of one twin, sometimes of both.	
$(\text{NH}_4)_2\text{SO}_4$ with Al, Cr, &c.	.. .. —	<i>See Alums.</i>					
$(\text{NH}_4)\text{LiSO}_4$	.. .. —	<i>See Li.</i>					
$(\text{NH}_4)_2\text{SO}_4\text{MnSO}_4 + 6\text{H}_2\text{O}$	.. .. —	<i>See Mn.</i>					
$(\text{NH}_4)_2\text{SO}_4\text{MgSO}_4 + 6\text{H}_2\text{O}$	.. .. —	<i>See Mg.</i>					
<b>RUBIDIUM.</b>							
$\text{Rb}_2\text{SO}_4$	.. .. 81		R	(a) Six-sided plates of hexagonal habit. (b) Lath-shaped with ragged ends. (c) Regular well-formed crystals with complex shapes round edge of drop.	4th order.	(b) <i>R.L.</i> to <i>e</i> . (c) Various.	(c) Absorption with single nicol. Multiple twinning almost invariable.
$\text{Rb}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O}$	.. .. —	<i>See Alums.</i>	R				
$\text{Rb}_2\text{SO}_4\text{MgSO}_4 + 6\text{H}_2\text{O}$	.. .. —	<i>See Mg.</i>					
$\text{RbLiSO}_4$	.. .. —	<i>See Li.</i>					
<b>STRONTIUM.</b>							
$\text{SrSO}_4$	.. .. 82	Celestine.	R	Globulites, round and almond-shaped disks, and in prisms.	White of 1st order.	In almond-shaped disks,    to longer axis.	
$(\text{SrBa})\text{SO}_4$	.. .. 83	Baryto-celestine.	R				
<b>TITANIUM.</b>							
$\text{Ti}(\text{SO}_4)_2$	.. .. 84	Normal sulph.	—				
$(\text{TiO})\text{SO}_4$	.. .. 85	Basic sulph.	—	White hard mass.			

Remarks.

No. 79.—Long rod-like liquid cavities containing air bubbles running with the length of the crystal are common. This salt is said to be isomorphous with  $\text{K}_2\text{SO}_4$ , but they may readily be distinguished under the microscope. There is a striking difference between them in their refraction; their double refraction is different, and the crystals of  $(\text{NH}_4)_2\text{SO}_4$  are much larger and flatter than those of  $\text{K}_2\text{SO}_4$ . No. 79 dissolves at  $0^\circ$  in 71 and at  $100^\circ$  in 97.5 parts of water.

No. 80.—Very deliquescent. Aqueous solution deposits crystals, but does not completely evaporate in the open air at the ordinary temperature.

No. 81.—See Remarks No. 53.

No. 82.—Solubility in water between  $\text{CaSO}_4$  and  $\text{BaSO}_4$ ; viz., 0.015 part dissolve in 100 of water at  $60^\circ\text{F}$ . It is less soluble in boiling than in cold water. When  $\text{SrSO}_4$  is dissolved in hot concentrated  $\text{H}_2\text{SO}_4$ , crystals of celestine are deposited on cooling. See Part 3.

No. 85.—Obtained by dissolving dry titanous acid in boiling  $\text{H}_2\text{SO}_4$  and evaporating.

No.	Name.	System.	Form.	Double refraction shows colours of.	Direction of major axis.	Other optical characters.
<b>TITANIUM.</b>						
Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> +3H <sub>2</sub> O..	86	—	A resinous transparent yellowish deliquescent mass.			
Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> +8H <sub>2</sub> O..	87	—	Crystals in tufts.			
<b>ZIRCONIUM.</b>						
Zr(SO <sub>4</sub> ) <sub>2</sub> +4H <sub>2</sub> O..	88	R	Spherulites, elongated lozenges, and six-sided micaceous-looking thin plates. Spherulites often constricted in the middle like dumb-bells.	3rd order.	to <i>e</i> . Spherulites    to axis of <i>Q.W</i> .	Absorption with single nicol. The elongated lozenges are deeply scored with numerous fine dark lines, which give them the appearance of bundles of micaceous plates.

*Remarks.*

No. 86.—Is formed by the oxidation of the sesquisulphate with nitric acid and evaporating.

No. 87.—Is obtained by dissolving the metal in dilute H<sub>2</sub>SO<sub>4</sub>.

No. 88.—Swells up on heating with alum. Decomposes at a red heat.

(To be continued).

**ELECTROLYTIC SEPARATIONS.**

By EDGAR E. SMITH and J. B. MOYER.

WE proved in a former communication that mercury and bismuth cannot be separated electrolytically. These observations agree with those made by Smith and Salter (*Journ. Analyt. Chem.*, vii., 128), since they proved conclusively that copper and bismuth cannot be separated under corresponding conditions, and, further, that the assertion that bismuth and lead are separable under these conditions is incorrect.

*Mercury from Lead.*

1. Ten c.c. of a nitric solution of mercuric oxide (=0.1150 gm. of metallic mercury), 1 c.c. of a nitric solution of lead (=0.0126 gm. lead peroxide), and 25 c.c. nitric acid of sp. gr. 1.3, were diluted to 175 c.c., and submitted to the action of a current giving 1.3 c.c. of detonating gas per minute. The mercury deposited weighed 0.1151 gm., and the lead peroxide 0.0123 gm. An examination of the mercury showed the absence of any admixture of particles of lead.

2. In this experiment the quantities of lead and mercury were the same as in 1; the volume of nitric acid was increased to 30 c.c., whilst the current indicated 1.8 c.c. detonating gas per minute. The deposit of mercury weighed 0.1150 gm. and the lead peroxide 0.0126 gm.

In three other experiments, in which the volumes of nitric acid (sp. gr. 1.3) added were respectively 5, 10, and 15 c.c.; the deposit of mercury contained metallic lead in varying but considerable quantities.

*Mercury from Lead and Bismuth.*

In former communications we mentioned the analysis of an alloy of tin, mercury, lead, and bismuth, which Classen indicates ("Quant. Analyse durch Electrolyse," 3rd edit., p. 147), and we showed that the analyst, if he pursues these instructions, will finally obtain very little bismuth, as beyond all doubt it will have been precipitated along with the mercury. Whilst disregarding tin, we submitted nitric solutions of the other three metals to the action of the current. The solution contained 0.1150 gm. mercury, 0.0126 gm. lead peroxide, 0.0718 gm. bismuth, and 15 c.c. nitric acid (sp. gr. 1.3), whilst the total solution amounted to 180 c.c. The current yielded 1.7 c.c. of detonating gas per minute. The deposit of

mercury weighed 0.1262 gm., and the increase of weight of the anode was 0.0164 gm. Bismuth was found to have appeared at both poles.

A second and a third experiment, with an increased volume of acid, had a similar result. This process must therefore be rejected if a satisfactory separation is required.

*Silver from Lead.*

The separation presented no especial differences in the two following experiments, if we work under conditions analogous to those given.

1. Ten c.c. of a nitric solution of silver (=0.1028 gm. silver), 1 c.c. nitric solution of lead (=0.0144 gm. lead peroxide), and 15 c.c. nitric acid (sp. gr. 1.3), with a total dilution to 200 c.c., were exposed to a current yielding 1.8 c.c. detonating gas per minute. The precipitate of silver weighed 0.1023 gm., and the lead peroxide 0.0144 gm.

2. The conditions as in No. 1. The precipitate of silver weighed 0.1028 gm., and the lead peroxide 0.0145 gm.

*Copper from Cadmium.*

This separation was carried out successfully by Smith some time ago. Classen mentions similar results. Smith's method is described in the *Amer. Chem. Journal* (ii. 41). The following results confirm those of Smith in every respect:—

1. Ten c.c. of a sulphuric solution of cupric oxide (=0.1341 gm. Cu), 5 c.c. of a nitric solution of cadmium (=0.1 gm. Cd), and 5 c.c. nitric acid (sp. gr. 1.2), with a total dilution of 200 c.c., were submitted to a current which produced 0.6 c.c. of detonating gas per minute. The deposit of copper weighed 0.1346 gm., and contained no cadmium.

2. Under similar conditions as in No. 1 the precipitated copper weighed 0.1341 gm.

*Copper from Zinc.*

The quantities of the metals were equal, the volume of nitric acid was 5 c.c. (sp. gr. 1.3), the total dilution 200 c.c., and the current gave 1 c.c. detonating gas per minute. The copper precipitated weighed 0.1345 gm. instead of 0.1341 gm.

*Copper from Zinc, Cobalt, and Nickel.*

The quantities of the metals were equal, the volume of

nitric acid 5 c.c. (sp. gr. 1.3). Total dilution 200 c.c. The current produced 0.4 c.c. detonating gas per minute. The precipitated copper weighed 0.1339.

*Copper from Iron and Zinc.*

The metals were present in equal quantities. The volume of nitric acid was 5 c.c. (sp. gr. 1.3). The current 0.7 c.c. of detonating gas per minute. The total dilution was 200 c.c. The precipitate of metal weighed 0.1340 gm.

The copper in each of these operations was tested for the metals which had been jointly present, but which were all now wanting.

*Bismuth from Cadmium,*

1. Five c.c. of a nitric solution of bismuth (=0.0718 gm. metallic bismuth), 5 c.c. of a nitric solution of cadmium (=0.1 gm. cadmium), and 15 c.c. nitric acid (sp. gr. 1.1), were diluted to 180 c.c., and treated with a current which gave 1.6 c.c. detonating gas per minute. The bismuth deposited weighed 0.0716 gm. instead of 0.0718.

2. The conditions of this experiment were the same as those of No. 1, with the exception that there was no further addition of acid to the nitric solution of the metals. The precipitated bismuth weighed 0.0719 gm.

*Bismuth from Zinc.*

0.0718 gm. bismuth and 0.1 gm. zinc in presence of 2 c.c. nitric acid (sp. gr. 1.3), with a total dilution to 200 c.c., gave 0.0712 gm. bismuth, if treated with a current of 0.4 c.c. detonating gas per minute. The anode was slightly coloured, and its increase of weight was 0.0003 gm.

In a second experiment, with the addition of 1 c.c. of acid, the precipitated bismuth weighed 0.0717. Hence we regard this separation as satisfactory.

*Bismuth from Nickel.*

1. 0.0718 gm. bismuth and 0.1 gm. nickel in presence of 2 c.c. nitric acid (sp. gr. 1.3) were diluted with water to 180 c.c. and treated with a current giving 0.5 c.c. of detonating gas per minute. The precipitation of the bismuth was complete, and the deposit of metal weighed 0.0724 gm.

2. In this experiment the weights of metals were the same as in 1; the total dilution 200 c.c., the nitric acid 3 c.c. (of sp. gr. 1.3), and the current yielded 0.2 c.c. of detonating gas per minute. The deposit of bismuth weighed 0.0716 gm.

A third experiment, under exactly the same conditions, gave 0.0716 gm. bismuth. It contained no nickel, and no precipitate was observed on the anode.

*Bismuth from Cobalt.*

The weights of the metals were 0.0718 gm. bismuth and 0.1 gm. cobalt. The nitric acid (spec. grav. 1.3) was 3 c.c., and the current gave off 0.2 c.c. detonating gas per minute. The precipitate of metallic bismuth weighed 0.0714 gm., and the anode was very slightly coloured. Further experiments showed that the separation is possible.

*Bismuth from Zinc, Cobalt, and Nickel.*

0.0718 gm. bismuth, 0.1 gm. zinc, 0.1 gm. cobalt, and 0.1 gm. of nickel were mixed with 2 c.c. nitric acid (specific gravity 1.3), diluted to 200 c.c., and submitted to the action of a current which gave off 0.8 c.c. of detonating gas per minute. The deposit of bismuth weighed 0.0739 gm., and on examination it was found that both nickel and cobalt were present. The anode was covered with a blue film.

A second, third, and fourth experiment, under almost identical conditions, gave deposits of 0.0729, 0.0738, and 0.0739 gm. of bismuth, contaminated in each case with nickel and cobalt.

*Bismuth from Cobalt and Nickel.*

Zinc was excluded in this experiment. The three metals were taken in the same proportions as above with 3 c.c. nitric acid (of specific gravity 1.3). The solution was exposed to a current which gave off 0.3 c.c. of detonating gas per minute. The deposit of bismuth weighed 0.0736 gm., and contained nickel.

*Bismuth from Cobalt and Zinc.*

0.0718 gm. bismuth, 0.1 gm. cobalt, and 0.1 gm. zinc in solution were mixed with 2 c.c. nitric acid (specific gravity 1.3), and submitted to a current giving 0.6 c.c. detonating gas per minute. The bismuth weighed 0.0747 gm., and contained cobalt. The anode was covered with a film of oxide.

*Bismuth from Cobalt, Nickel, and Zinc.*

On employing the same quantities of metals as in the above experiments, and increasing the nitric acid to 5 c.c. the precipitate of bismuth weighed 0.0728 gm., and contained both cobalt and nickel.

In an experiment under the above conditions we succeeded in separating all the metals present; 0.0718 gm. bismuth, 0.1 gm. zinc, 0.1 cobalt, 0.1 nickel, 8 c.c. nitric acid (specific gravity 1.3), total dilution 200 c.c., and a current which gave 0.4 c.c. detonating gas yielded a deposit of bismuth of 0.0718 gm. On examination the absence of the other metals was ascertained. The anode remained unaffected. Subsequent experiments were equally successful as regards the separation of the metals, though in some of them the anode appeared slightly coloured, its weight was not increased by more than 0.0004 gm.

The bismuth was deposited on platinum capsules of from 60 to 70 grms. in weight. In all the successful experiments the deposit was adherent and uniform. It was washed with warm water, alcohol, and ether. The strength of the current was ascertained by means of a voltameter, and the electrolyte was introduced in the circuit. The use of a nitric solution does not give such satisfactory results as the treatment of the metals in a sulphuric solution in presence of free sulphuric acid.—*Zeit. Anorganische Chemie.*

ON THE PHOTOGRAPHY OF THE  
LUMINOUS RAYS OF THE SHORTEST  
WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 93).

CD, No. 23, 231.35; No. 24, 226.55; No. 25, 219.45; No. 26, 214.41. Zn, No. 27, 209.88; No. 28, 206.10; No. 29, 202.43. Al, No. 30, 198.81; No. 31, 193.35; No. 32, 185.22. No. 28, No. 31, and No. 32 are double lines.

The photography of the cadmium spectrum formed the beginning of my investigation.

With a slit of the width of 0.020 m. m. and an exposure of one minute, the Leyden jar spark of cadmium gave all the main lines but the two most refrangible, No. 25 and No. 26, in contrast to the others, strikingly pale. As it might have been expected, this difference in intensity did not disappear, even on prolonged exposure, until solarisation became perceptible in the more intense lines. The difference in intensity which regularly followed on normal exposure would not have attracted my notice if I had not had at my disposal several cadmium proofs of extraneous origin—three original plates for which I am indebted to the kindness of Mr. W. N. Hartley, of Dublin—which have also been taken upon silver bromide gelatin with a quartz prism and quartz lenses.

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

These proofs showed the difference in the intensity of the above-named lines decidedly less than my plates. They therefore justify the assumption that Hartley's experimental arrangement had in some manner relatively assisted the photographic action of the lines No. 25 and No. 26. I was confirmed in this conclusion by three other cadmium photos. by the same spectroscopist; good photographic reproductions of which accompany one of his treatises (*Scientific Transactions of the Royal Dublin Society*, "Photos. of the Spark-spectra of Twenty-one Elementary Substances," vol. i., Series 2, pp. 231—238, 1882), and which, in contrast to the above named original plates, are in harmony with my plates; whence, therefore, the difference among Hartley's proofs? This question was of essential import for the continuation of my work.

Hartley, on the ground of the plates of his two negatives above named, had marked with a diamond the date 1880; his treatise appeared in 1882. My investigation began in the year 1889. As regards the arrangement in taking Hartley's plates above-mentioned, I merely know that an apparatus with quartz prisms had been employed. Hartley's treatise explained his arrangements in taking the other spectra. From reasons the exposition of which would prove tedious I have below, in the solution of the above question, kept myself exclusively to the proofs. This was admissible, since they display a difference palpable for the present case; the length of the spectra is different; if measured between the cadmium lines No. 9 and No. 26 it amounts in the plates to 82 m.m. and in the figures to 157 m.m. As both spectra show no appreciable difference in the re-resolution of their crowded lines, it was permissible to assume that the dispersion of Hartley's spectral apparatus was the same, and that merely the focal distance of the lenses was different. Therefore the lengths of the aerial transit of the rays of both apparatus must have differed from each other approximately in the same proportion as the focal lengths. It has been already proved by Cornu (*D'Almeida F.*, x., pp. 5—17, 1881) that the transparency of the air decreases with the wave-lengths of the rays, especially in the ultra-violet, though certainly in strata of much greater thickness than those of Hartley's apparatus. Still, I have felt compelled to uphold the resistance of the air as the sole cause of the above named difference in the intensity of the two most refrangible lines of cadmium. On the one hand, because Miller's proofs already showed that a stratum of air, even of moderate thickness, may prove an insuperable difficulty in the photography of the ultra-violet; and, on the other hand, because all further experiments which I instituted to detect other causes for this phenomenon proved fruitless. An experimental strengthening of this assumption, the necessity for which seemed more urgent on every new photo, had to be postponed until the conclusion of the connected examination of the spectra of zinc and aluminium, on account of procuring the necessary instruments.

The zinc spectrum in its most refrangible part acted still more feebly than the cadmium spectrum. For instance, an exposure of three minutes was required for the appearance of the most refrangible line, No. 29. Like the efficacy, the intensity showed a further decrease. Of all the main lines of cadmium and zinc, none appeared so slightly as the zinc line No. 29. The combined spectrum of both metals showed better than any other that the intensity decreased with the wave-length as yielded by a spark springing over between these electrodes. (When employing three electrodes, I connect the pair of electrodes with the current-circuit, whilst the single electrode of the other metal was introduced with its extreme end into the track of the spark, where it then took part in the discharge in a normal manner). Few metals are here at all suitable like zinc and cadmium.

Contrasts in the intensity of adjacent ultra-violet lines are shown in the inflection spectrum better than in the refraction spectrum, since the deflection of the rays does

not succeed progressively with the wave-length as with the prism, but proportionally. Hence the lines towards the more refrangible end are more and more crowded together, whilst in the refraction spectrum they recede further from each other. Proofs which I took with a concave grating revealed still better the decrease of the intensity and efficacy of the lines in question.

According to Cornu's hypothesis (*Comptes Rendus*, lxxxviii., pp. 1285—1290, 1879), a stratum of air of the thickness of 10 metres suffices for the absorption of the rays of the wave length  $211\cdot84 \mu\mu$ .

The rays Nos. 27, 28, and 29, the wave-lengths of which are smaller, are consequently absorbed by such a stratum of air in a still stronger degree.

(To be continued).

## THE SPECIFIC HEATS OF THE METALS.\*

By JOS. W. RICHARDS, Ph.D.,  
Instructor in Metallurgy, &c., in Lehigh University.

(Continued from p. 72.)

### APPENDIX.

#### Aluminum.

[SEE a résumé on this subject by J. W. Richards, in *Journ. Franklin Institute*, February, 1892.]

First investigated by Regnault, in 1855, on very impure metal, obtaining  $0\cdot2056$  between  $25^\circ$  and  $97^\circ$ , and, allowing for the impurities present, he made the figure for pure aluminum  $0\cdot2181$ . Had he used the correct specific heat of silicon in making this allowance he would have obtained  $0\cdot2200$ .

Investigated again by Regnault, a year after, on purer metal, obtaining a corrected value of  $0\cdot2143$  ( $14^\circ$ — $97^\circ$ ).

Kopp used ordinary commercial aluminum, and obtained  $0\cdot2020$  ( $20^\circ$ — $52^\circ$ ), as the mean of four determinations which varied from  $0\cdot1970$  to  $0\cdot2070$ . This determination is, therefore, of very little value.

Mallet used chemically pure aluminum, and found by the Bunsen calorimeter  $0\cdot2253$  ( $0^\circ$ — $100^\circ$ ).

Naccari (purity of metal not stated) investigated up to  $300^\circ$ , by the method of mixtures. His results lead to the formulæ—

$$S = 0\cdot2116 + 0\cdot000095 t$$

$$S_m = 0\cdot2116 + 0\cdot0000475 (t + t_1).$$

The mean  $0^\circ$ — $100^\circ$  would be  $0\cdot2164$ .

Richards used metal which analysed 99·93 per cent aluminum, the rest silicon. Temperatures pushed to  $600^\circ$ . Formulæ arrived at—

$$S = 0\cdot2220 + 0\cdot0001 t$$

$$Q = 0\cdot2220 t + 0\cdot00005 t^2.$$

(Mean  $0^\circ$ — $100^\circ$ ,  $0\cdot2270$ , being less than 1 per cent from Mallet's value. The rate of increase with the temperature is similar to Naccari's observation. Total heat contained in the solid metal to its melting-point ( $625^\circ$ ), by this formula, 158·3 calories.

Le Verrier finds the specific heat between  $0^\circ$  and  $300^\circ$  to be invariable, and =  $0\cdot22$ ; between  $300^\circ$  and  $530^\circ$  also constantly =  $0\cdot30$ ; between  $530^\circ$  and  $560^\circ$  an absorption of about 10 calories rendered latent; between  $540^\circ$  and  $600^\circ$  the specific heat again constant and equal to  $0\cdot46$ . For the total quantities of heat in the metal he gives the following formulæ:—

$$\begin{array}{ll} \text{Between } 0^\circ \text{ and } 300^\circ & \dots Q = 0\cdot22 t \\ 300^\circ \text{ ,, } 530^\circ & \dots Q = 65 + 30\cdot0 (t - 300) \\ 540^\circ \text{ ,, } 600^\circ & \dots Q = 139 + 0\cdot46 (t - 530). \end{array}$$

Q becomes about 170 calories towards  $600^\circ$ , and rises rapidly, passing 200 before fusion at  $620^\circ$ .

\* A Lecture delivered before the Franklin Institute, Jan. 30, 1893.

Pionchon has recently published the following results:—

$$\begin{aligned} \text{Between } 0^\circ \text{ and } 580^\circ \quad & \cdot Q = 0.393 t - \frac{291.86 t}{1517.8 + t} \\ 625^\circ \quad \text{,,} \quad 800^\circ \quad & \cdot Q = 0.308 t - 46.9. \end{aligned}$$

Specific heat at  $0^\circ = 0.2010$ ; in the liquid state, above  $625^\circ$ , constant and equal to  $0.308$ . He states that beginning at  $580^\circ$  the fusion starts, the metal losing its solidity, and between  $623^\circ$  and  $628^\circ$  the heat curve  $Q$  is nearly vertical. Pionchon's first formula gives for the total heat in the solid metal at the melting-point  $160.49$  calories.

*Latent Heat of Fusion.*—In 1890 the writer determined the amount of heat in solid aluminum as near as possible to its melting-point as  $199.5$  calories, and the heat in the molten metal as  $229$ , from which he concluded that the latent heat of fusion was close to  $30$  calories. Since then two sources of errors have been disclosed in this determination.

(1.) The metal above  $600^\circ$  absorbs in advance some of its latent heat of fusion, the writer's observation in this regard agreeing with Le Verrier's, who states that the total heat exceeds  $200$  calories before real fusion occurs. If this phenomenon did not occur the writer's formula would give the heat content at the melting-point as  $158.3$ , while Pionchon's formula gives  $160.49$ , and it is these numbers which must be used in calculating the total heat absorbed during the change of state.

(2.) The heat in the molten metal at its setting-point is very greatly modified by impurities present. The writer found the following heats in impure and pure metal:—

Per cent Pure.	Calories.
96.9 .. .. .	229.0
99.9 .. .. .	254.0
99.93 .. .. .	258.3

The writer's results must then be considerably modified, in order to get the total latent heat. For the metal of greatest purity the total calculated absorption between  $600^\circ$  and  $625^\circ$ , due to change of state, would be—

$$258.3 - 158.3 = 100 \text{ calories.}$$

Pionchon's formula for the heat in liquid aluminum evaluated for the melting-point gives  $239.4$  calories, and subtracting his lower value of  $160.49$  there is left  $78.91$  units as the latent heat. The writer's experiments would show that Pionchon's upper figure,  $239.4$ , is probably nearly  $20$  units too low, since four experiments have given me  $258.2$ ,  $258.9$ ,  $259.3$ , and  $259.2$  respectively.

#### Antimony.

Prof. Wilcke gave  $0.063$ ; Crawford,  $0.0645$ ; Kiiwan,  $0.086$ .

Dulong and Petit give  $0.0507$  ( $0^\circ - 100^\circ$ ) and  $0.0549$  ( $0.300^\circ$ ), or in formulæ—

$$\begin{aligned} S &= 0.0486 + 0.000042 t \\ Q &= 0.0486 t + 0.000021 t^2. \end{aligned}$$

F. E. Neumann, using commercial metal, found its specific heat by the method of cooling as  $0.0470$ .

Regnault—

$$0.05077. \quad (61^\circ - 97^\circ).$$

Bède gives the formulæ—

$$\begin{aligned} S &= 0.0466 + 0.000040 t \\ Q &= 0.0466 t + 0.000020 t^2. \end{aligned}$$

Kopp gives—

$$0.0523 \text{ at } 31^\circ \text{ (unreliable).}$$

Bunsen—

$$0.0495 \text{ at } (0^\circ - 100^\circ).$$

L. Pebal and H. Jahn found the following mean values:—

$$\begin{aligned} Sm \text{ (} -21^\circ \text{ to } -76^\circ) &= 0.0496 \\ Sm \text{ (} -21^\circ \text{ to } 0^\circ) &= 0.0486 \\ Sm \text{ (} 0^\circ \text{ to } -33^\circ) &= 0.0495. \end{aligned}$$

Naccari derives the formulæ—

$$\begin{aligned} S &= 0.04864 + 0.0000167 t \\ Q &= 0.04864 t + 0.0000084 t^2 \end{aligned}$$

#### Beryllium.

Emerson Reynolds found  $0.642$  ( $20^\circ - 100^\circ$ ); while Nilson and Pettersson obtained  $0.408$  ( $0^\circ - 100^\circ$ ).

T. S. Humpidge investigated carefully through a range of temperatures, and gives the formula—

$$S = 0.3756 + 0.00106 t - 0.00000114 t^2.$$

This formula evaluated for ( $0^\circ - 100^\circ$ ) would give  $0.4248$ . It is therefore probable that Reynolds's value is much too high.

#### Barium.

The Russian chemist Mendeléeff gives  $0.05$ .

#### Bismuth.

Prof. Wilcke made its specific heat  $0.043$ .

Dulong and Petit found  $0.0288$ , and Neumann  $0.027$  by the method of cooling.

Regnault made it  $0.03084$  ( $14^\circ - 99^\circ$ ).

Bède made experiments up to  $200^\circ$ , from which he calculated the formula—

$$Sm = 0.0269 + 0.00002 t,$$

which would give for ( $14^\circ - 99^\circ$ )  $0.0292$ , about 5 per cent lower than Regnault's result.

Kopp found  $0.0305$  ( $12^\circ - 60^\circ$ ), close to Regnault's figure.

Person found the specific heat of molten bismuth between  $280^\circ$  and  $360^\circ$  to be  $0.0363$ .

*Latent Heat of Fusion.*—Dr. Irvine, Jun., determined that the latent heat would raise the temperature of  $550$  parts of solid bismuth  $1^\circ F.$ , equal to  $305.5$  parts  $1^\circ C.$  He then assumed Wilcke's figure for the specific heat of bismuth which gives its latent heat as  $11.92$  calories. Had he used the specific heat found since by Regnault, his experiments would give  $10.3$ . Or, had he used the specific heat at the melting-point as determined by Bède's formula, he would have obtained  $10.8$  calories.

Person made experiments with molten bismuth, from which he calculated that at its melting-point ( $266.8^\circ$ ) it contained  $94.88$  calories. But, assuming Regnault's value to be true to the melting-point for solid bismuth, the heat in solid bismuth is  $82.24$  calories, from which the latent heat of fusion is  $12.64$  calories. If, however, we take Bède's determination of its increasing  $0.00002$  for every degree rise in temperature, the mean specific heat to the melting-point would be  $0.0322$ , the heat in solid bismuth at its melting point  $86.00$  calories, and the latent heat of fusion  $8.88$ .

#### Cadmium.

Regnault found  $0.0567$  ( $16^\circ - 98^\circ$ ) on metal containing 1 per cent of impurities.

De la Rive and Marcet found  $0.0576$ , at ordinary temperatures, by the method of cooling.

Kopp found  $0.0542$  ( $15^\circ - 60^\circ$ ) in method of mixtures.

Bunsen found  $0.0548$  ( $0^\circ - 100^\circ$ ) by the ice calorimeter.

Naccari experimented up to  $300^\circ$ , and gives the following formula:—

$$Sm = 0.0546 + 0.000012 t.$$

This evaluated for Regnault's range of temperature gives  $0.0560$ .

*Latent Heat of Fusion.*—Person found  $31.83$  calories in molten cadmium at the melting-point ( $320.7^\circ$ ), and subtracting the heat in solid cadmium at that point, using Regnault's value, the latent heat of fusion became—

$$31.83 - 18.17 = 13.66.$$

Had he used Naccari's formula for the heat in solid cadmium he would have obtained  $18.7$ , and for the latent heat of fusion  $13.13$ .

#### Calcium.

Bunsen found  $0.1722$  and  $0.1686$ , mean  $0.170$  ( $30^\circ - 100^\circ$ ), by the ice calorimeter.

#### Cerium.

Dr. W. F. Hillebrand gives  $0.0448$ , at ordinary temperatures, determined on metal 95 per cent pure, allowing for the impurities, which were mostly iron and didymium.

*Chromium.*

Kopp found 0.1000 (15°—60°); but since he found that of iron, with a larger atomic weight, to be greater than this, he concluded that this number must be too small, and supposed it due to the impurity of the material he was working with.

*Cobalt.*

Dulong and Petit found 0.1498, by the method of cooling.

Regnault gives 0.10696 (13°—99°).

De la Rive and Marcet obtained 0.1172 as the mean of three experiments by the method of cooling. Regnault observes, however, that specimens containing carbon gave him as high as 0.117, but he took the smallest value as belonging to the purest metal.

Pionchon investigated up to 1160°. He found the specific heat at 0° to be 0.10584, his formula up to 900° being—

$$Sm = 0.10584 + 0.00002287 t + 0.0000000219427 t^2.$$

This formula evaluated for Regnault's range gives  $Sm$  (13°—99°) = 0.1086, about 15 per cent higher than Regnault's value. At about 900°, however, Pionchon observed a sudden change in the specific heat, so that above 900° the mean specific heat to 0° is expressed by the formula—

$$Sm = 0.124 + 0.00004 t - \frac{14.8}{t}.$$

He could not definitely determine just how much heat was rendered latent in this change at 900°.

*Copper.*

Wilcke found 0.114; Dr. Crawford, 0.1111; and Dalton gave 0.11, the latter by the method of cooling.

Dulong and Petit found 0.0949 (0°—100°) and 0.1013 (0°—300°), from which follows the formula—

$$Sm = 0.0917 + 0.000032 t.$$

Regnault gives 0.09515 (17°—98°); Dulong and Petit's formula evaluated for this range gives 0.09535.

Bède obtained a considerably lower result, giving up to 250°,—

$$Sm = 0.0910 + 0.000023 t,$$

which gives values at (15°—100°) about 2 per cent lower than Regnault.

Kopp obtained values between 0.0895 and 0.0949; average 0.0925 (15°—60°).

Naccari worked up to 325°, and gives the formula—

$$Sm = 0.0921 + 0.0000105 t,$$

which gives, at 17°—98°, 0.0933. This result is almost the same as Bède's, but for higher temperatures would be much below his.

Le Verrier says that the specific heat of copper does not increase regularly with the temperature, but is constant between certain limits, that is,—

Between 0° and 360°	.. .. .	0.104
360° „ 580°	.. .. .	0.125
580° „ 780°	.. .. .	0.090
780° „ 1000°	.. .. .	0.118

Further, that at the points where the changes occur there is heat rendered latent, about 2 calories towards 350°, 2 calories towards 580°, 3.5 calories towards 780°. He states that the total heat in the copper is 117 calories towards 1020°.

In connection with Prof. B. W. Frazier, the writer has made a particular study of copper, reaching the conclusion that none of the above critical points occur, and that the specific heat increases regularly with the temperature according to the equations—

$$\begin{aligned} S &= 0.0939 + 0.00003556 t \\ Sm &= 0.0939 + 0.00001778 t \\ Q &= 0.0939 t + 0.00001778 t^2. \end{aligned}$$

These formulæ were the true expressions of the results obtained up to 900°, and at none of the temperatures designated as critical points by Le Verrier were any deviations noticed. It would have been impossible for an absorption of 0.5 calorie to have occurred without having been detected. The ratio of the specific heat of copper to that of platinum throughout this range did not vary one-half of 1 per cent from 2.96, showing that the ratio of increase of specific heat with the temperature is the same in both metals.

*Latent Heat of Fusion.*—The mean value of six experiments on the amount of heat in molten copper at the melting point have given us 162.0 calories. The above formula evaluated for 1054° gives for the solid copper 118.7 calories. We have therefore determined the latent heat of fusion as 43.3 calories.

*Didymium.*

Hillebrand obtained 0.04563 (0°—100°) in the ice calorimeter, allowing for 0.4 per cent of silicon, 0.3 per cent of iron, and 0.1 per cent of aluminum, which were in the specimen.

*Gallium.*

Bettendorf obtained 0.079 (12°—23°) for solid gallium. Tomassi ("D'Electrochimie," p. 226) gives the specific heat of liquid gallium as 0.0802, and the latent heat of fusion as 19 calories. I do not know the name of the investigator who determined these.

*Germanium.*

Nilson and Pettersson found the following mean specific heats:—

0° to 100°	.. .. .	0.0737
0° to 211°	.. .. .	0.0773
0° to 302°	.. .. .	0.0768
0° to 440°	.. .. .	0.0757

As there is evidently first an increase and then a decrease, no simple formula can be derived to express these results.

*Gold.*

Kirwan first made its specific heat 0.05; Dalton gave it as the same; Dulong and Petit obtained 0.0298 by the method of cooling.

Regnault obtained 0.03244 (12°—98°) with gold 999 fine. Violle worked with gold 1000 fine, and obtained for 0°—100° 0.0316. This is stated to remain sensibly constant up to 600°, and then to increase gradually towards the melting-point (1035°). At 900° Violle makes its specific heat 0.0345, and at 1020° 0.0352. It would appear from these figures that the specific heat of gold is more nearly constant, or rather changes less with the temperature than that of any other metal.

*Iridium.*

Bunsen has found with the ice calorimeter 0.0574 and 0.0565, mean 0.0570 between 0° and 100°.

*Iridium.*

Regnault found 0.03672 (17°—98°), but remarks that the metal he used was impure.

Kopp obtained 0.0358 (15°—60°) with metal of greater purity.

Violle found for it exactly the same value as for platinum:—

$$Sm = 0.0317 + 0.000006 t.$$

He verified this formula up to 1400°. Violle further determined the heat in solid iridium just set as 84.2, 85.3, and 83.9 calories; mean 84.5, which, by the above formula, would indicate a maximum fusing-point of 1950°.

*Iron.*

Wilcke gave 0.126; Crawford, 0.1269; Irvine, 0.143; Kirwan, 0.125; Dalton, 0.13; and Dulong, 0.11.

Dulong and Petit experimented up to 350°, obtaining the values—

0° to 100° .. .. .	Sm=0·1098
0° to 200° .. .. .	Sm=0·1150
0° to 300° .. .. .	Sm=0·1218
0° to 350° .. .. .	Sm=0·1255

which would lead to the formulæ—

$$S = 0·1062 + 0·000028 t + 0·0000008 t^2$$

$$S = 0·1062 + 0·000056 t + 0·00000024 t^2.$$

It may be here remarked that all later investigators have reached similar formulæ of three terms, which means that the specific heat of iron increases more rapidly than the first power of the temperature. It should be borne in mind that these formulæ were verified only to 350°.

Regnault found 0·11352 (19°—98°), and, after the same piece had been heated to redness, 0·11380.

Bède obtained the following results :—

15° to 100° .. .. .	0·11230
16° to 142° .. .. .	0·11533
20° to 247° .. .. .	0·12331

From these observations he deduces the formula—

$$S = 0·1053 + 0·000071 t,$$

but it can be seen from the data obtained that the value for 247° was higher than it should have been if the rate of increase had remained constant. A formula of three terms should, therefore have been derived to fit the data, and he should have given—

$$S = 0·1050 + 0·000065 t + 0·00000018 t^2.$$

It will be observed that the coefficient of  $t^2$  is smaller than in Dulong and Petit's formula, showing the curve to be nearer to a straight line.

Byström gives the true specific heat of iron, as deduced from his experiments, at every 50° up to 300°, as follows :—

Temperature	Specific Heat (S)	Differences.
0° .. ..	S=0·111641	0·000728
50° .. ..	0·112369	0·001426
100° .. ..	0·113795	0·002154
150° .. ..	0·115949	0·002872
200° .. ..	0·118821	0·003590
250° .. ..	0·122411	0·004308
300° .. ..	0·126719	

These data would lead to the formulæ—

$$S = 0·11164 + 0·00000718 t + 0·0000001436 t^2$$

$$S = 0·11164 + 0·00000359 t + 0·0000000479 t^2.$$

This formula differs from the previous ones in having a much larger value of the constant, a much smaller coefficient of  $t$  and a larger coefficient of  $t^2$ , which is shown on the diagram by the curve starting higher, being quite flat for a distance and then rising rapidly. This formula evaluated for Regnault's range gives Sm (19°—98°) 0·1127, about 0·75 per cent below Regnault's value.

Kopp obtained results from iron, the average of eight experiments at 15° to 60° being 0·1120. His minimum value was 0·108, and maximum 0·114, showing here especially the roughness of his experiments and the general unreliability of his results, although the mean, in this case, comes very near the probably true value.

(To be continued.)

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 4, July 24, 1893.

**Researches on Samarium.**—Lecoq de Boisbaudran.—This paper will be inserted at some length.

**Density of Sulphurous Acid, its Compressibility, and its Expansion under Normal Conditions.**—A. Leduc.—The author finds the density of sulphurous acid = 2·2639.

**Oxidation of Nickel Sulphide.**—Ph. de Clermont.—The oxygen of the atmosphere cannot entirely oxidise the sulphur of this compound, and leaves a minimum quantity of nickel sulphide unattacked. This residue forms a fairly stable compound with the neutral sulphite.

**Crystalline Cuprous Phosphide.**—A. Granger.—The composition of this phosphide is  $Cu_2P_2$ . In appearance it is like graphite. It is attacked in the cold by chlorine and bromine. Dilute nitric acid dissolves it readily. If mixed with oxidising agents, such as potassium nitrate or chlorate, it detonates on percussion. If heated in contact with air it is oxidised and converted into copper phosphate. It is slightly soluble in hydrochloric acid; its solution gives with potassa a precipitate of cuprous oxide.

**Bismuth Sub-gallate.**—This compound is more generally known by its pharmaceutical name dermatol. Its composition is  $C_7H_3O_5Bi \cdot 2H_2O$ . In it bismuth oxide is combined with the acid function and the phenolic functions of gallic acid.

**Condensation of the Alcohols of the Fatty Series.**—A. Brochet and P. le Boulenger.—This paper does not admit of useful abstraction.

No. 5, July 31, 1893.

**Benzoylnicotine.**—A. Etard.—Benzoylnicotine is a colourless alkaloid, slightly viscid and having no tendency to crystallise. It is insoluble in water, and dissolves only in an excess of dilute hydrochloric acid. Its chloroplatinate, a light yellow crystalline precipitate, has the composition  $[C_{10}H_{13}N(C_7H_5O)HCl]_2PtCl_4$ .

**Fixation of Iodine by Starch.**—G. Rouvier.—If to known and equal volumes of starch water, the strength of which in starch is known, we gradually add larger and larger quantities of starch, there remains free iodine as soon as we pass the proportion  $(C_6H_{10}O_5)_{16}I_3$ .

**Preparation of Normal Caproic and Hexylic Acids.**—J. Tripiet.—The oxidation of castor oil by a dilute mixture of sulphuric and nitric acids gives much more abundant yields than those obtained with nitric acid alone. The volatile products consist entirely of normal hexylic and heptylic acids, and a small quantity of pure heptylic nitrile.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. viii., No. 89.

**Report by Z. Roussin on M. Buisine's Memoir on the Purification of Sewage by means of Ferric Salts.**

**Purification of Sewage by means of Ferric Salts.**—M. Buisine.—The process described in these papers is thoroughly known in Britain.

## MISCELLANEOUS.

**The Cape Agricultural Journal.**—It is not often that an editor feels pleasure in acknowledging himself in the wrong. Such, however, is decidedly our case as regards our notice of the (Cape) *Agricultural Journal* inserted in CHEM. NEWS, vol. lxxvii., p. 314. Our reviewer, being misled by the names of the analysts in question, supposed them to be aliens. Like ourselves, he is very glad to salute them as British subjects.

**Bibliography of Alcoholic Fermentation.**—The writer wishes to call the attention of fellow-workers to the fact that he is preparing a bibliography of alcoholic fermentation, with special reference to vegetable physiology. He will be very glad to receive notes concerning the literature of this question from botanists, chemists, and physiologists in this country who are interested in having bibliographies of this kind as complete as possible.—J. CHRISTIAN BAY, Missouri Botanic Garden, St. Louis, Mo., U.S.A.

**A New Pathogenic Organism.**—At the recent meeting of the British Institute of Public Health, Edinburgh, Sir Charles A. Cameron, of Dublin, read a paper (by himself and Dr. McSweeney) on an organism isolated from a water which was supposed to have caused a local epidemic of enteric fever. The water proved to be polluted, and to contain a bacterium, which by culture proved to be intermediate between the *Bacterium coli communis* and the *Bacterium typhosum*. It resembles the latter in its cultivation on fuchsine agar, and its occasional exhibition of energetic mobility. It resembles the former in giving the indol reaction. In its mode of growth on potato it resembles closely *B. typhosum*, and in its energetic power of fermentation and its appearance on gelatin plates it resembles *B. coli communis*. This organism resembles in appearance both *B. typhosum* and *B. coli communis*; it is only by its behaviour under cultivation and its action on glucose, lactose, &c., that it can be differentiated from those bacteria. As it was found in water at Miltown, near Dublin, it may provisionally be termed the *Miltown bacterium*.

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SESSION 1893—94.

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SESSION 1893—94.

The Matriculation Examination of the CITY AND GUILDS CENTRAL INSTITUTION will be held on September 19—22nd, and the Entrance Examination of the Day Department of the CITY AND GUILDS TECHNICAL COLLEGE, Finsbury, on September 26th.

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THE CHEMICAL NEWS.

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ON THE  
ACTION OF IODINE ON SOME  
PHENOLS AND ALLIED COMPOUNDS IN  
PRESENCE OF FREE ALKALI, AND  
A NEW CLASS OF DERIVATIVES  
RESULTING THEREFROM.

By THOS. R. CARSWELL.

BEYOND the simple statement found in most text-books, that the action of iodine and iodic acid, in presence of free alkali, on phenol results in the formation of the three mon-iodophenols together with a tri-iodophenol, little of importance seems to have been known until I. Messinger and G. Vortman reported on a new class of "iodine phenols" which they had obtained by modifying this reaction, which report appeared in the *Berichte Deut. Chem. Gesell.*, No. 12, 1889.

This latter class of "iodine phenols" have come to be of considerable importance, since some of them have been introduced into medicine, prominent amongst them being the article known as Aristol, which was originally introduced under the name annidalin. Messinger and Vortman studied the general reaction more minutely in order to find a volumetric method for the quantitative estimation of the phenols as a class, together with some allied compounds. This latter paper was published at a more recent date (1890) than the one referred to above and was abstracted by various English contemporaries. These abstracts originally attracted my attention to the subject, and to the British Pharmaceutical Conference Meeting of 1892 I contributed a paper, in which I dealt chiefly with the reaction as a method of assay, from a practical point of view, and in that sense criticised it. I was not then aware of the 1889 paper dealing with the composition of the compounds resulting.

In order to explain the large disappearance of iodine relative to the quantity substituted in the phenol molecule, I dealt very roughly with the probable composition of the compounds formed; my object being simply to show that the iodine percentages of the compounds were not commensurate with the consumption of iodine as found by titration, and more especially to show that where the greater consumption was indicated the compounds formed actually contained less iodine. I now propose to supplement that paper, to criticise other communications relative to the subject, to treat exhaustively a few typical cases, to deduce the *rationale* of the reaction in general, and prove the composition of a number of the compounds resulting. It must be borne in mind, however, that the substances as a class are of an exceedingly ill-defined nature, and therefore presented great difficulties in deciding whether a particular portion was a single substance or a mixture.

For the purposes of this paper, in estimating iodine the method of Carius was used throughout. Only one set of results will be given in each case. In the constitutional representations used throughout the following, the carbon atom symbols of the nuclei will not be inserted; and, indeed, such representations are used more because they show at a glance differences, than for any proved reason for choosing any particular structure.

*Phenol* (C<sub>6</sub>H<sub>6</sub>O).

A quantity of the reddish violet precipitate was prepared as follows:—A solution containing 8 grms. phenol in 300 c.c. was prepared (solvent, water). 20 c.c. of this

solution, together with 35 c.c. of normal solution of caustic soda, were diluted to about 1 litre, heated to 60° C., and decinormal solution of iodine run in to large excess, the whole allowed to stand for thirty minutes, and then acidified with dilute sulphuric acid. This process was repeated until a sufficient quantity was obtained.

Total iodine of this precipitate (air dried)—

Quantity taken = 0.1584 grm.  
Silver iodide found = 0.2136 ,, = 72.85 p.c. iodine.

The precipitate was treated with cold ether as long as anything dissolved out, the ethereal solution was allowed to evaporate, and the residue recovered and powdered. This residue was of a yellowish brown colour, perfectly amorphous, resinous consistence, and readily fusible. The presence of iodine, other than that of substitution, being suspected, an attempt was made to drive it off by simple air heating, but fusion took place, accompanied with decomposition, and rendered this impossible. It was therefore placed in a tube together with metallic copper and water, sealed, and heated for a few hours at a temperature of about 120° C. The contents were then washed out, dried on water-bath, and dissolved out with ether. The recovered product was boiled with alcohol, and the alcoholic solution filtered off, the portion soluble in alcohol recovered and powdered. This was of a dirty white colour. It was dried in desiccator for two days, and finally at 50° C. in air-oven. It was then taken for analyses.

Total iodine of alcohol, soluble portion:—

Quantity taken = 0.1660 grm.  
Silver iodide found = 0.2334 ,, = 75.96 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1276 grm.  
Water found = 0.0137 ,, = 1.19 p.c. hydrogen.  
Carbon dioxide found = 0.0773 ,, = 16.52 ,, carbon.  
By difference .. .. = 6.33 ,, oxygen.

No very good formula can be derived from those analyses, probably owing to slight admixture, although it may roundly be represented thus, C<sub>20</sub>H<sub>12</sub>I<sub>9</sub>O<sub>6</sub>, showing that its constitution may be represented similarly to that of the following substance, assuming that one of the original benzene nuclei entering into its constitution had been, or became, tri-substituted, whilst only two of the original oxidised carbon atoms had become further oxidised.

The insoluble residue from the boiling alcohol treatment was dried; it appeared of a dirty white colour, and melted with decomposition (180° C.).

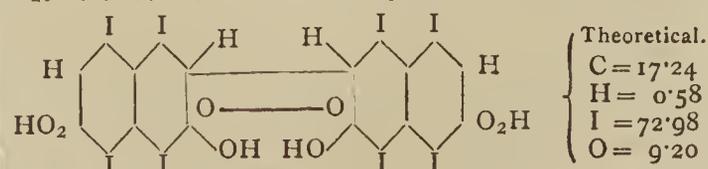
Total iodine of the alcohol-insoluble portion:—

Quantity taken = 0.1002 grm.  
Silver iodide found = 0.1350 ,, = 72.79 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1312 grm.  
Water found = 0.0124 ,, = 1.05 p.c. hydrogen.  
Carbon dioxide found = 0.0838 ,, = 17.42 ,, carbon.  
By difference .. .. = 8.74 ,, oxygen.

Those results may be represented by the formula C<sub>20</sub>H<sub>8</sub>I<sub>8</sub>O<sub>8</sub>; or, constitutionally, thus—



It is somewhat difficult to reconcile with theory the large percentage of hydrogen found without assuming the existence of hydrogen at the junction of the benzene ring, but this is extremely unlikely.

The remainder of the original precipitate insoluble in

ether was treated similarly with chloroform, the chloroform solution filtered, and the chloroform allowed to evaporate. The residue was of a bright violet-red colour, perfectly amorphous, and pulverulent. An attempt was made to free it from alleged loosely-combined iodine by treating with a weak alcoholic solution of caustic potash on the water-bath, but this was unavailing. The alcoholic potash was therefore filtered off and the residue washed. It was found that the potash had extracted a very small portion, readily fusible, which was thrown out on acidification. The quantity was too small for examination. The washed residue was heated with water and copper in sealed tube until decolorised, rinsed out, dried on water-bath, and dissolved out with carbon disulphide, recovered from the solvent and dried, then taken for analyses.

## Total iodine :—

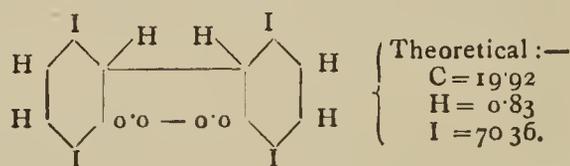
Quantity taken = 0.1173 gm.  
Silver iodide found = 0.1507 ,, = 69.42 p.c. iodine.

## Combustion of same :—

Quantity taken = 0.1010 gm.  
Water found = 0.0103 ,, = 1.13 p.c. hydrogen.  
Carbon dioxide found = 0.0748 ,, = 20.19 ,, carbon.  
By difference .. .. = 9.26 ,, oxygen.

These results may fairly well be represented by the formula  $C_{12}H_6I_4O_4$ , although the iodine percentage is rather low, which might easily be accounted for by the heating at a high temperature in sealed tube, the carbon being correspondingly high.

It may be constitutionally represented thus :—



The remainder of the original precipitate insoluble in chloroform was treated similarly with carbon disulphide, in which it almost entirely dissolved, the carbon disulphide was evaporated off, and the residue which occurred in brittle scales—of a reddish violet colour—was powdered and dried. This latter residue constitutes the greater portion of the whole original precipitate. It does not fuse, but simply decomposes between 360° and 380° C. Any former portion of the original precipitate, extracted by a particular solvent in the order given, is also soluble in any solvent used for extraction after its removal. For instance, the whole precipitate is soluble in carbon disulphide. No part of the original precipitate is soluble in glacial acetic acid, whilst strong sulphuric acid only exerts a very slight solvent action on the more readily soluble portions.

## Total iodine of the alcohol-ether-chloroform insoluble portion :—

Quantity taken = 0.1840 gm.  
Silver iodide found = 0.2485 ,, = 72.95 p.c. iodine.

## Combustion of same :—

Quantity taken = 0.2387 gm.  
Water found = 0.0161 ,, = 0.75 p.c. hydrogen.  
Carbon dioxide found = 0.1797 ,, = 20.53 p.c. carbon.

A quantity of the same portion of precipitate was heated in sealed tube, together with copper and water, at a temperature of about 140° C., for three days. When taken out the red colour had disappeared, the suspected loosely combined iodine having been apparently eliminated. The mixture was evaporated to dryness on the water-bath, the dry residue washed with ether-chloroform and then dissolved out with carbon disulphide, the solution filtered and allowed to evaporate. The residue was again

deposited in its scaly character, but now almost colourless. This was powdered, dried, and taken for analyses.

## Total iodine :—

Quantity taken = 0.3015 gm.  
Silver iodide found = 0.4009 ,, = 71.84 p.c. iodine.

## Combustion of same :—

Quantity taken = 0.1818 gm.  
Water found = 0.0141 ,, = 0.86 p.c. hydrogen.  
Carbon dioxide found = 0.1402 ,, = 21.03 p.c. carbon.

A new batch of the red-violet precipitate was prepared and treated as before with ether, chloroform, and carbon disulphide in succession. A quantity of the carbon disulphide residue was air-dried, and the total iodine estimated.

Quantity taken = 0.3418 gm.  
Silver iodide found = 0.4651 ,, = 73.52 p.c. iodine.

Another batch of the red-violet precipitate was prepared in presence of lead (in this case the colour of the precipitate was lighter).

The precipitate was separated by solvents as before, and a quantity of the carbon disulphide residue estimated for total iodine.

Quantity taken = 0.2376 gm.  
Silver iodide found = 0.3163 ,, = 71.08 p.c. iodine.

Another batch of the red-violet precipitate was prepared under the ordinary conditions, and the total iodine of the whole precipitate estimated.

Quantity taken = 0.2073 gm.  
Silver iodide found = 0.2789 ,, = 72.69 p.c. iodine.

The total iodine percentages of the whole precipitates being so much less than those reported by Messinger and Vortman, namely, 78.95 and 79.70, a quantity was prepared, with a dilution equal to about an eighth of that used in the above preparations, and the iodine estimated.

Quantity taken = 0.1238 gm.  
Silver iodide found = 0.1680 ,, = 73.32 p.c. iodine.

The differences may possibly be explained, by assuming that they had obtained mixtures containing larger quantities of a tri-substituted compound.

The quantity of "loosely-combined iodine" taken up is intimately connected with the quantity of free iodine existing in the mixture after the substances have all been satisfied, which fact can easily be demonstrated.

A new batch of the red-violet precipitate was prepared and separated as before. The alcohol-ether-chloroform insoluble portion, recovered from its solution in carbon disulphide, was taken for further experiment.

## Total iodine :—

Quantity taken = 0.1501 gm.  
Silver iodide found = 0.2111 ,, = 75.98 p.c. iodine.

A quantity of the same was heated together with water and copper in sealed tube, at a temperature of about 180° C., for three days. The product was then taken out, dried, and washed with ether and chloroform, then treated with carbon disulphide, the portion soluble in carbon disulphide recovered and dried. This was of the physical character as the similar product already treated of, and, like it, did not fuse, but decomposed on the temperature reaching about 360° C., carbon separating and iodine coming off free.

A small quantity of a dark greyish-brown substance remained, insoluble in carbon disulphide.

## Total iodine of the carbon disulphide soluble portion :—

Quantity taken = 0.2557 gm.  
Silver iodide found = 0.3400 ,, = 71.84 p.c. iodine.

## Combustion of same :—

Quantity taken = 0.1935 gm.  
Water found = 0.0145 ,, = 0.83 p.c. hydrogen.  
Carbon dioxide found = 0.1547 ,, = 21.80 p.c. carbon.  
By difference = 5.53 p.c. oxygen.

As the quantity of the greyish-brown insoluble part was so small, no satisfactory examination could be made of it; but an iodine assay and combustion were attempted, in order if possible to obtain some evidence of admixture of the original taken or some clue to the above discordant results:—

Total iodine:—

Quantity taken = 0.0411 gm.  
Silver iodide found = 0.0342 „ = 44.96 p.c. iodine.

Combustion of same:—

Quantity taken = 0.0460 gm.  
Water found = 0.0055 „  
Carbon dioxide found = 0.0212 „ = 12.57 p.c. carbon.  
Ash (consisting chiefly of CuO and Fe<sub>2</sub>O<sub>3</sub>) = 39.56 p.c.

This result, although valueless in itself, is of some use, in so far as it furnishes evidence that the portion retained by the copper was essentially of the same composition as the soluble portion, differing probably by its containing less oxygen. It also tends to dispel the possibility that the iodine percentages, although agreeing with those of the di-substituted compounds, were not really derived from mixtures of mono- and tri-substituted compounds.

A further quantity of the same separated portion as that used in the last series of experiments, together with a quantity of a previously “deiodised” portion (the quantity of material having become rather scant), were placed in a tube, together with water, finely divided silver, and copper, sealed, and heated for eight days between 180° and 200° C. The product was then taken out, dried, washed with ether-chloroform, and treated with carbon disulphide, which latter dissolved out the greater part of it. This soluble portion when recovered and powdered was of a light yellowish-white colour, and, like the other similar portions decomposed, without melting on the application of heat.

Total iodine of this portion:—

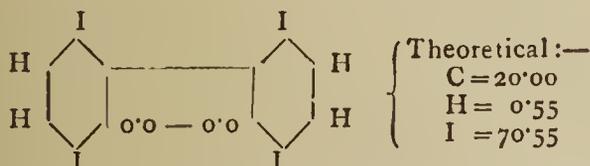
Quantity taken = 0.2179 gm.  
Silver iodide found = 0.2859 „ = 70.89 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1152 gm.  
Water found = 0.0085 „ = 0.81 p.c. hydrogen.  
Carbon dioxide found = 0.0848 „ = 20.07 p.c. carbon.  
= 8.23 p.c. oxygen.

Those results answer well to the formula C<sub>12</sub>H<sub>4</sub>I<sub>4</sub>O<sub>4</sub>, although the analyses would indicate slight contamination with a similar compound of lower oxidation.

The compound may be represented constitutionally thus:—



The remainder of the heated product, insoluble in carbon disulphide (cold), was boiled with successive quantities of carbon disulphide as long as anything dissolved out. The soluble part, which was very scanty, was recovered and dried, and the whole taken for iodine assay.

Total iodine:—

Quantity taken = 0.0599 gm.  
Silver iodide found = 0.0643 „ = 58 p.c. iodine.

The fixed portion had evidently undergone decomposition.

(To be continued).

## ON THE DETERMINATION OF VANADIC ACID.\*

(Continued from p. 77).

ON the prolonged passage of carbonic acid through the solution, boiled and treated with sulphurous acid, a distinct oxidation of the vanadium tetroxide is perceived, occasioned by the air contained in the carbonic acid.

Arthur Rosenheim (Inaugural Dissertation, Berlin, 1888), in a research on vanadic-tungstic acid, has given communications on the determination of vanadic acid and its separation from tungstic acid.

Wolcott Gibbs (*Zeit. Anal. Chemie*, xxiii., 543), in the analysis of the vanadic tungstates, uses for separating vanadic and tungstic acids the process first employed by Berzelius, according to which the vanadic acid, after the decomposition of the vanadic-tungstic salt by prolonged boiling with ammonia, potassa, or soda lye, is eliminated as ammonium vanadate by means of a concentrated solution of ammonium chloride.

Rosenheim, in verifying this method, arrived at the following results:—

Vanadic acid is precipitated by ammonium chloride from very concentrated solutions of vanadates. Small quantities, however, as Roscoe has shown, remain in solution. If about 0.2 gm. of vanadic acid is used, there results a loss of about 0.3 per cent.

Tungstic acid is not appreciably precipitated by ammonium chloride, even from strongly concentrated solutions of tungstates.

The ammonium vanadate precipitated by ammonium chloride from mixtures of tungstates and vanadates occludes small quantities of ammonium tungstic. Larger quantities of vanadic acid remain in the solution, and the tungstic acid separated is converted on expulsion of the ammonium chloride into a black tungsten nitride not easily transformed.

Hence for accurate quantitative determinations, such as the analysis of vanadic tungstates, the separation of vanadic and tungstic acids by means of ammonium chloride is not available, as small quantities of vanadic acid are always present along with large proportions of tungstic acid.

For determining vanadic acid along with tungstic acid, Gibbs (*Zeit. Anal. Chemie*, xxiii., 543) has made use of a method depending on the circumstance that vanadic acid, whether free or combined, evolves chlorine if boiled with concentrated hydrochloric acid, and undergoes reduction. The free chlorine is determined in the usual method.

F. Mohr (“Lehrbuch der Titrimethode,” 5th edition, p. 314) first pointed out this method; and Gibbs probably assumes, according to the statements of Mohr, that vanadic acid is reduced by hydrochloric acid according to the following equation:—



Rosenheim first sought to determine whether the reaction, in fact, ensues according to the above equation. To this end he studied the action of concentrated hydrochloric acid upon certain pure vanadates and upon pure vanadic acid.

From his experiments it appears that vanadic acid is never reduced by hydrochloric acid to V<sub>2</sub>O<sub>4</sub> or one of its derivatives, and that consequently a volumetric method which depends on the above equation must give false results. There are probably formed some of the numerous oxides or their chlorine derivatives which lie between V<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>4</sub>. The results of the numerous experiments do not justify us in establishing a fixed equation, and the method is therefore rejected by the author for quantitative determinations.

Attempts at founding a method of determining vanadic acid upon its behaviour with potassium iodide in a slightly acid solution had no better success.

\* *Zeitschrift für Analytische Chemie.*

The volumetric method with permanganate is also applicable to the determination of vanadic acid along with tungstic acid.

According to the proposal of Gibbs (*Zeit. Anal. Chemie*, xxv., 544), the solution of the salts is first strongly acidified with a mixture of sulphuric acid and phosphoric acid in order to produce the phospho-tungstic acid which is not precipitable by acids; it is then reduced with sulphurous acid or hydrogen sulphide, and finally titrated with permanganate.

In testing this method the author arrived at the following results:—If vanadates and tungstates are simultaneously present the reduction of the vanadic acid takes place more slowly than in solutions of pure vanadates. The light blue vanadyl colour is masked by the violet-grey of the somewhat reduced phospho-tungstic acid. The transitions of colour in titration are modified, and the recognition of the permanganate colour is impeded.

For removing these difficulties the author dilutes the solution of the vanadic tungstate as far as possible. The more dilute the purer is the colour on reduction. When titrating, the flask should be set on a white support. The final reaction is recognised by a distinct reddish shine, which is visible by reflected light at the margin of the solution. When this reaction appears the level of the reagent is read off, and we ascertain by adding one or two more drops that the reaction is completed. The solution of permanganate should be very dilute. The author uses a solution 1 c.c. of which represents about 0.008 gm.

On observing the above precautions the results were very accurate, ranging between 100.05 and 100.18 per cent. The method is unexceptionable in the analysis of the vanadic tungstates.

(To be continued).

#### STUDY OF CERTAIN NOVEL PHENOMENA OF FUSION AND VOLATILISATION PRODUCED BY MEANS OF THE HEAT OF THE ELECTRIC ARC.\*

By HENRI MOISSAN.

(Concluded from p. 77).

*Silicon*.—With a current of 380 ampères and 80 volts we may effect the volatilisation of silicon. We find in the cold tube small spheres of silicon attackable by a mixture of nitric and hydrofluoric acids. These spheres are mixed with a grey dust and with a small quantity of silica. If we collect the vapours upon asbestos pasteboard we see that the chief part of the silicon has been converted into silica.

*Carbon*.—Duration of the experiment, twelve minutes; intensity of current, 370 ampères and 80 volts. If we heat under these conditions a crucible filled with coarse fragments of coke, all the mass of the latter is soon transformed into graphite. After the experiment we find in the cold tube thin, light, translucent plates of carbon of a maroon colour by transmitted light.

M. Berthelot in his numerous experiments on the progressive condensation of carbon has already indicated the existence of a light carbon of a maroon colour. This substance is separated by means of dilute hydrochloric acid from the lime, which has been volatilised at the same time. The residue thus obtained, which we are studying, burns readily in oxygen with the production of carbonic acid.

*Oxides*.—The researches which we have already indicated on the crystallisation of oxides demonstrate superabundantly the volatility of these compounds. We are about to show it for the oxides,—regarded heretofore as infusible,—lime, and magnesia.

\* From the *Comptes Rendus*.

*Lime*.—With a current of 350 ampères and 70 volts we effect the volatilisation of lime in from eight to ten minutes. Under these conditions we collect in the cold tube lime in the form of an amorphous dust presenting no spherules. Abundant vapours of calcium oxide escape from the furnace. With a current of 400 ampères and 80 volts the experiment is completed in five minutes. With a current of 1000 ampères and 80 volts 100 grms. of calcium oxide may be volatilised in five minutes.

*Magnesia*.—Magnesia is less easily volatilised than lime, and its boiling-point lies near its melting-point. When the magnesia is melted it emits vapours which may be condensed upon the cold tube. This experiment is effected with a current of 360 ampères and 80 volts. The distillation becomes very beautiful and rapid if we use currents of 1000 ampères and 80 volts.

In fine, at the high temperature of the electric arc both the metals and the non-metals, hitherto regarded as refractory, are volatilised. The most stable compounds of mineral chemistry disappear in the electric furnace either by dissociation or by volatilisation. Nothing remains to resist these high temperatures except a series of new, perfectly crystalline compounds of exceptional stability, the properties of which we shall soon describe. These are the borides, the silicides, and especially the metallic carbides.

M. Daubrèe has already pointed out that the carbon of all our present organic compounds has originally existed in the state of metallic carbides. The electric furnace seems to realise the conditions of that remote geological epoch. It seems to us probable that these compounds may exist in the stars of high temperatures. At that same period the nitrogen would be found in the state of metallic nitrides, whilst the hydrogen was probably in a free state in a complex gaseous medium containing hydrocarbons and perhaps compounds of cyanogen.

#### NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.\*

By Lieut.-General C. A. McMAHON, F.G.S.

(Continued from p. 80).

#### PART III.

##### Aluminium.†

CÆSIUM chloride is usually recommended as a test for the salts of aluminium, the reaction yielding cæsium-aluminium-alum (cubic); but inasmuch as CsCl itself crystallises in the cubic system, there is serious danger of the reagent being mistaken for the desired product. The sulphates of Cs or Rb are more suitable (Cs<sub>2</sub>SO<sub>4</sub> is recommended), as they both crystallise in the rhombic system, and cannot therefore be mistaken for cæsium-alum. See Alum *ante*.

It is essential that samples of the sulphates obtained from the mineral under examination should be crystallised on glass slides prior to the addition of Cs<sub>2</sub>SO<sub>4</sub> or Rb<sub>2</sub>SO<sub>4</sub>, in order to be sure that the mineral does not yield an alum without the addition of the reagent. When Mg as well as Al is present, as MgSO<sub>4</sub> forms monoclinic double salts with Cs<sub>2</sub>SO<sub>4</sub> and Rb<sub>2</sub>SO<sub>4</sub> (see Nos. 61 and 62, Part II.), sufficient of the reagent must be used to satisfy any MgSO<sub>4</sub> that may be present and leave sufficient over to convert the Al-sulphate into Cs- or Rb-alum. The advantage of Cs<sub>2</sub>SO<sub>4</sub>, or Rb<sub>2</sub>SO<sub>4</sub>, is that neither of these reagents forms alums with the sulphates of other metals (see Alums).

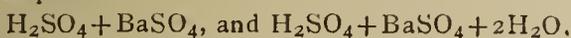
##### Barium.

The sulphate of barium is almost insoluble in water

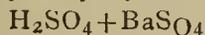
\* *Mineralogical Magazine*, vol. x., No. 46, p. 79.

† The bases in Part III. are arranged alphabetically with reference to their symbols; soda, for instance, being under the letter N.

(1 in 400,000), and barium precipitated by  $\text{H}_2\text{SO}_4$  has no crystalline form under the microscope. The sulphate, however, dissolves to a considerable extent in hot concentrated  $\text{H}_2\text{SO}_4$ , and deposits on cooling crystals having the composition—



Very frequently both are deposited together, the character of the deposit depending a good deal on the condition of the atmosphere at the time. If the air is damp the hydrous salt may predominate; if it is dry the anhydrous salt may be the one principally found on the glass slide.



is in microscopic four-sided\* transparent crystals (*a*). One of the four sides is very commonly a little longer than the others, and this side is frequently curved inwards like a concave lens. These small transparent crystals have straight extinction. More rarely crystals of hexagonal and more complex outline are formed. When the hot acid is exposed to a current of air, especially damp air, large skeleton crystals (*b*) are formed, which bear considerable resemblance to negative ice crystals. These are the skeleton forms of tabular rhombic crystals, and every transitional form up to a perfect rhomb may be seen. The skeletons extinguish in a line bisecting two arms. This is a very interesting fact, it seems to me, which throws light on the process of crystal building. Each molecule of these embryo crystals appears to be orientated not with reference to its present, but with reference to the ultimate form of the perfect crystals. Each molecule appears to have been endowed with what (for want of a better term) we must call polarity, and to have attached itself to its neighbour in a way that needed no subsequent modification as the mineral grew from a crystallite into a perfect crystal.† The fact that some embryo crystals of doubly refracting minerals show very little or no double refraction is, I think, due to the fact that owing to their excessive thinness they do not show colours between crossed nicols.

The sulphuric acid test is a delicate and sure one. It may be combined with ordinary testing in the following way:—Place some of the liquid to be tested in a test-tube or watch-glass. If  $\text{H}_2\text{SO}_4$  gives a white precipitate, evaporate to dryness. Add concentrated  $\text{H}_2\text{SO}_4$ ; heat for some time; draw off some of the clear, hot  $\text{H}_2\text{SO}_4$  with a pipette, and place a few drops on a warm slide. If anhydrous crystals (*a*) be desired, allow the  $\text{H}_2\text{SO}_4$  solution to cool gradually in a warm dry room. If the hydrous salt (*b*) be desired, allow the  $\text{H}_2\text{SO}_4$  to cool in or near an open window or exposed to steamy air. If the preparation is to be mounted in Canada balsam, allow the slide to stand for twenty-four hours, then cautiously drain off the free  $\text{H}_2\text{SO}_4$  with strips of filter paper.

2. If barium is present as sulphate I convert it into the chloride by the following process:—Evaporate solution to dryness; mix powder in agate mortar with sufficient charcoal to make the mixture dark grey in colour. Heat in small covered earthenware crucible strongly for one hour over a Bunsen burner. This converts the sulphate into the sulphide. Dissolve in dilute  $\text{HCl}$ , and heat until all the sulphuretted hydrogen is given off; filter, evaporate to dryness; dissolve in water, and allow a few drops to evaporate on a glass slide. The crystals of  $\text{BaCl}_2 + 2\text{H}_2\text{O}$  (*Monoc.*) thus obtained are in square prisms, very much resembling those of augite in shape. They almost always exhibit a very characteristic polysynthetic twinning, closely resembling the albite-baveno and albite-pericline twins of feldspar. Two sets of these twins may sometimes be seen. Each set of multiple twins is apparently parallel to a pinacoidal face, and they intersect at about  $90^\circ$ . A third and fourth set may also be seen, which appear to be parallel to the prismatic faces.

\* By this and similar expressions it is intended that, as seen in transmitted light, the crystal has a four-sided outline.

† For another illustration of the same principle see Calcium (2).

3. With a solution of tartar-emetic barium chloride yields tabular rhombs with two acute angles of about  $50^\circ$  each. Sometimes one or both of the acute angles are cut off, giving six-sided forms. They extinguish parallel to a line bisecting the acute angles, and the major axis is parallel to that line. They polarise brilliantly in colours of the 1st and 2nd order. These crystals very commonly exhibit multiple twinning, the twinning plane being parallel to a line bisecting the obtuse angles of the rhomb.

#### Beryllium (*Glucinum*).

The principal reaction mentioned in Clement and Renard's "Réactions Micro-chimiques" is the bichloride of platinum; but I do not think this is to be relied on when the beryllium to be tested is in the form of sulphate, for this salt and the chloroplatinate of beryllium both yield crystals belonging to the tetragonal system, and consequently one might be mistaken for the other.

1. The monoclinic salt may be obtained by dissolving the normal salt (tetragonal) in  $\text{H}_2\text{SO}_4$ . See Part II.

2. The double salt with  $\text{K}_2\text{SO}_4$  is very characteristic. See Part II.

3. On the addition of  $\text{KOH}$  solution a precipitate of white flocculent  $\text{Be}(\text{OH})_2$  forms, which dissolves in an excess of the precipitant or on application of heat. A precipitate re-forms on addition of a few drops of ammonium chloride. The precipitate formed by  $\text{KOH}$ , on being allowed to crystallise spontaneously, deposits crystals of  $\text{K}_2\text{SO}_4$  imbedded in  $\text{Be}(\text{OH})_2$ . The latter appears in radiating sheaves, apparently monoclinic. Extinction  $0^\circ - 25^\circ$  to  $e$ , and this is also the major axis. Double refraction very high, reminding one of calcite.

4. By treating a solution of the sulphate with a solution of ammonium carbonate very remarkable crystals of beryllium carbonate may be obtained, which I think have not yet been described. If too much of the ammonium carbonate is used the mixture will yield a white, opaque, amorphous mass; if too little is used the result will be a structureless glass; but if the right proportion of the reagent is added a carbonate is obtained that gives crystals which resemble bivalve shells in a remarkable manner. This resemblance is increased by the fact that they project, sometimes standing up on edge, sometimes lying more on their sides, from a ground-mass of granular ill-formed crystals that look extremely like a matrix of broken shells. The large and perfect crystals have two discoidal faces (resembling the upper and lower valves of shells) joined by a sharp edge, which is very frequently truncated at one side in a way to simulate the hinge of a bivalve shell. Straight extinction—viz.,  $\parallel$  to axis of elongation. Major axis  $\parallel$  to  $e$ . Between crossed nicols these crystals polarise in the blue of the 2nd order. Twinning is not uncommon. The combinations presented are varied. After mounting in Canada balsam the crystals gradually become more or less corroded.

5. The reagent recommended by Behrens is potassium oxalate, but the objection to this is that the results vary greatly with the proportion of the reagent to the beryllium salt. I obtained with one drop of the reagent a mass of globulites showing a cross under crossed nicols; and with from two to six drops: *a*, massive crystals; *b*, dendritic arrangements bristling with very sharply pointed spear-heads (rhombs with one of the acute angles projecting); *c*, lenticular crystals (with rather sharp terminations) shaped like a Zulu shield; and *d*, rosette-like groups of *c*, composed of two or more individuals. Extinction in *b* oblique; in *c* and *d* straight, viz.,  $\parallel$  to  $e$ . Double refraction: *b*, *c*, and *d* polarise brilliantly in the blues and reds of the 2nd order. Refraction strong. I have not observed any twinning in *c* or *d*; the groups of crystals, *d*, are not in my specimens penetration twins, but thin plates overlapping each other.

#### Calcium.

Gypsum ( $\text{CaSO}_4 + 2\text{H}_2\text{O}$ ), the form in which the sulphate crystallises from aqueous solution under ordinary

conditions, is soluble in the proportion of 1 part in 500 parts of water at the ordinary temperature. The maximum solubility is attained at about 35°, after which it declines. I find in practice that by boiling powdered gypsum in water for from ten to fifteen minutes sufficient of the sulphate is taken up to give good typical crystals when a few drops of the solution are allowed to evaporate on a glass slide. The crystals usually lie on the 010 face, and are commonly elongated in one direction (apparently 110). Gypsum prisms are often very slender, and radiate from a common centre like the rays of a star. This grouping of slender needle-shaped prisms is very characteristic of the mineral, but it must not be accepted as conclusive evidence of its identity, as several other salts have a similar habit, and some of these have an oblique extinction similar to gypsum.

More important, to my mind, is the presence of very peculiar twins, which have always been present when I have allowed an aqueous solution to evaporate spontaneously on a glass slide. The re-entering angles appear to be formed by the prism faces (110), as a fibrous striping (110 cleavage) is very distinct on almost every twin crystal. Sometimes this has a curious resemblance to polysynthetic twinning. The twin crystals disappear when they are mounted in Canada balsam. Owing to their thinness, and the consequent feebleness of their double refraction, they rarely show even between crossed nicols.

Another very common and characteristic form is that of a prism. These prisms are usually isolated from other crystals, but sometimes they appear in combination with other forms. The major axis of elasticity is theoretically 37° 28' from the axis of elongation, measured towards the acute angle of the rhomb, but it varies, I find, from 33° to 43°.

The above characteristic forms are often seen together on the same glass slide.

2. If a few drops of calcium sulphate in aqueous solution are placed on a glass slide, and a couple of drops of ammonium carbonate are added, the solution becomes clouded. On spontaneous evaporation numerous grains and congeries of grains of calcite are left on the glass. Long filamentous crystals, or strings of grains, are not uncommon, and these occasionally form skeleton rhombs, the obtuse angle of which varies from 105° to 108°. The high refraction and double refraction of calcite makes the detection of calcite crystals very easy. Being thin they usually polarise in brilliant colours. I have not succeeded in making magnesium carbonate in the above way, otherwise the latter might be mistaken for CaCO<sub>3</sub>.

3. Concentrated H<sub>2</sub>SO<sub>4</sub> raised to the boiling-point dissolves CaSO<sub>4</sub> to a certain extent, and deposits, on cooling, a salt which, according to Roscoe and Schorlemmer (vol. ii. [1], p. 203), consists "of microscopic prisms which have the composition CaSO<sub>4</sub>+H<sub>2</sub>SO<sub>4</sub>." The results obtained by me are as follows:—A little of the hot acid solution allowed to cool slowly on a glass slide, and to stand for some time, deposits embryonic crystals consisting of round and oval disks and moss-like clumps, the latter of which, under high powers, are seen to be composed of spicules sticking out in all directions. More rarely microscopic crosses consisting of four arms and obscurely shaped crystals may be seen. Straight extinction, viz., parallel to the longer axis of the oval disks and to the arms of the cross. Major axis at right angles to the longer axis of the oval disks; relief good; the disks polarise in the yellow of the 1st order. The round disks in transmitted light are rather suggestive of silk-worms' eggs; in reflected light they are a dull dead white.

Sometimes I have obtained a quantity of well-shaped crystals of the form shown at fig. 5 (see *Mineralogical Magazine*, x., No. 46); the sharp bows of these boat-shaped prisms meet at an angle of about 62°. At other times I have obtained crystals of the shapes shown at figs. 1 to 4. That at fig. 1 is not a thin platy crystal;

but owing to the action of free H<sub>2</sub>SO<sub>4</sub> on the balsam, and other causes, it is very difficult to make out the precise shapes of the side faces. Sometimes the top seems to be four-sided, and the side faces to be six-sided like the outline of fig. 5; but they cannot be made out exactly. All these crystals appear to belong to the orthorhombic system, and the mineral I doubt not is anhydrite (CaSO<sub>4</sub>).

#### Cerium.

Klement and Renard put in the foreground as tests oxalic acid and ammonium oxalate, but I have not obtained any very reliable results from these. I prefer ammonia as a test. This does not yield crystals, but its results are striking. If a drop of CeSO<sub>4</sub> solution is placed on a glass slide, and a drop of liquid ammonia is placed near it, the vapour from the latter, even when the drops are not allowed to touch each other, causes the CeSO<sub>4</sub> drop to assume a beautiful opalescent appearance. If the drops are allowed to evaporate side by side, or if ammonia be added to the CeSO<sub>4</sub>, an isotropic deposit is formed which shrinks considerably as evaporation proceeds and becomes scored with cracks that give it the appearance of a slice of serpentine. When unmounted the dried deposit generally exhibits, like opal, a blue and red sheen.

2. With ammonium formate crystals of cerium formate, Ce<sub>2</sub>(CO<sub>2</sub>H)<sub>6</sub>, are deposited in rounded, or six-sided, generally opaque white clumps, made up of micro-prisms which usually project from the edge of the mass. They have straight extinction. Direction of major axis doubtful. On mounting in balsam a few become translucent, and show colours up to the blue of the 2nd order. They look like radiating bunches of feathers, each feather with a central shaft and side barbs.

3. With K<sub>2</sub>SO<sub>4</sub> (see Remarks, Part II.) cerous sulphate forms double salts. Under the microscope these form transparent hexagonal disks, microscopic crystals of complicated structure, some of which have pyramidal terminations, globulites, and irregular hexagonal disks made up of overlapping or irregularly grouped crystals. The apparently heterogeneous internal structure is increased by numerous inclusions of opaque matter. When the globulites are densely packed together so as to form an opaque crust, they often appear in reflected light like branching stalks of coral. Refraction high; double refraction never higher than blue of 2nd order.

4. With Na<sub>2</sub>SO<sub>4</sub> and Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in the right proportion, we obtain small four-sided prisms terminated by sharp pyramids at both ends, or lenticular granules with sharp ends often arranged in groups like flowers with four petals. Extinction || to *e*. Major axis at right angles to *e*.

5. With potassium ferrocyanide, cerous sulphate yields (a) hexagonal disks; (b) short hexagonal prisms lying on their sides; and (c) stars with six rays, each star being an embryo hexagonal disk. The passage of the star into the hexagonal disk may often be seen, the almost complete forms being a hexagonal disk with a dark line running from the centre of each face towards the centre of the crystal. Other forms also occur, viz.—(d) four-rayed stars passing into; (e) short prisms of cube-like aspect; (f) bundles of bud-shaped crystals; (g) rounded complexes of small crystals suggestive of marigold flowers; and some variations of the skeletal form (d). (a) and (c) remain dark between crossed nicols; (b) and (e) have straight extinction; (d) polarises parallel to a line bisecting the rays of the star, and (f) to the axis of bundle. Major axis || to length of prism in (b) and at right angles to longer axis of (f).

#### Cobalt.

1. If potassium nitrite solution be added to the aqueous solution of CO<sub>2</sub>SO<sub>4</sub>, and then acetic acid to strong acid reaction, and the mixture gently warmed, a beautiful yellow precipitate (resembling the colour of chrome yellow) is formed. Under the microscope this yellow deposit (K<sub>6</sub>CO<sub>2</sub>N<sub>12</sub>+3H<sub>2</sub>O) is seen to be made up of very

small isotropic crystals in the shape of four-rayed stars or crosses with short arms. These are said to be the skeletons of crystals belonging to the cubic system. They require a 1-5th inch objective and 2nd eye-piece for their definition.

2. Solutions of cobalt that do not contain nickel, as an impurity, are said in Klement and Renard's work to give with oxalic acid the oxalate of cobalt ( $\text{CoC}_2\text{O}_4 + 2\text{H}_2\text{O}$ ) in rectangular flat prisms (straight extinction), which are often grouped as rosettes, and one is referred to Plate VI., fig. 11, of their work for the form of these rosettes. Oxalic acid (straight extinction) itself, however, sometimes occurs in radiating groups of fine prisms exactly as those represented, and it seems possible that, in this case, the reagent may have been mistaken for the oxalate of cobalt. In my experiments this reaction has yielded white opaque globules with rough edges suggestive of a resemblance to the spores of ferns. Among these there are also numerous slender crystals of oxalic acid, some of which are in radiating star-shaped groups.

(To be continued.)

## THE SPECIFIC HEATS OF THE METALS.\*

By JOS. W. RICHARDS, Ph.D.,  
Instructor in Metallurgy, &c., in Lehigh University.

(Continued from p. 85.)

### Iron (continued).

NACCARI made experiments similar to Byström's, arriving at the formulæ—

$$S = 0.1072 + 0.000116 t + 0.0000001466 t^2$$

$$Sm = 0.1072 + 0.000058 t + 0.0000000489 t^2$$

The diagram shows clearly the relative position of Naccari's results.

Pionchon experimented up to  $1150^\circ$  with the soft iron of "Berry," which contained no manganese or phosphorus, and only a trace of carbon and silicon. Pionchon found two points at which heat was rendered latent, about 5.3 calories being absorbed between  $660^\circ$  and  $720^\circ$ , and 6.0 calories between  $1000^\circ$  and  $1050^\circ$ . He gives the following formulæ for the mean specific heat from temperatures within the designated limits to zero:—

$$(0^\circ \text{ to } 660^\circ) Sm = 0.11012 + 0.000025 t + 0.0000000547 t^2$$

$$(660^\circ \text{ to } 720^\circ) Sm = 0.57803 - 0.001436 t + 0.000001195 t^2$$

$$(720^\circ \text{ to } 1000^\circ) Sm = 0.218 - \frac{39}{t}$$

$$(1050^\circ \text{ to } 1160^\circ) Sm = 0.19887 - \frac{23.44}{t}$$

It will be seen that the first formula is of the same nature as the preceding ones, the subsequent ones are complicated by having to include the heat rendered latent. The values of the true specific heat at any temperature are best seen by reference to the diagram. It increases gradually up to the first critical point, after which it remains constantly 0.218 until the second critical point is reached, after which it is again constant at 0.1989.

Pionchon remarks that these critical points coincide with sudden changes in the magnetic and conductive properties of iron, and also calls attention to the fact that from  $720^\circ$  to  $1000^\circ$  the specific heat is almost exactly double what it is at zero.

The presence of carbon and silicon in iron increase its specific heat, so that steel and cast iron are superior to pure iron in calorific capacity. The study of these bodies is therefore of interest, but can only be referred to briefly here. Regnault found the specific heat of cast steel (Hausman's) 0.11848, cast iron 0.12728, white iron 0.12983. Byström found that of cast steel 0.11850, and

of pig iron 0.1283, and also found the variations of these with the temperature up to  $300^\circ$ ; for full statement of which the reader is referred to his original paper.

### Lanthanum.

Dr. Hillebrand found 0.04485, using metal containing 4.6 per cent of didymium, 1.2 per cent of iron, 0.3 per cent of silicon, and a little aluminium, and calculating the allowance for these impurities.

### Lead.

Wilcke found 0.042; Crawford, 0.0352; Kirwan, 0.05; Dalton, 0.04; and Dulong and Petit, 0.0293; the last two by the method of cooling.

Regnault gives 0.03140 ( $15-98^\circ$ ).

Bède deduced from his experiments up to  $200^\circ$  the formulæ—

$$Sm = 0.0286 + 0.000019 t$$

This evaluated for Regnault's range gives 0.03075, two per cent below Regnault's value.

Kopp obtained 0.0308, 0.0302, 0.0293, and 0.0302; mean, 0.0301 ( $15-60^\circ$ ). Bède's formula gives for this range 0.0300.

Person found the specific heat of molten lead ( $335-430^\circ$ ) 0.0402.

Naccari experimented to  $300^\circ$ , and deduced the formulæ:—

$$S = 0.02972 + 0.0000136 t$$

$$Sm = 0.02972 + 0.0000068 t$$

This gives for Regnault's temperatures 0.03049, even a little below Bède.

Le Verrier finally states that the specific heat of lead is constantly 0.038 between  $0^\circ$  and  $230^\circ$ , that between  $220^\circ$  and  $250^\circ$  it is almost zero, for the metal absorbs almost no heat in traversing this interval of temperature, and between  $250^\circ$  and  $300^\circ$  the specific heat is constantly 0.0465. These results are so unexpected and differ at ordinary temperatures so greatly from Regnault's value (22 per cent difference), that we must conclude that they are quite improbable.

It is seen that there is some uncertainty as to the specific heat of lead at ordinary temperatures. On examining the diagram, it is seen that Bède's value for the specific heat increases until near the melting-point it is very nearly that observed by Person in the molten state. Now, since it has been observed in other metals that the specific heat in the solid state, near the melting-point, approaches the specific heat in the molten state, the writer is disposed to consider Bède's and Person's results as corroborating each other. I would, therefore, modify Bède's formula by using Regnault's value as affecting the constant, and write as the probably correct formulæ for lead—

$$Sm = 0.02925 + 0.000019 t$$

$$S = 0.02925 + 0.000038 t$$

This curve will pass through Regnault's value, and have the rate of increase determined by Bède.

*Latent Heat of Fusion.*—Dr. Irvine, jun., determined that the latent heat would raise the temperature of an equal weight of solid lead at the melting-point  $162^\circ$  F., and, using Crawford's value for the specific heat, this equals 5.6 calories F., or 3.1 C. If we use the value given by the above formula, 0.042415, his determination would give the latent heat as 3.8 calories.

Rudberg worked by the method of cooling also, and assuming that solid lead at its melting-point had a specific heat of 0.0352, he obtained 5.858 calories as the latent heat. If we use 0.042415 instead of 0.0352, the latent heat would become 7.058.

Person found molten lead at its melting-point to give out 15.61 calories. Assuming Regnault's value to be constant to the melting point, he obtained 5.37 calories as the latent heat. Had he used Bède's formula he would have obtained 4.27 calories, or with Naccari's formula 5.18 calories, or Bède's corrected formula 3.94. Or using the

\* A Lecture delivered before the Franklin Institute, Jan. 30, 1893.

total amount of heat in solid lead at its melting-point as found by Le Verrier (11.68 calories), the latent heat would be 3.93

I think the best conclusion to be drawn from this discussion is that the latent heat of fusion of lead is about this latter figure, 3.95 calories.

#### Lithium.

Regnault gives 0.941 at 20–98°.

#### Magnesium.

Regnault found 0.25 (22–98°); Kopp obtained results varying between 0.240 and 0.249; mean, 0.245 (15–55°).

#### Manganese.

Regnault first found 0.1441 (14–98°), but remarked that the metal was impure. Afterwards he obtained 0.1330 with a specimen which showed important quantities of carbon and silicon. Still later he found 0.122 (12–98°) for a specimen containing still a little silicon.

#### Mercury.

Crawford found 0.0357; Leslie, 0.0290; and Kirwan, 0.033. Dulong and Petit found 0.033 (0–100°), and 0.035 (0–300°), giving the formula—

$$S_m = 0.0320 + 0.00001 t.$$

Regnault found 0.03332 (12–98°), and 0.0319 at –59°, in the solid state.

Winkelman found 0.03312 (20–50°), and 0.03278 (25–142°). This last result would indicate a decrease in the specific heat with rise of temperature, and lead to the formula—

$$S = 0.0336 - 0.0000069 t.$$

Pettersson found—

0° to –5° .. ..	0.033266
–5 to –16 .. ..	0.033262
–5 to –26 .. ..	0.033300
–5 to –36 .. ..	0.033299

Naccari has recently determined the following values for the true specific heat:—

0° .. .. .	0.03337
50 .. .. .	0.03310
100 .. .. .	0.03284
150 .. .. .	0.03259
200 .. .. .	0.03235
250 .. .. .	0.03212

These data show a regularly decreasing specific heat, and lead to the formulæ—

$$S = 0.03337 - 0.0000055 t + 0.000000002 t^2$$

$$S_m = 0.03337 - 0.00000275 t + 0.00000000667 t^2.$$

It will be noticed that Naccari's figures agree well with those of Winkelman, giving for 20–50°, 0.03322; and for 25–142°, 0.03309. Naccari's formula gives for Regnault's temperatures (12–98°) 0.03314, which is only 0.5 per cent different.

Milthaler has found as the mean of his experiments the formula—

$$S = S_0 (1 - 0.000138 t)$$

If  $S_0$  (the true specific heat at zero) be taken as 0.033266 (Pettersson's value) the formula becomes—

$$S = 0.033266 - 0.0000046 t.$$

Or, if Naccari's value for  $S_0$  is taken—

$$S = 0.03337 - 0.0000046 t.$$

Or, if Regnault's value for  $S$  at 60° is taken—

$$S = 0.033596 - 0.00000461 t.$$

If Pettersson's results are reliable, they show that the specific heat of mercury between 0° and 36° is practically constant. The most recent experiments agree in showing

that above 0° the specific heat decreases with the temperature.

Kundt and Warburg have determined the specific heat of vapour of mercury, which is found to be 0.1714 at constant pressure and 0.102843 at constant volume. Since these quantities are to each other in the proportion 5:3, it follows from the mechanical theory of heat that the molecule of mercury must consist of only one atom; a conclusion which agrees with that deduced from the density of mercury vapour, thus confirming in a remarkable manner one of the deductions from Clausius's theories.

*Latent Heat of Fusion and Vaporisation.*—Person found the latent heat of fusion by reversing the method of cooling, as 2.84 calories. Fabre and Silbermann found the latent heat of vaporisation in an indirect way by means of iodine vapour as 77.5 calories.

#### Molybdenum.

Regnault found 0.07218 (12–98°), but the specimen contained an undetermined amount of carbon.

De la Rive and Marcet found 0.0659 at ordinary temperatures by the method of cooling.

#### Nickel.

Dalton found 0.10 and Dulong 0.1035, both by the method of cooling.

Regnault found 0.10863 (13–99°).

Pionchon investigated up to 1050°. He found a gradual increase in the specific heat up to 230°, but between that and 400° a very rapid increase, but after 400° the former rate resumed. He therefore concluded that between those two temperatures there is a gradual change of state, which would represent the absorption of 4.64 calories as latent heat. The diagram shows this break clearly. Pionchon gives the following formulæ for the mean specific heat to zero from any temperature within the designated limits.

Between—

$$0^\circ \text{ and } 230^\circ \quad S_m = 0.10836 + 0.00002233 t$$

$$230 \text{ ,, } 400 \quad S_m = 0.183493 - 0.000282 t + 0.000000467 t^2$$

$$440 \text{ ,, } 1050 \quad S_m = 0.099 + 0.00003375 t + \frac{6.55}{t}$$

Pionchon remarks that this change of state corresponds to known variations in nickel's magnetic and conducting properties.

Naccari experimented up to 320°, and deduces the formulæ—

$$S = 0.1043 + 0.0000946 t$$

$$S_m = 0.1043 + 0.0000473 t$$

Naccari remarks that all tests showed this metal to be pure, and that as far as he went he found no trace of the phenomenon mentioned by Pionchon.

#### Osmium.

Regnault found 0.0311 (22–98°).

#### Palladium.

Regnault gives 0.05928 (11–98°).

Violle investigated it up to 1265°, and found results agreeing to the formula—

$$S_m = 0.0582 + 0.000010 t$$

This formula gives for Regnault's range 0.05929, a remarkable coincidence.

The amount of heat in solid palladium as near as possible to its melting-point was found to be 109.8 calories, which, according to the above equation, would indicate a maximum fusing-point of 1500°.

*Latent Heat of Fusion.*—Three experiments to find the heat in molten palladium at its setting-point gave 146.0, 145.8, and 146.4 calories respectively, mean 146.1. Subtracting from this the heat in solid palladium at that temperature leaves 36.3 calories as the latent heat of fusion.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 15th, 1893.

Dr. ARMSTRONG, President, in the Chair.

MR. T. H. EASTERFIELD was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Henry Ormsby Hale, B.A., Oundle School, Northamptonshire; Thomas Beilby Rawlins, 2, Leven Street, Pollockshields, Glasgow; Herbert Santer, Albion Brewery, Caledonian Road, N.; William Gilchrist White, Lamb Roe, Whalley, Lancashire; Edward Humphreys Winder, 37, Vincent Square, S.W.

The following were duly elected Fellows of the Society:—John Bateman, Henry Bailey, Douglas T. C. Berridge, Robert S. Cahill, John Henry Coste, S. W. M. Davy, Arthur Henry Green, Ernest Albert Hancock, James John Howitt, John Walter Leather, Alexander Mitchell Martin, Charles Mills, Charles Alexander McKerrow, K. P. McElroy, John Watson Napier, William Ridgely Orndorff, Alexander Orr, George Ritchie, Wilfred Sessions, Henry Thomas Sorrel, Frank Ernest Thompson, Claude Theodore Vautin, Edward Augustus Warmington, Thomas Whittaker, Sydney Whally.

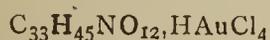
Of the following papers those marked \* were read:—

\*33. "Contributions to our Knowledge of the Aconite Alkaloids. Part VI. Conversion of Aconitine into Isaconitine." By WYNDHAM R. DUNSTAN, M.A., F.R.S., and FRANCIS H. CARR.

In a previous communication it has been shown that the roots of *Aconitum napellus* contain, besides the highly poisonous aconitine, an almost non-poisonous isomeride—isaconitine. These alkaloids are evidently intimately related, as both furnish aconine and benzoic acid on hydrolysis. The authors now show that when an aqueous solution of aconitine hydrobromide (m. p. 163°) is heated, change very gradually takes place, the isomeric *isaconitine hydrobromide* (m. p. 282°) being produced. The change is facilitated by the addition of a small quantity (1–2 per cent) of hydrogen bromide, but is not assisted if sufficient is present to induce hydrolysis of a large proportion of aconitine. The isaconitine was identified not only by the high melting-point of its salts, but also by the formation and analysis of the characteristic aucthorisaconitine. No similar change could be detected in the case of aconitine nitrate, either when neutral or acid solution was used, nor could the conversion be effected by heating aconitine with glacial acetic acid, although in this case anhydraconitine is produced if the heating be continued during eighteen hours at 120°. Aconitine may be dissolved in concentrated sulphuric acid, and the solution gently heated without the conversion into isaconitine taking place; nor does aconitine sulphate undergo conversion into the isomeride when it is heated many hours in contact with very dilute sulphuric acid. No isaconitine seems to be produced during the hydrolysis of aconitine by cold soda solution. The authors are making further experiments in the hope of gaining information with regard to the mechanism of the conversion of aconitine hydrobromide into isaconitine hydrobromide.

\*34. "Contributions to Our Knowledge of the Aconite Alkaloids. Part VII. Some Modifications of Aconitine Aurichloride." By WYNDHAM R. DUNSTAN, M.A., F.R.S., and H. A. D. JOWETT.

Certain irregularities having been observed in the melting-point of aconitine aurichloride,—



(see Part I.) prepared under different conditions from pure

aconitine, the subject was fully investigated, the result being that three distinct isomeric modifications have been isolated differing in melting-point and crystalline form.

When auric chloride is added to a solution of aconitine hydrochloride, a yellow amorphous precipitate is thrown down, from which directly or indirectly the three crystalline modifications can be obtained by employing different solvents. *Aconitine  $\alpha$ -aurichloride* is most readily produced in rosettes of needles by crystallisation from a mixture of acetone and water, or less readily and certainly in rectangular plates from dilute alcohol. The crystals melt at 135.5°. When re-crystallised from strong alcohol, this compound changes into the  $\beta$ -modification.

*Aconitine  $\beta$ -aurichloride* is obtained by crystallising from strong alcohol. It forms rosettes of needle-shaped crystals which melt at 152°. When this substance is re-crystallised from a mixture of chloroform and ether it changes into the  $\gamma$  modification, and when re-crystallised from a mixture of acetone and water it appears as the  $\alpha$ -modification.

*Aconitine  $\gamma$ -aurichloride* cannot apparently be formed directly from the amorphous precipitate or from the  $\alpha$ -aurichloride. It is, however, easily prepared by re-crystallising the  $\beta$ -aurichloride from a mixture of chloroform and ether, when it separates in prisms melting at 176°. When crystallised from strong alcohol, this substance is converted into needles of the  $\beta$ -aurichloride; and on crystallising it from a mixture of acetone and water, the  $\alpha$ -modification is obtained. When the  $\beta$ - and  $\gamma$ -modifications are melted they pass into the  $\alpha$  aurichloride. From each of the modifications one and the same crystalline aconitine (m. p. 188–189°) may be recovered. They behave, then, as true "physical" isomerides, no chemical difference being detectable between them.

\*35. "Note on the Stereoisomerism of Nitrogen Compounds." By S. U. PICKERING.

Hantzsch and Werner's suggestion that the isomerism of some triad nitrogen compounds may be explained by referring them to a tetrahedron and assuming that the nitrogen occupies one corner instead of the centre is tantamount to representing one side only of the nitrogen atom as capable of entering into combination. It leads to further difficulties when the nitrogen becomes pentad, as, in order to preserve the tetrahedral form, the nitrogen atom has to be placed in the centre of the tetrahedron together with one of the monad atoms. An alternative explanation which has been offered is based on the supposition that the isomerides are produced according as one of the bonds of the nitrogen atoms inclines towards one or other of the groups in its vicinity, an explanation for which the study of compounds of other elements affords no justification. In suggesting an arrangement of atoms in space, our ignorance of the matter renders the simplest possible arrangement the only justifiable one. This, in the case of an atom combining with three or five others, is that three of these should be arranged in one plane at equal distances around the central atom, the other two being placed in a plane at right angles, so that each of them is equidistant from the first three. This arrangement, though not symmetrical, is the most nearly symmetrical one possible. It affords, in the author's opinion, a perfect explanation of the stable character of ammonia derivative, and of the fact that in ammonium derivatives two of the group can be very easily split off. It explains the isomerism found in the hydroximes and hydrazones by one of the groups present being united by different bonds in the two cases (two of the five bonds being always free), just as in the isomerism of carbon compounds, and it agrees well with the facts as to isomerism and optical activity observed in the case of ammonium derivatives. Moreover, as the nitrogen atom can form a symmetrical compound with any two, as well as with three, of its bonds occupied, it also affords an explanation of the existence of nitric oxide and peroxide.

\*36. "A Study of the Properties of Some Strong Solutions." By S. U. PICKERING.

The depressions of the freezing-points of the three solvents water, acetic acid, and benzene by a number of non-electrolytes (methyl, ethyl, and propyl alcohols, diethylamine, pyridine, ethyl ether, carbon bisulphide, acetic anhydride) were examined, the determinations being extended to the strongest solutions possible. The results showed that the slight irregularities which are observable in the results afforded by weak solutions become one of the most marked features in the case of strong solutions, and any theory which attempts to explain the nature of solutions while ignoring the existence of these irregularities must necessarily be imperfect. The nature of the dissolved substance has an obvious effect on the character of the results, but it is impossible to ascribe this character to the nature of the dissolved substance only, as the peculiarities exhibited by a particular substance in one solvent are often absent when another solvent is used; these peculiarities would appear to be explicable only on the assumption that every solution contains substances peculiar to itself—*i.e.*, compounds of the solvent and substance—and does not consist merely of the juxtaposed free solvent and free substance.

In the various series, 29 breaks were observed in the regions embracing fairly simple molecular proportions (1:4 to 4:1 mols.), and of these, 24 agree within experimental error with molecular proportions, the remaining 5 being breaks whose existence or position was doubtful. Additional evidence is thus afforded as to the existence and significance of these breaks, and their occurrence is shown not to be confined to cases in which the solvent is water.

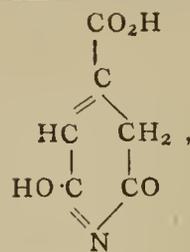
\*37. "Studies on Citrazinic Acid." By W. J. SELL and T. H. EASTERFIELD.

A new method of preparing citrazinamide is described, which consists in fusing a mixture of citric acid and urea. The alkali salts of the amide and the normal and acid alkali salts of the acid are described, and an account is given of trichlorocitrazinic acid and its behaviour with phenylhydrazine.

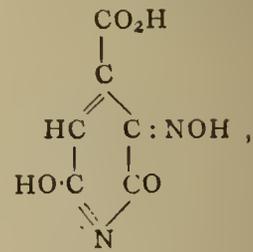
The authors find that the production of a blue colour when citrazinic acid is warmed with dilute solutions of potassium nitrite is due to the formation of a quinhydroketopyridine, a substance whose alkaline solution has an intense blue colour; this, however, is only the final stage of a series in which isonitrosocitrazinic acid is first formed. The isonitroso-compound is very unstable; it is oxidised by nitric or nitrous acid and converted into a stable yellow acid of the formula  $C_6H_2N_2O_5 \cdot 4H_2O$ ; hence, if an excess of nitrite be employed in applying the colour test for citrazinic acid, no blue colour results. The yellow acid is dibasic, and its solutions precipitate potassium or ammonium salts from solutions of the chlorides of those metals.

By the action of dilute sulphuric acid or of reducing agents, isonitrosocitrazinic acid is converted into  $\alpha\beta$ -quinhydro- and  $\alpha$ -ketopyridine, which crystallises in lustrous, bronze-green coloured prisms. The same substance may be produced by reducing the yellow acid. The quinhydrone is easily converted by oxidation into the corresponding quinone, which resembles ordinary quinone in many of its properties, and may be reconverted by sulphurous acid and other reducing agents to the quinhydrone. On reduction the quinhydrone gives a colourless solution which probably contains the quinol, as, on exposure to air, the liquid begins at once to deposit crystals of the quinhydrone; the quinol has not yet been isolated.

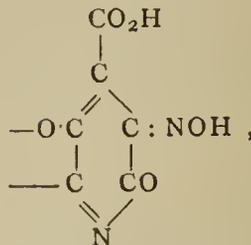
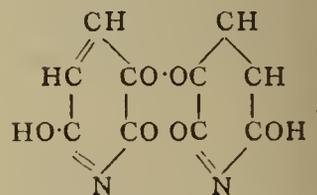
A bright red-coloured phenylhydrazocitrazinic acid, corresponding to the above isonitroso-derivative, is obtained by the action of diazobenzene chloride on citrazinic acid; this substance forms characteristic salts. The following formulæ are provisionally suggested for the substances described:—



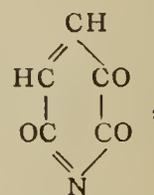
Citrazinic acid.



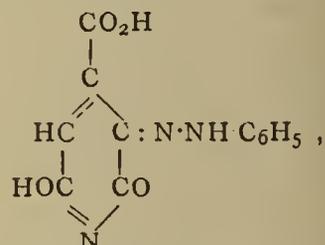
Isonitrosocitrazinic acid.

Yellow acid,  $\frac{1}{2}$  mol.

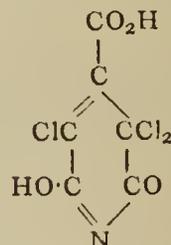
Quinhydroketopyridine.



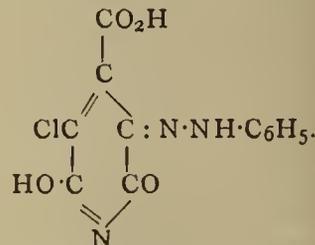
Quinoketopyridine.



Phenylhydrazocitrazinic acid.



Trichlorocitrazinic acid.

Chlorphenylhydrazocitrazinic acid  
(as salts).

#### DISCUSSION.

Dr. KIPPING said the published statements regarding citrazinic acid agree in assigning to it the property of fluorescence, which, according to Dr. Armstrong's views on the origin and nature of colour, it should not possess, assuming it to have the usually accepted constitution. At Dr. Armstrong's suggestion, Mr. O. F. Russell and himself undertook to settle, if possible, this question of fluorescence, and for this purpose they prepared citrazinic acid by two methods, of which that described by Behrmann and Hofmann was found to give the better results, the acid obtained by Ruhemann's process from ethylic acetyl citrate being difficult to purify.

A freshly-prepared alkaline solution of the crude product is highly fluorescent, but when the acid is carefully purified by converting it into the ethylic salt and crystallising the latter from acetic acid, this is no longer the case. A small quantity of pure citrazinic acid dissolved in concentrated soda gives a colourless solution without visible fluorescence; on shaking for a few minutes in contact with air a slight but gradually increasing blue fluorescence is observed, caused doubtless by the presence of some oxidation or decomposition product of the acid. A solution containing pure ethylic citrazinate, together with sodium carbonate, becomes fluorescent on exposure to the air, but apparently more slowly than a solution of the acid.

Some further experiments were made with citrazinic acid with the object of elucidating its constitution. Ethylic citrazinate gave with acetic anhydride a colourless crystalline diacetyl derivative,  $C_{12}H_{13}NO_6$ , the composition of which was determined by the ordinary

methods and by direct estimation of the quantity of acetic acid produced on decomposition with sulphuric acid. Attempts to prepare a hydrazone and a hydroxime from citrazinic acid were unsuccessful. By suspending citrazinic acid in water and passing nitrous fumes into the ice-cold mixture, a substance of the composition  $C_6H_6N_2O_6$ , which is evidently identical with the authors' isonitrosocitrazinic acid, was obtained; this compound can be obtained in almost colourless crystals by recrystallisation from ethylic acetate and petroleum. The action of potash and methyl iodide on citrazinic acid seems to be quite abnormal, but the nature of the product, which was of an uninviting character, was not determined. Citrazinic acid combines with dry bromine, yielding a crystalline substance which is readily soluble in water and ethylic acetate; it is, however, unstable, and loses hydrogen bromide very readily, being converted into a yellowish powder which is practically insoluble in ethylic acetate.

\*38. "The Essential Oil of Hops." Preliminary Notice. By ALFRED C. CHAPMAN.

About 80 kilos. of hops, some of which had been grown in Burgundy, some in Alsace, and the remainder in Kent and Sussex, were submitted to steam distillation in quantities of about 1 kilo. at a time.

When the greater part of the oil had been prepared the author was compelled, owing to pressure of other work, to discontinue its examination, and it was placed aside in a well-stoppered bottle, which it filled; at the end of about ten or eleven months, the remainder of the oil (about 30 c.c.) was prepared, and the whole was then twice steam-distilled to free it from resin; about 140 c.c. were obtained. On submitting the oil to distillation it commenced to boil at  $170^\circ$ , the thermometer rapidly rising to  $230^\circ$ , the greater part distilling over between  $230^\circ$  and  $270^\circ$ . After several fractionations, finally over sodium, about 40 c.c. of oil were obtained, boiling between  $256^\circ$  and  $261^\circ$  (uncorr.). This was found, on examination, to be a sesquiterpene, three combustions giving numbers closely agreeing with those required by the formula  $C_{15}H_{24}$ .

Two vapour density determinations by Hofmann's method gave 6.91 and 7.1, the vapour density required by  $C_{15}H_{24}$  being 7.1. The boiling-point of the sesquiterpene corrected for the emergent mercurial column was  $261$  to  $265^\circ$ . Its relative density was found to be 0.8987 at  $15^\circ/15^\circ$ , and 0.8955 at  $20^\circ/10^\circ$ ; when examined in a tube 100 m.m. long at  $20^\circ$ , it produced a rotation of  $1^\circ 5'$  to the right, corresponding to a specific rotatory power of  $+1.2^\circ$ .

Its index of refraction for the red hydrogen line,  $hH_a$ , was 1.4978, corresponding to a specific refractive energy of 0.555.

Another freshly-distilled sample of hop oil, which was examined soon after its preparation, was found to boil at much lower temperatures, and consisted of lower boiling-point terpenes, together with an oxygenated constituent, and contained but little of the sesquiterpene. It is proposed both to continue the study of the sesquiterpene and to examine in detail the other constituents of oil of hops in the hope of gaining some insight into the nature of the changes which occur during the ageing of the essential oil.

\*39. "The Sulphides and Polysulphides of Ammonium." By W. P. BLOXAM.

After calling attention to the uncertain state of our knowledge of the changes which solutions of ammonia saturated with hydrogen sulphide undergo when oxidised by exposure to the air, the author describes qualitative experiments, from which he infers that in addition to polysulphide such solutions contain *thiosulphate*, but never more than traces of sulphite, and that no sulphate is produced. These conclusions are based on the application of the method of testing recommended by Fresenius ("Qual. Anal.," Eng. trans. of 15th German ed., p. 193),

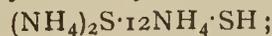
using cadmium chloride in place of zinc chloride to remove sulphides, as this proved to be a more effective agent, but adding the latter salt, as its presence was found to be essential to the production of the colouration characteristic of sulphite. It is pointed out that the presence of excess of ammonia enhances the delicacy of the test for sulphite.

In order to follow with success the changes undergone by solutions of "ammonium sulphide" on oxidation, the author has endeavoured to prepare the various sulphides and polysulphides in a pure state, and describes the results of a large number of experiments. In analysing the solutions of ammonium sulphides, the total sulphur was determined after oxidation by alkaline hypobromite; to determine the polysulphide sulphur, the solutions were boiled with excess of chlorhydric acid to expel sulphuretted hydrogen, and the residual sulphur was then oxidised by hypobromite, &c.; ammonia was estimated by boiling with excess of standardised chlorhydric acid, and then determining the amount of acid in excess.

A concentrated solution of ammonia ( $d=0.880$ ) does not absorb the amount of hydrogen sulphide required to convert the whole of the ammonia into sulphhydrate,  $NH_4 \cdot SH$ , a solution saturated at air temperature taking up only about 75 per cent of that amount, and having a composition which may be represented by the formula  $(NH_4)_2S \cdot 2NH_4 \cdot SH$ . Less concentrated solutions of ammonia absorb a larger proportion of hydrogen sulphide, a mixture of one volume of ammonia solution ( $0.880$ ) with four volumes of water taking up sufficient to form a solution of the composition corresponding with the formula  $NH_4 \cdot SH$ , the strongest solution of this substance which is obtainable containing only about 16 per cent. The author infers, however, from the results obtained on passing hydrogen sulphide into various mixtures of water and ammonia solution cooled with ice water, that the solutions do not progressively take up more hydrogen sulphide as they become weaker, but that the amount absorbed is constant within certain well-defined limits, viz. :—

Ammonia sol.	:	Water.	Composition of sol.
3	:	1	$(NH_4)_2S, 4NH_4 \cdot SH$
2	:	1	$(NH_4)_2S, 8NH_4 \cdot SH$
1	:	1	$(NH_4)_2S, 8NH_4 \cdot SH$
1	:	2	$(NH_4)_2S, 18NH_4 \cdot SH$
1	:	3	$(NH_4)_2S, 18NH_4 \cdot SH$
1	:	4	$NH_4 \cdot SH$

The author attributes this remarkable behaviour to the actual formation of double sulphides, and states that he has obtained several such in crystals. Thus, by cooling, the solution having a composition corresponding with the formula  $(NH_4)_2S \cdot 2NH_4 \cdot SH$ , crystals of this composition were obtained; whereas a concentrated solution of ammonia, saturated at air temperature with hydrogen sulphide, then cooled to  $0^\circ$  and further saturated with the gas, gave highly hydrated crystals of the formula—



and a concentrated solution of ammonia, cooled to  $0^\circ$  and then saturated with hydrogen sulphide, gave well-defined crystals, the composition of which is represented by the formula  $(NH_4)_2S \cdot 18NH_4 \cdot SH$ .

What appears to be ammonium sulphhydrate,  $NH_4 \cdot SH$ , may be obtained in the solid state by passing the two gases into a vessel surrounded with ice, the hydrogen sulphide being maintained in slight excess; compounds of the type  $(NH_4)_2S \cdot xNH_4 \cdot SH$  are also formed if the ammonia be in excess.

By exercising great care in adjusting the volumes of the two gases and the rate of flow, operating at  $18^\circ$ , micaceous crystals are obtained, which, when rapidly dissolved in ice-cold water, yield a solution the composition of which sufficiently approximates to that required by the formula  $(NH_4)_2S$  to justify the conclusion that they consist of this compound; but if a large excess of ammonia passes through the bottle, a more volatile sulphide is ob-

tained in the form of an oil, which appears to be a compound of the formula  $(\text{NH}_4)_2\text{S}\cdot 2\text{NH}_3$ .

When an alcoholic solution of ammonia is saturated with hydrogen sulphide, crystalline compounds of the formula  $(\text{NH}_4)_2\text{S}\cdot x\text{NH}_4\cdot \text{SH}$ , containing alcohol of crystallisation, are obtained, the value of  $x$  depending on the concentration, as in the case of aqueous solutions.

The formation of definite polysulphides appears to be attended with considerable difficulty; "ammonium sulphide" solutions dissolve, at most, the amount of sulphur required to form a polysulphide of the formula  $(\text{NH}_4)_4\text{S}_9$ , and the author is inclined to regard the simpler polysulphides as secondary products resulting from the decomposition of this compound or of analogous lower compounds.

(To be continued.)

## CORRESPONDENCE.

### OZONE.

To the Editor of the Chemical News.

MONSIEUR,—Je suis français, et non italien. Déjà, lors de la publication de mes articles dans *l'Electrical Review*, le "Microbe phylloxera," s'était glissé dans un paragraphe que je traduisais de Fröhlich; on a justement critiqué l'expression; j'ai soigneusement fait la correction et malgré cela, le "Microbe phylloxera" a reparu dans la brochure. Ce n'est pas moi qui ai suggéré l'extermination du Phylloxera et la purification des Eaux d'égoût par l'ozone, c'est le Dr. Fröhlich.

Quant aux microbes inoffensifs qui se trouvent dans des endroits infectés par des microbes dangereux, si l'ozone les tue, ce n'est pas mafaute, c'était à eux de ne pas fréquenter mauvaise compagnie, et ils ont le soir des autres.

Agréez mes remerciements pour votre critique bien-vieillante.

E. ANDREOLI.

18, Somerleyton Road,  
12 Aout, 1893.

## BRITISH ASSOCIATION ANNOUNCEMENTS.

To the Editor of the Chemical News.

SIR,—Many of your readers will be interested to know that M. Moissan has kindly undertaken to arrange a demonstration of the properties of fluorine for a meeting of the Chemical Section of the British Association, at Nottingham, in September next.

We hope also to have at least two important discussions—one on Bacteriological Work, and the Chemical Problems connected with it; the other on Explosions in Coal Mines, with special reference to the Dust Theory. Professor Percy Frankland will open the former discussion and Professor Harold Dixon the latter.

It would be a considerable convenience to the Organising Committee if chemists, physicists, or biologists who wish to take part in the discussions and to contribute papers will be so good as to send an early intimation to the Secretaries, Burlington House.—I am, &c.,

J. EMERSON REYNOLDS.

University of Dublin, Trinity College,  
August 21, 1893.

Constitution of the Di-cyanides of Di-molecular Acids.—L. Bouveault.—The cyanides of di-molecular acids are substituted  $\beta$ -ketonic nitriles. If they present an analogous reaction they may be transformed into monoximes of triketones, the analogues of which are only found in the aromatic series.—*Bull. de la Soc. Chim. de Paris*, ix.-x., No. 14.

## 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. cxvii., No. 6, August 7, 1893.

Origin of Atmospheric Oxygen.—Dr. T. L. Phipson.—The substance of this paper has already been inserted as a communication from the author.

Isomorphism in the Anhydrous Alums.—T. Klobb.—The anhydrous alums, as well as the corresponding hydrated compounds, are isomorphous, and crystallise together in all proportions. Their crystalline form is that of a regular hexagonal prism. It is difficult to decide if this form is simply pseudo-hexagonal. These conclusions have been verified on the one hand for the oxides  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and on the other hand for  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}(\text{NH}_4)_2\text{O}$ .

*Bulletin de la Société Chimique de Paris.*

Series 3, Vols. ix. and x., No. 14.

Fixation of the Group =  $\text{CH}_2$  in Certain Amidic Derivatives.—A. Trillat.—It must be supposed from analogy that when formaldehyd acts upon an amidic substance, in which only a single hydrogen is free, two mols. of this substance enter into combination.

A New Series of Colouring Matters.—A. Trillat.—The author describes derivatives of rosaniline, of sulphorosaniline, chrysaniline,  $\beta$ -amidoalizarine, and the azo-derivatives.

Some Acetones Derived from Acrylic Acid.—Ch. Moureu.—The author has obtained and described phenylvinylacetone,  $\text{C}_6\text{H}_5\text{—CO—CH=CH}_2$ .

Soluble Gums.—Pietro Palladino.—The author has published a complete monograph of the gums of commerce with reference to their use in medicine, their falsifications, their constitution, and their origin. Tables are given which summarise their behaviour with iodine, oxalic acid, ammonium oxalate, ammonia ferric chloride, borax, albumen, nitric acid, ammonium molybdate, basic lead acetate, potassa, orceine, mercurous nitrate, stannous chloride, potassium silicate, tannic acid. To detect dextrine the author heats the sample to ebullition for a minute with aniline sulphate, chlorobrucine, pure brucine, orceine, or orceine. With these reagents gum, in an alkaline solution (KOH), gives a pale straw colour, which sometimes becomes a little greenish, whilst gums containing dextrine take a yellowish orange or a brownish red colour.

Preparation of Silver Monedate.—E. J. Maumené.—In this paper, which is not suitable for abstraction, the author gives silver formiate the name "silver monedate," whilst the oxalate is spoken of as monaedate.

The Chromosulphuric, Chromodisulphuric, and Chromotrisulphuric Acid and the Chromosulphates.—A. Recoura.—Already noticed.

Determination of the Fixed and Volatile Acids of Wines.—J. A. Müller.—This paper will be inserted at length.

Salts of Diamidophenol (Orthopara 1.2.4) and Triamidophenol 1.2.4.6.—A. Lumière and A. Seyewetz.—Not adapted for abstraction.

Phenylallylcarbinol.—H. Fournier.—The author finds that a procedure similar to that of Saytzeff may be generalised for the preparation of the secondary alcohols of the aromatic series.

Action of Zinc and Magnesium on Metallic Solutions and on the Determination of Potassa.—A. Villiers and F. Borg.—This paper will be inserted in full.

THE CHEMICAL NEWS.

VOL. LXVII., No. 1762.

ON THE  
ACTION OF IODINE ON SOME  
PHENOLS AND ALLIED COMPOUNDS IN  
PRESENCE OF FREE ALKALI, AND  
A NEW CLASS OF DERIVATIVES  
RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 89).

WHEN the red-violet precipitate is prepared in presence of lead a considerable proportion of the resulting precipitate remains insoluble on treatment with carbon disulphide and contains a large quantity of lead. A similarly insoluble portion is obtained frequently containing the metals iron and calcium if the solution in which the precipitation takes place contains a relatively large proportion of those metals in an available condition. One would be naturally inclined to the opinion that such metals existed in a state of true chemical combination, but from various experiments made in this direction I think that the combination is at most of a very loose molecular kind—of the metal oxide with the compound. All attempts to prepare a metal compound approaching saturation failed.

A quantity of such "lead compound" was treated as follows:—

Weight of crucible .. .. .	= 7.5225 grms.
" " + substance .. .. .	= 7.6203 "
Substance taken .. .. .	= 0.0978 "

The crucible with substance was then heated in a mercury bath to about 340° C. until the substance had almost lost its maroon colour, which colour is due to the "loosely-combined iodine" which I have already proved.

Weight of crucible + substance after heating ..	Grms. = 7.6176
" " " before .. .. .	= 7.6203
Iodine lost .. .. .	= 0.0027
	= 2.8 p.c.

Total iodine of original:—

Quantity taken .. .. .	= 0.0974 gm.
Silver iodide found = 0.1068 .. .. .	= 59.24 p.c. iodine.
∴ 56.44 is equal to the percentage of true substituted iodine (approx.).	

Combustion of the heated portion:—

Quantity taken .. .. .	= 0.0869 gm.
Water found .. .. .	= 0.0071 .. = 0.90 p.c. hydrogen.
Carbon dioxide found .. .. .	= 0.0488 .. = 15.31 p.c. carbon.
Ash (chiefly PbO with a trace of silica) .. .. .	= 13.35 p.c.

Attempted Reduction of the Alcohol-Ether-Chloroform Insoluble Portion of Red-Violet Precipitate Soluble in Carbon Disulphide.

In this case it was also treated with boiling chloroform prior to solution in carbon disulphide. The carbon disulphide solution was placed in a stoppered vessel, together with a quantity of a solution of caustic soda and treatment with sodium amalgam, carried on for a period extending over five days. The mixture quickly assumed a muddy appearance and lost its red colour. As the

reaction proceeded the magma became stiffer, the addition of water making little difference. The aqueous layer ultimately assumed a yellowish brown colour. The whole mixture was then thrown into a large volume of water and shaken up. The brown watery solution was filtered off and the operation repeated a number of times, a dark brownish watery solution being obtained each time, whilst a considerable volume of gas escaped after each shaking. The brown aqueous washings were acidified, when the brown colour disappeared, giving place to a yellowish milky fluid having a fetid penetrating odour. The milky-looking fluid was shaken up with ether, which extracted nearly all the visible substance; the ethereal solution was then shaken up with a solution of caustic potash, into which the substance passed. This operation was repeated a second time. During this transaction a black caoutchouc-looking substance fell out which contained mercury. The alkaline solution was evaporated, and a small quantity of needle-shaped crystals were obtained mixed with a quantity of a dark brownish non-crystalline substance, from which the crystals were separated and washed.

The crystals (a sulphur determination only could be made):—

Quantity taken .. .. .	= 0.0732 gm.
Barium sulphate found .. .. .	= 0.0536 .. = 10.06 p.c. sulphur.

This result furnishes the evidence required, since the percentage of sulphur found is sufficient to show that the compound could only contain one atom of sulphur to two benzene nuclei; thereby confirming the existence in the original of the di-phenol molecule, which has been assumed throughout the constitutional representations already given, largely on account of their analogy with the thymol compounds yet to be considered.

The blackish coloured insoluble mass which was filtered out from the brown aqueous solution was treated with ether, when a yellowish solution was obtained having a particularly fetid odour. The remainder was then treated with carbon disulphide, which dissolved out a considerable portion.

The Ethereal Solution.—This was shaken up with a weak solution of caustic potash, when a portion passed into the solution (alkaline), whilst another yellowish coloured portion separated out solid at the junction of the fluids, not soluble to any extent in one or the other. This was separated and washed. When washed and dried it was of a yellowish white appearance and brittle; it did not melt, and was quite odourless.

Total iodine of this insoluble portion:—

Quantity taken .. .. .	= 0.0961 gm.
Silver iodide found .. .. .	= 0.1011 .. = 56.84 p.c. iodine.

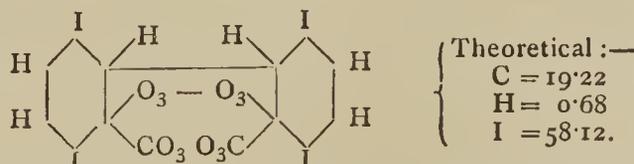
Combustion of same:—

Quantity taken .. .. .	= 0.1218 gm.
Water found .. .. .	= 0.0116 .. = 1.05 p.c. hydrogen.
Carbon dioxide found .. .. .	= 0.0830 .. = 18.58 p.c. carbon.
Ash .. .. .	= 3.40 p.c.
No sulphur.	

Allowing for ash we would have per cent:—

$$C = 19.19, H = 1.10, I = 58.71, O = 21.00,$$

which may be represented by the formula  $C_{14}H_6I_4O_{12}$ , and admitting this to be true might be represented constitutionally thus:—



This would, indeed, appear to be a somewhat startling product to be taken from a reduction mixture, but it must

be remembered that the carbon disulphide had also entered into the reaction. However as this may be, I have no reason to doubt the analyses, and, indeed, the iodine percentage was controlled by a check experiment, but as further confirmatory work outlay the line of this research I merely give the data.

The portion dissolved out by the carbon disulphide when recovered was of a whitish colour and brittle scaly character.

Total iodine of this portion :—

Quantity taken = 0.1644 grm.

Silver iodide found = 0.2217 „ = 73.47 p.c. iodine.

Combustion of same :—

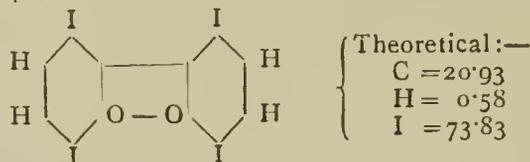
Quantity taken = 0.1184 grm.

Water found = 0.0098 „ = 0.92 p.c. hydrogen.

Carbon dioxide found = 0.0921 „ = 21.21 p.c. carbon.

By difference .. .. = 4.4 p.c. oxygen.

Those results may be represented by the formula  $C_{12}H_4I_4O_2$ , and constitutionally thus—



(To be continued).

### NEW METHOD FOR THE PRODUCTION OF SODIUM AND POTASSIUM FERROCYANIDE.

By H. N. WARREN, Research Analyst.

THE alloy now known as zinc-eisen, and which at the present time is largely used in pyrotechny, the which has already been briefly described by the author in subsequent pages of this journal, will be remembered is produced by the action of ferrous chloride upon metallic zinc; giving rise to a brittle regulus of zinc, containing up to 15 or 20 per cent of iron. The same compound, in return, is now being experimented with as a reducing agent for the sulphocyanides.

The potassium or sodium salt, as the case may be, is procured by the action of ammonia upon carbon disulphide dissolved in petroleum. If this mixture is kept below  $212^{\circ}$  F., there is produced ammonium sulphocarbamate, which, if briskly boiled for a short time, is resolved into ammonium sulphocyanate; this being afterwards converted into its equivalent of either potassium or sodium salts by the introduction of either of those bases; the ammonia thus evolved being collected in the usual manner and employed in a further operation.

If the calcined sodium or potassium salt thus prepared is intimately mixed with an equivalent proportion of the zinc alloy and heated to redness, the sulphur present is gradually absorbed by the zinc, whilst the iron remains for the production of the ferrocyanide. The mass thus obtained is lixiviated and evaporated; the ferrocyanide crystallising out as the liquid cools, which may be further purified by re-crystallisation.

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18, Albion Street, Everton, Liverpool.

**Crystalline Basic Copper Seleniate and an Analogous Salt of Cobalt.**—M. Bogdan.—The salt in question has the composition  $2SeO_3, 3CuO, 4H_2O$ . It forms very small crystals insoluble in water and freely soluble in air. At  $250^{\circ}$  they are decomposed, losing water and selenium, which forms a reddish deposit on the cold parts of the tube. The cobalt salt has the composition  $3SeO_3, 4CoO, 11H_2O$ . It forms red acicular crystals, which, if heated, behave like the corresponding salt of copper.—*Bull. de la Soc. Chim. de Paris*, ix.-x., No. 14.

### ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 82).

I UTILISED this fact in order, even before the completion of the above-named new apparatus (see *ante*), to procure a more certain basis for the measurement of the absorption of the more refrangible rays in the air than was afforded by the former observations. To this end I executed some proofs with the quartz apparatus, in which the sparks and the photographic plate were distant from each other, not 10, but 17 metres. The light was conducted directly into the apparatus. Two quartz lenses placed at the focal distance of the rays arriving at the plate in front of the slit and the sparks co-axially with the collimator, collected these rays in the aperture of the slit of the collimator. After fifteen minutes' exposure all the zinc lines appeared, contrary to expectation, although very thin and devoid of expression, which, however, was this time unimportant. The important part of the result was the fact that the atmospheric air, as tested by brom-silver gelatin, is far more pervious to light than might have been expected according to Cornu. In addition, the thickness of the stratum of air employed by no means corresponded to the limit of transparency. According to my firm conviction a much thicker stratum of air would have led to the same result. How did my assumption of the influence of the air upon the photographic efficacy of the most refrangible rays agree with this result? Little as I could bring them in harmony, the cadmium phenomena furnished ground enough to uphold them unaltered. That the numerical values which Cornu has given for the aerial absorption could no longer serve as a basis after they had been found doubtfully trustworthy in my photographs of the zinc spectrum need not surprise us. Cornu's statements are founded on the behaviour of the wet collodion plate, whilst my proofs were taken only with the gelatin plate. The sensitiveness of both plates is fundamentally different, and in that part of the spectrum which exclusively concerns us it is totally unknown. How the sensitiveness of both plates may vary in the ultra-violet we have hitherto no observations to show.

I next proceeded to take the spectrum of aluminium. The first experiments were fruitless. Not until I had enlarged the slit to the unusual extent of  $1\frac{1}{2}$  m.m. and had exposed for twenty minutes did I succeed for the first time in recognising on the fixed plate at least traces of the line No. 30 and the less refrangible components of the double line No. 31. The image of lines was certainly so faint that under ordinary circumstances it was visible neither by transmitted nor by reflected light. To perceive it distinctly especial precautions are required. In the same manner I subsequently obtained, after an exposure of forty-five minutes, the remaining aluminium lines. Thus I had arrived at the region of the smallest wave-lengths, but had by no means attained my purpose. My proofs certainly supplied evidence that the most refrangible aluminium rays after traversing a stratum of air of 2 metres in thickness could still exert upon silver-bromide gelatin an impression capable of development; but an application of such proofs in spectroscopy, at which I was aiming, was not to be thought of. The clearness of the lines was insufficient.

An attempt to obtain better results by elevating the energy of the rays failed completely. What I effected with an induction apparatus of unusual size, constructed by Keiser and Schmidt, of Berlin (length of sparks 50

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., Apr. 1, 1893).

c.m.), expressly for these proofs, demonstrated merely that the object could not be approached in this direction.

More for the sake of completeness than with a hope of success I executed an aluminium proof with the above-mentioned grating apparatus. I never obtained even a trace of a line. The grating was well suited for taking the zinc lines, but with the aluminium lines of the shortest wave-length it failed entirely.

Nothing remained but to take a photograph with a thicker air stratum. After I had studied the behaviour of my plate in the aluminium light under normal conditions, the thickening of the stratum of air seemed a more suitable expedient for the direct demonstration of the influence of the air upon the photographic efficacy of the most refrangible rays than previously. I employed for this purpose the same experimental arrangement which I had used in taking the zinc spectrum. The track of the rays in the air up to the photographic plate measured consequently again 17 mètres.

Not a single exposure now left an impression upon the plate, not even when I exposed for an hour and a half with very energetic sparks. The thickening of the stratum of air had therefore caused all the light-rays, which in the former case had left an impression, to become enfeebled on their passage to the plate to complete inefficiency. Thus I had at last obtained experimentally the confirmation of my supposition on the aerial resistance in the most refrangible ultra-violet, and at the same time the certainty that if with the resources of the present day a further advance is feasible, this can be effected only after sufficient diminution of the resistance of the air. No apparatus in my possession could be adapted to this condition. The continuance of the experiment was therefore effected chiefly with newly-acquired instruments, mentioned under "Cadmium," the arrangement of which had been brought into accord with the experience collected in photographing the most refrangible rays.

(To be continued.)

## ON THE DETERMINATION OF VANADIC ACID.\*

(Continued from p. 90).

IN the analysis of the vanadio-tungstates the author proceeded as follows in accordance with the results of the above investigations.

The determination of the vanadic acid was effected by the process last mentioned. The very dilute solution of the salt was strongly acidified with phosphoric and sulphuric acid, the vanadic acid was reduced with sulphurous acid, the excess of the latter expelled by boiling in a current of carbonic acid, and the vanadic acid then determined by titration with permanganate, observing the prescribed precautions.

The tungstic acid was determined indirectly, the author finding the joint weight of vanadic and tungstic acid, and then determining the latter as difference.

The vanadic and tungstic acid were precipitated with mercuric nitrate in a moderately dilute solution, as neutral as possible, and the liquid was then mixed with a few drops of ammonia until the reaction was distinctly alkaline. The precipitate was filtered off and washed with a very dilute solution of mercurous nitrate. After acidulation with sulphuric acid, the excess of mercury was precipitated by sulphuretted hydrogen, or by the mere addition of hydrochloric acid, and the precipitate was filtered off. The two mercurial precipitates were dried, and after the most careful combustion of the filters ignited in a porcelain crucible (first gently and then very strongly), and weighed. Before the check weighings the precipitate is

again ignited in an atmosphere of ammonium nitrate in order to oxidise any vanadyl which may have been formed. Both precipitates were ignited together, because it was found that in the first precipitation the acids were not entirely separated, and that in general a portion is precipitated along with the mercury sulphide or chloride.

Occasionally a little vanadic acid has been still detected in the filtrate of the second mercurial precipitation. Such traces were then determined by titration with permanganate.

The author proceeded in the manner described in the analysis of the alkali and the barium salts of the vanadio-tungstic acid. For the determination of the barium a solution of potassium sulphate was added to the boiling solution of the salts in order to precipitate the barium sulphate. An addition of sulphuric acid would cause a separation of tungstic acid. Silver-vanadio-tungstate was melted with sodium-potassium carbonate for the determination of the vanadic acid, and the titration of the vanadic acid was undertaken in the usual manner in the aqueous solution of the melt. For determining the sum of both acids the salt was entered in a boiling solution of sodium nitrate, with which it is transformed into silver nitrate and sodium-vanadio-tungstate. The silver was then precipitated by a calculated quantity of solution of sodium chloride, and the sum of both acids was determined in the filtrate in the manner described above.

C. Friedheim (*Berichte Deutsch. Chem. Gesellschaft*, xxiii., p. 353) considers the determination of vanadic acid along with tungstic acid, by titration with permanganate, uncertain, as the recognition of the final reaction is attended with too great difficulties. He recommends the following method for the direct determination of both acids.

To the concentrated solution of the alkaline vanadio-tungstate he adds, in a roomy porcelain capsule placed upon a boiling water-bath, a concentrated solution of mercurous nitrate as neutral as possible, until the precipitate settles readily, and digests then with an excess of freshly-precipitated mercuric oxide for about twenty minutes, in order to neutralise the free acid. When the solution is cold, the precipitate—a mixture of the mercury salts of both acids with an excess of mercuric oxide—is filtered through a plain filter, washed with water (to which a few drops of mercurous nitrate have been added), which is effected in a short time, as the precipitate filters very readily. It is then rinsed back from the filter into the capsule, and the liquid is evaporated to the consistence of a paste. When cold it is treated, with careful stirring, with an excess of the most concentrated hydrochloric acid, covered with a watch-glass, and heated for five minutes on the boiling water-bath. Thus all the vanadium (as vanadyl chloride), almost all the tungstic acid, and the main quantity of the mercury pass into solution, as the bulk of the mercurous chloride passes into mercuric chloride in consequence of the generation of chlorine due to the action of hydrochloric acid upon the vanadic acid. To the blue solution obtained there is now added much water, by which the dissolved tungstic acid is precipitated almost quantitatively, whilst vanadium and mercury remain in solution. This solubility of the freshly-precipitated mercurous tungstate in fuming hydrochloric acid depends probably on the circumstance that, in contact with hydrochloric acid, tungstic acid behaves like a base. The author has not completed his examination of such solutions. If recently precipitated tungstic hydrate is boiled with fuming hydrochloric acid, it is likewise partially dissolved and can be re-precipitated by water. In the analysis of tungstates we must avoid mixing the acid when once separated with much hydrochloric acid, as it is often done to prevent it from running through the filter. The solution is preferably acidified with dilute sulphuric acid. The remnant of the precipitate left upon the filter is dissolved in hot sulphuric acid of sp. gr. 1.12, and the solution transferred to the capsule. After standing for twenty-four hours,

\* *Zeitschrift für Analytische Chemie.*

during which time a little more tungstic acid is deposited, the precipitate is filtered off, washed with water, very faintly acidulated with hydrochloric acid, the residue adhering to the capsule is brought into a weighed porcelain crucible by means of a little ammonia, the contents of the crucible are evaporated to dryness; the filter, whilst still moist—if previously dried it is readily corroded—is placed in the crucible, dried in the air-bath at 120°, and ignited under the draught-hood, when pure yellow tungstic acid is obtained.

From the filtrate, after heating to 80°, the mercury is precipitated as sulphide by the prolonged introduction of sulphuretted hydrogen until the precipitate is completely deposited; the filtrate, containing vanadyl chloride, is evaporated to dryness on the water-bath, oxidised with concentrated nitric acid on the water-bath whilst covered with a watch-glass, again evaporated—repeating the operation at least twice,—and the brown hydrated vanadic acid is dissolved in water with the addition of a few drops of nitric acid.

(To be continued).

## NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.\*

By Lieut.-General C. A. McMAHON, F.G.S.

(Concluded from p. 93).

### Chromium.

1. For the following test the chromium salt should be converted into an alkaline chromate by ignition with potassium nitrate and an alkaline carbonate. Dissolve the resulting chromate in water, and then neutralise the alkaline solution with acetic acid. Add a drop or two of a solution of nitrate of silver. The liquid turns blood-red. On spontaneous evaporation microscopic crystals of chromate of silver are deposited ( $\text{Ag}_2\text{CrO}_4$ ). Sometimes these crystals are in very minute and short rods, and remind one of a clotted mass of some species of microbe; at other times they are of larger size and more irregular shape. They are then seen to be of blood-red colour in transmitted light, and to be transparent or translucent. In any case they require a  $\frac{1}{2}$  inch objective and the second eye-piece. As the chromate of silver is insoluble in water, all trace of the chromate of potash can be removed by washing. The residue dissolves readily on the addition of a few drops of ammonia to the slide, and on evaporation thin, branching, moss- or lichen-like clumps and tufts of  $\text{Ag}_2\text{CrO}_4 + 4\text{NH}_3$  are deposited. These tufts are opaque to translucent, the latter being of blood-red colour in transmitted light. Powerful absorption with a single nicol (blood-red to nearly black), but between crossed nicols the double refraction is so feeble as to be nearly *nil*. In reflected light the crystals have a brilliant metallic lustre. These crystals are said (Haushofer, quoted by Klement and Renard, p. 44) to occur in elongated rhombic plates, but I have not obtained any that exhibit a definite crystallographic form.

2. To the dichromate add a drop or two of barium chloride. On evaporation the chromate of barium ( $\text{BaCrO}_4$ ) will be found on the slide. This is insoluble in water, and is of yellowish-white colour and of granular texture. If the solution was strong the deposit will be opaque and dotted over with the cubic crystals of potassium chloride. If very dilute the barium chromate commonly yields skeleton crystals in the form of four-armed crosses. The arms of these crosses are varied and irregular in shape, but they all more or less resemble the fronds of a fern with transverse lobes. They require 1.5th inch objective, and have only a feeble action on polarised light.

\* *Mineralogical Magazine*, vol. x., No. 46, p. 79.

### Cæsium (Cs).

Stannic chloride\* gives with  $\text{Cs}_2\text{SO}_4$  (orthorhombic system) a multitude of micro-crystals belonging to the cubic system (principally octahedrons) and star-shaped skeleton crystals, shaped like negative ice crystals, but consisting usually of three (occasionally four) rays.

Cæsium chloride gives with the above reagent small octahedrons and colourless crystals of the cubic system. The latter usually predominate. Cæsium chloride itself crystallises in the cubic system ( $\text{Cs}_2\text{SO}_4$  is therefore to be preferred), but its habit is different from  $\text{Cs}_2\text{SnCl}_6$ . I have always found cæsium chloride crystallise in cubes like common salt.

The bichloride of platinum gives with the salts of  $\text{NH}_3$ , K, Cs, and Rb crystals similar in shape to those of  $\text{Cs}_2\text{SnCl}_6$ .

### Iron (Fe).

The ferro- and ferri-cyanides of potassium give such delicate and characteristic reactions that hardly any other tests are required to detect the presence of iron. Basic sulphates, about which little seems to be known from a microscopic point of view, are numerous, and they form on the application of heat or on a solution being allowed to oxidise in the air; and this renders the determination of iron with the aid of the microscope very difficult. Of microscopic tests the following may be mentioned:—

1. With oxalic acid, ferrous sulphate gives greenish-yellow crystals of ferrous oxalate ( $\text{FeC}_2\text{O}_4 + 2\text{H}_2\text{O}$ , solution 1 in 3800). They are of microscopic size, belong to the orthorhombic system, and have their major axis of elasticity at right angles to *e*. They are ordinarily rectangular in shape, but are sometimes prisms with six sides terminated by domes. They polarise rather brilliantly.

2. With ferrous sulphate, ammonia throws down a whitish precipitate, which at first turns green and ultimately a dull red colour. When dried on the glass slide it closely resembles a drop of dull red sealing-wax on which a plain seal has been impressed. It is only translucent here and there, being in transmitted light of bright orange-red colour. With ferric sulphate, ammonia throws down at once a foxy-red precipitate, which forms on evaporation an amorphous translucent glass of much brighter red than that formed by  $\text{FeSO}_4$ .

3. When ferric sulphate is dissolved in boiling water several salts seem to be formed. When allowed to evaporate on glass slides my specimens contained (a) needle-like prisms in groups radiating from an opaque amorphous centre—these seem to be No. 34, Part II.; (b) hexagonal scaly plates of micaceous habit—these seem to agree with No. 39, Part II.; and (c) spherulite rounded disks composed of radiating platy crystals resembling two open fans arranged so as to form a circle. They polarise brilliantly, and show radiating stripes of colour. Major axis  $\parallel$  to axis of quartz wedge. It is difficult to say whether these disks are No. 34 or No. 39 of Part II., or some other basic salt.

4. The ferrous sodium double salt (Part II., No. 41) on first crystallising forms an isotropic structureless glass. After standing for some little time it parts with some of its water and passes into the crystalline condition, forming masses of long prisms radiating from different centres, which polarise brilliantly. After further exposure to the air, and further loss of water, the salt gradually becomes a white opaque mass. This process, which is attended with loss of weight, takes place in a somewhat capricious manner, drops from the same solution evaporated side by side, behaving differently. Some take a short cut to the white opaque stage at once; others take as much as from six to ten days to accomplish it. The process may be stopped by mounting in Canada balsam.

5. The ferrous and the ferric sulphates treated with ammonium fluoride yield numerous small octahedra, cubes

\*  $\text{SnCl}_4 + 3\text{H}_2\text{O}$  (in needles);  $\text{SnCl}_4 + 5\text{H}_2\text{O}$  (opaque acute prisms);  $\text{SnCl}_4 + 8\text{H}_2\text{O}$  (large transparent crystals). These hydrates all crystallise in the monoclinic system.

and other forms of the cubic system, the octahedra being by far the most numerous. Interesting cases of penetration twinning frequently occur.

#### Potassium (K).

A very delicate test is the reaction with the bichloride of platinum ( $\text{PtCl}_4$ ). It is absolutely indispensable that this reagent should be pure, and that its purity should be tested by evaporation on a glass slide and microscopic examination before it is used. The bichloride commonly sold contains potash, and yields crystals of chloroplatinate of potash, described below. The pure bichloride (that is to say, the purest I have been able to obtain) crystallises in long slender prisms like blades of grass. Extinction takes place nearly parallel to the length of the blade. Major axis parallel to  $e$ . The blades polarise brilliantly, usually in the blue and pink of 2nd order. The reagent must not be kept in glass bottles. I use a gutta-percha one. If a drop or two of this reagent be added to a few drops of the sulphate of potassium (or to a neutral or feebly acid solution of any other K-salt) yellow crystals of chloroplatinate of potash ( $\text{K}_2\text{PtCl}_6$ , solution 1 in 100) are formed. These are either octahedrons or combinations of the octahedron and dodecahedron, or some other form of the cubic system. The complex forms, however, almost always exhibit a six-sided face (a triangle with the corners cut off) of deep orange-yellow colour; the other faces of the crystal at various angles to the plane of the glass slide, owing to the high refraction of the mineral, remain dark in transmitted light. Sometimes skeleton crystals in trefoil form, or with four arms arranged as a cross, are formed.

An excess of free  $\text{H}_2\text{SO}_4$  is unfavourable to this reaction.

The salts of ammonium, caesium, and rubidium give, with the bichloride of platinum, crystals belonging to the cubic system similar in shape to those of  $\text{K}_2\text{PtCl}_6$ .

#### Lithium.

1. Phosphate of soda produces a precipitate of phosphate of lithium,  $\text{Li}_3\text{PO}_4 + \text{H}_2\text{O}$  (solution 1 in 2500), which forms in dagger-shaped crystals (two short transverse arms representing the hilt), or in star-shaped crystals composed of four or five rays. These crystals are interspersed among numerous globulites, which give a dark cross between crossed nicols. Most of these globulites are divided into approximately two halves; and when resolved between crossed nicols, in parallel light, the cross opens up into two hyperbolic branches like axial sections of some biaxial crystals in converging polarised light. The curvature is greatest when the axis of the hyperbola is at right angles to the dividing line. In elongated individuals the result between crossed nicols is an elongated cross with two transverse arms, one on either side of the dividing line. These elongated twins are very suggestive of the multiplication of organic cells by fission. Indeed the resemblance is so close that one may readily obtain on the same slide illustrations of this supposed fission at every stage. The optical phenomena noted above are very curious, but, pending the completion of some investigations which I am carrying on, I think it better to postpone any attempt to explain them.

The crystals of lithium phosphate possess strong refraction, which shows itself in the dark boundaries of the globulites and in the strongly wrinkled surface of the crystals. The latter have straight extinction. The addition of acetic acid increases the number of globulites.

2. With the reagents mentioned below (see Magnesium, No. 2) crystals isomorphous with those of struvite are obtained. They also exhibit similar optical properties. A little warmth assists the reaction, and the phosphate of soda should be added in crystalline form. Manganese salts also yield similar results with these reagents.

#### Magnesium.

1. With ammonia the sulphate yields a gelatinous pre-

cipitate which on spontaneous evaporation forms a colourless mass with a silky gloss on it. This is the monoclinic double salt  $\text{MgSO}_4(\text{NH}_4)_2\text{SO}_4 + 6\text{H}_2\text{O}$  (see Part II.). Prepared on a glass slide this salt usually appears in crystals arranged like the shaft and web of a bird's feather. Mounting in Canada balsam appears to decompose the double salt. In every instance in which I have tried the experiment the monoclinic crystals of the double salt have broken up into needle-shaped orthorhombic prisms, presenting the appearance and optical properties of  $\text{MgSO}_4 + 7\text{H}_2\text{O}$ .

2. Add a little ammonium chloride (cubic) to a dilute solution of  $\text{MgSO}_4$  (orthorhombic) in water. Place a few drops of this mixture on a glass slide. Place a drop of an aqueous solution of sodium phosphate (monoclinic) on the slide near it, and to the latter add one or two drops of ammonia. Then join the two drops. On evaporation struvite crystals will be found on the glass slide. As hemimorphism is common the shapes of the crystals are varied. The struvite crystals,  $\text{Mg}(\text{NH}_4)\text{PO}_4 + 6\text{H}_2\text{O}$  (solution 1 in 15,000), belong to the orthorhombic system. They polarise brilliantly in the colours of the 1st and 2nd order. Major axis  $R.L.$  to  $e$ .

Most writers recommend the gentle warming of the drops prior to mixing, but I have not found it necessary. Behrens adds the phosphate of soda solid. This may be useful in some cases. The reaction requires a little practice.

Crystals similar in shape and optical properties are also produced by the action of the above reagents on the sulphates of lithium and manganese.

3. On adding some drops of the aqueous solution of potassium antimonate to the aqueous solution of  $\text{MgSO}_4$  (the proportion of the latter to the antimonate should not be too great), numerous microscopic crystals of the acid pyro-antimonate of magnesia ( $\text{MgH}_2\text{Sb}_2\text{O}_7 + 9\text{H}_2\text{O}$ ) are formed on the slide. These occur, for the most part, in six-sided disks lying on their basal planes, but also, not unfrequently, on one of the sides of the hexagonal prism. They also occur in cube-like prisms (sometimes slightly elongated in one direction), and in the form of little flowers, like primroses, with four (occasionally five) uniform petals. The hexagonal disks sometimes pass into globulites, and the latter are doubtless the immature form of the former. Penetration twins are not uncommon, and their forms are very varied. Double refraction is not strong, and sometimes it is *nil*. Fock refers the crystals of pyro-antimonate of magnesia to the hexagonal system.

#### Manganese.

The blowpipe and ordinary chemical tests are the most reliable for the detection of manganese.

1. Manganous sulphate (or other manganous neutral or feebly acid salt) treated with oxalic acid yields crystals of oxalate of manganese ( $\text{MnC}_2\text{O}_4 + 3\text{H}_2\text{O}$ ) in radiating groups of elongated prisms with straight extinction; but as oxalic itself forms similar prisms, and groups of prisms with straight extinction,\* this reaction is not recommended.

2. Ammonia produces a white precipitate, which on exposure to the air becomes of dark brown colour (chloride of ammonium prevents this precipitation). On allowing this to evaporate spontaneously on a glass slide, the crust formed is partly transparent and partly opaque. Under the microscope in transmitted light the crust becomes a very beautiful object, and is seen to be made up of fern-like fronds arranged in groups on a rich yellow-brown background. The transparent portions (sometimes the fronds are transparent, sometimes opaque) extinguish in a direction oblique to the stems of the fern-like forms.

3. With phosphate of soda  $\text{MnSO}_4$  gives the same results as  $\text{Li}_2\text{SO}$  and  $\text{MgSO}_4$ . For details see Mg, Part III., No. 2.

\* Oxalic acid is said to crystallise in the monoclinic system, but the prisms obtained on a glass slide have straight extinction. Double refraction very high. Major axis  $\parallel$  to  $e$ .

*Sodium (Na).*

The blowpipe and flame reactions are principally to be relied on for the detection of soda. Szabo's well-known method is a most useful one. The following is the process for microscopic testing which I follow. It is a good, but a somewhat troublesome, method.

1. Reduce the mineral to a fine powder in an agate mortar; ignite in platinum crucible; re-grind in mortar; ignite; add hydrofluoric acid and stir; heat gently for some time in platinum dish or crucible (agitating the liquid from time to time and adding more HF aq. if necessary) until the powder, or as much of it as is soluble in HF aq., is dissolved; cool, add water, and then heat again. This operation converts the soda and silica present into sodium fluo-silicate ( $\text{Na}_2\text{SiF}_6$ ). Should the mineral operated on not contain silica, pure silica must be added. A glass slide must now be prepared by giving the central portion of it a thin coating of hardened Canada balsam. A few drops of the liquid are then removed by means of a platinum spoon (all the platinum employed must be pure from all surface trace of soda), and transferred to the prepared glass slide. If the liquid does not completely evaporate in forty-eight hours, the surplus can be removed by bringing a strip of filter-paper into contact with the outer edge of the drop. When this has been done the crystals left on the slide can be mounted in the usual way.

The most characteristic crystals of sodium fluo-silicate are six-sided prisms; sometimes short and terminated with rather flat pyramids (in which case they much resemble micro-crystals of quartz); sometimes comparatively long and terminated at both ends by flat basal planes. Penetration twins are not uncommon, and other forms also occur. Before mounting, the crystals sometimes lie with the apex of the flat terminal pyramid turned towards the eye of the observer. In the process of mounting they get turned over on their sides. Straight extinction. Major axis parallel to length of prism. Double refraction—white of the 1st order.

Crystals of fluo-silicate of soda are isomorphous with those of the fluo-titanate of soda.

*Rubidium.*

1. The reaction of the salts of rubidium with platinum bichloride is the same as that of the salts of potassium, caesium, and ammonium. See Potassium.

2. For reaction with fluoride of titanium see Titanium, No. 2, Part III.

*Silica.*

The reaction for silica is the same as that for sodium (see *ante*). If the mineral to be tested does not contain soda, some soda must be added. Crystals of fluo-silicate of soda are isomorphous with those of fluo-titanate of soda.

*Strontium.*

Strontium sulphate dissolves in hot concentrated  $\text{H}_2\text{SO}_4$  like  $\text{BaSO}_4$  (see *ante*). On cooling, embryo crystals are deposited, the lowest form of which is the micro-globulite. More advanced forms present themselves in the shape of disks, oval crystals, and acicular prisms (often forked), which sometimes arrange themselves in rosettes. The prisms and almond-shaped bodies occasionally develop radiating tufts at one or both ends. The most developed is the arrangement of almond-shaped bodies in the form of a short cross with oval arms, which gradually grows, by the filling up of the re-entering angles, into a four-sided tabular crystal. Not unfrequently we get either a combination of lenticular crystals or two disks at right angles to each other. The suppression of one half of one of the disks produces a hat-like form, which is not uncommon. In all these crystals the unit is clearly a globulite. Even the most advanced forms (the four-sided tabular crystals) may sometimes be distinctly seen to be built up of globulites.

The double refraction is feeble, showing only the grey-

white of the 1st order. Major axis parallel to  $e$  in oval disks. Straight extinction, viz., parallel to  $e$  in oval disks. In the cross-like forms extinction is parallel and at  $R.L.$  to each arm. The more gradual the cooling the more the cross-like forms abound. After mounting in balsam I have obtained comparatively large crystals of celestine (orthorhombic).

Klement and Renard state on the authority of Haushofer that a mixture of equal parts of the sulphates of Sr and Ba dissolved in hot concentrated  $\text{H}_2\text{SO}_4$  gives on cooling crystals in the form of  $\text{SrSO}_4$  only. Behrens says the same. My experiments do not confirm this. I have under the above circumstances obtained typical crystals of  $\text{BaSO}_4$ .

*Titanium.*

1. Titanium dioxide dissolved in hydrofluoric acid\* gives with the salts of potassium monoclinic crystals of fluotitanate of potassium ( $\text{K}_2\text{TiF}_6 + \text{H}_2\text{O}$ ) in rectangular crystals, rhombs, and elongated six-sided prisms. The truncation of the corners of the former give six- and eight-sided outlines. Polarisation feeble. The best results are obtained by placing a crystal of the K-salt in contact with the acid solution. Crystals of fluoride of potassium cannot be mistaken for those of the fluotitanate, as the extinction of the former is straight and the latter decidedly oblique.

2. Strong solutions of rubidium chloride (cubic) and caesium chloride (cubic) both give similar reactions.

3. The fluotitanate of sodium,  $\text{Na}_2\text{TiF}_6$  (obtained by melting the substance to be analysed in a bead of sodium fluoride, treating with cold water first, and afterwards with hydrofluoric acid, and crystallising on a glass slide), is isomorphous with sodium fluosilicate (see Sodium, *ante*). This reaction, therefore, is of no use when silica is present.

*Zirconium.*

1. Two or three drops of an aqueous solution of potassium binocalate added to a solution of zirconium sulphate on a glass slide yield, on evaporation, crystals probably tetragonal (Behrens); they are in: (a) rectangular and six-sided prisms, principally the former, lying apparently on their basal plane with the apex of a pyramid turned towards the eye of the observer; (b) crystals showing a six-sided face parallel to the plane of the glass slide and bounded by faces that remain black in transmitted light. (a) Remain dark between crossed nicols; (b) the central portion polarises and exhibits a limpid gentian blue of very beautiful tone; at the margin of the drop, where the crystals are massive, the blue passes through violet into red. None of the above crystals will bear mounting in Canada balsam.

2. Zircon (and other varieties of the silicate of zirconium) is decomposed by fusion† with about five times its weight of pure anhydrous sodium carbonate. A little hydrous sodium carbonate (pure) should be added when fusion is nearly complete. After fusion treat the mass with cold water for the removal of soluble silica; dissolve the insoluble residue with hydrochloric acid; evaporate to dryness; dissolve in water acidulated with hydrochloric acid; the solution contains nearly pure zirconium chloride. Oxalic acid throws down zirconium oxalate. The crystals I have obtained in this way appear, like those described under No. 1, to belong to the tetragonal system. They present rectangular outlines with pyramids pointing to the eye of the observer truncated by a plane, the outline of which is a rhomb, the diagonals of which bisect the faces of the rectangle. Two of the edges of the pyramids are sometimes truncated towards their apex by planes which are apparently the pyramids of the 2nd order, and these planes also truncate the acute angles of

\* When HF aq., or a fluoride, is evaporated on a glass slide, the glass must be protected by a thin coat of hardened Canada balsam, as otherwise Ca, K, and other bases would be extracted from the glass.

† Behrens recommends fusion with sodium fluoride and evaporating down with sulphuric acid.

the rhomb producing a six-sided outline. The rhomb alluded to polarises in the whitish yellow of the 1st order. Major axis parallel to a line bisecting the acute angles of the terminal rhomb. Extinction parallel to the sides of the rectangle.

THE SPECIFIC HEATS OF THE METALS.\*

By JOS. W. RICHARDS, Ph.D.,  
Instructor in Metallurgy, &c., in Lehigh University.

(Concluded from p. 94.)

Platinum.

DR. IRVINE found 0.03, and Dulong and Petit 0.0314 by the method of cooling.

Dulong and Petit found 0.0335 (0—100°) and 0.0355 (0—300°), which lead to the formula—

$$Sm = 0.0325 + 0.00001 t.$$

Pouillet made a careful study of platinum in 1836, using the air thermometer up to 1200°. The data which he gives lead to the formulæ—

$$Sm = 0.03308 + 0.0000042 t$$

$$S = 0.03308 + 0.0000084 t.$$

Regnault found 0.03243 (12—99°).

Byström obtained rather anomalous results. He found that up to 250° the rate of increase was uniform, according to the formulæ—

$$S = 0.032386 + 0.0000094 t + 0.00000183 t^2$$

$$Sm = 0.032386 + 0.0000047 t + 0.000000627 t^2$$

Above 250° Byström observed a very sudden rise, which no other observer has noted. The formula would give the true specific heat at 300°, 0.034360, while Byström records 0.034750, a sudden rise of 1.2 per cent above the curve which fits all his lower results.

Kopp obtained results varying from 0.0316 to 0.335 (15—60°), so that his observations are of no interest in comparisons of accurate data.

Weinhold also investigated platinum, but his results vary so greatly among themselves as to be worthless.

Violle has made a most careful study of platinum up to 1200°. He remarks that Pouillet's observations were in error chiefly because he used a platinum bulb for his air thermometer, which gives erroneous results because of transference of gases through the platinum at high temperatures. Violle used a porcelain bulb, and all the precautions possible to take in such experiments. Since these determinations and formulæ are so greatly relied on in using platinum as a pyrometer, I have considered it important that Violle's results should be thoroughly understood. The diagram of Violle's results shows the particular values found by him for the mean specific heat to zero, and their proximity to the line which he chooses as best representing his results. The greatest difference between his experiments was about 1.1 per cent at any given temperature, the greatest deviation from the assumed mean line 0.8 per cent.

$$Sm = 0.0317 + 0.000006 t.$$

Violle found by direct experiment  $Sm$  (0—100°) 0.0323, which would become 0.0324 for Regnault's range of temperatures, results practically identical. We must regard Violle's results as being altogether the best we possess for platinum.

*Latent Heat of Fusion.*—Violle made five determinations of the heat in solid platinum as near to its melting-point as possible, the mean value obtained being 75.21 calories to zero. (By the formula this would indicate a maximum point of fusion of 1775°). Four experiments were made on the heat in molten metal at its setting-point, the mean value obtained being 102.39 calories to

0°. From these data the latent heat of fusion is 27.18 calories.

Potassium.

Regnault found 0.1660 between -78° and +10°.

Rhodium.

A specimen containing iridium gave Regnault 0.0553 (12—98°); another purer specimen 0.0580.

Ruthenium.

Bunsen found 0.0611 (0—100°).

Silver.

Wilcke gave 0.082; Dalton, 0.08.

Dulong and Petit found 0.0557 (0—100°) and 0.0611 (0—300°), which would give the formula of two terms.

$$Sm = 0.0530 + 0.000027 t.$$

Regnault obtained 0.05701 (14—99°), almost 2 per cent higher than given by the above formula.

Byström investigated up to 300° and gives his results calculated for the true specific heats at every 50° up to 300°. His figures are represented by the equations—

$$S = 0.05698 + 0.0000023 t + 0.00000032 t^2$$

$$Sm = 0.05698 + 0.00000115 t + 0.000000107 t^2.$$

This equation would give for Regnault's temperatures 0.05725, about identical with Regnault's value.

Kopp obtained values varying from 0.0552 to 0.0574; mean, 0.0560 (15—65°).

Bunsen obtained 0.0559 (0—100°), a value almost identical with Dulong and Petit's.

Pionchon investigated up to 1020°. He found up to the melting-point a regular formula of three terms, viz.,—

$$Sm = 0.05758 + 0.0000044 t + 0.00000006 t^2.$$

This equation gives for Regnault's range of temperature 0.05815, which is 2 per cent above his value. In the molten state, Pionchon found the following formula for the mean specific heat to zero:—

$$Sm = 0.0748 + \frac{17.20}{t}$$

the true specific heat in this condition being constantly 0.0748. The formula for the solid state would give its true specific heat at the melting-point as 0.075; we thus have another example of the specific heat in the solid state approaching equality to that in the liquid state as the melting-point is approached.

Naccari's experiments up to 300° led to the following formulæ:—

$$S = 0.05449 + 0.0000214 t$$

$$Sm = 0.05449 + 0.0000107 t$$

The latter, evaluated for Regnault's temperatures, gives 0.0557, which is almost identical with Dulong and Petit's value.

Le Verrier claims that the specific heat is constant up to 260°, then changes suddenly and is again constant up to 660°, then changes again and is constant to the melting-point. He gives between 0° and 260°, 0.0565; between 260° and 660°, 0.075; between 660° and 900°, 0.066. As no other observer has observed any such sudden changes, it is probable that Le Verrier is mistaken in his results. Le Verrier states that silver contains 62 calories of heat towards 930°, a little before the fusion. Pionchon places the fusing-point at 907°, and gives 60.32 calories as the amount of heat in the metal at this temperature.

It is difficult to decide just where the truth lies in this case of the specific heat of silver. If it were allowable to do so, an average of all the results at ordinary temperatures would come close to Regnault's value. But, since Pionchon made no experiments below 400°, I should be disposed to place less reliance on his values for temperatures from 0° to 100°. I would suggest for use below 400°, a formula based on the mean of Regnault's and

\* A Lecture delivered before the Franklin Institute, Jan. 30, 1893.

Bunsen's observations at 0° to 100° and on Pionchon's results at 0° to 400. Such a formula would be—

$$S = 0.0555 + 0.00001886 t$$

$$Sm = 0.0555 + 0.00000943 t$$

This gives for Bunsen's range 0.05644; for Regnault's range, 0.0566; being in each case about 1 per cent from their figures. At 220°, the point where it will be seen from the diagram that the lines of Byström and Naccari meet, at the value for S of 0.0590, the above formulæ gives 0.0596. At 400° the line joins in with Pionchon's curve, and above 400° Pionchon's formula may be assumed as probably accurate.

*Latent Heat of Fusion.*—Person determined this by the method of cooling to be 21.07 calories. Pionchon's formula for solid silver evaluated for the melting-point gives 60.32, and his formula for liquid silver evaluated for that temperature gives 85.04; the difference between these would therefore be the latent heat of fusion, or 24.72 calories. Pionchon's number is probably the nearest right.

#### Sodium.

Regnault obtained 0.293 (38° to +10°).

#### Thallium.

Regnault obtained 0.0335 (18—98°).

#### Thorium.

Nilson obtained 0.0276 (0—100°).

#### Tin.

Crawford found 0.0704; Wilcke, 0.06; and Kirwan, 0.068. Dalton obtained 0.07 by the method of cooling.

Dulong and Petit obtained 0.0514 by the method of cooling.

Regnault found for impure English tin 0.05695 (16—97°), and for pure Banca tin 0.05623 (14—99°).

Bède obtained results up to 213°, from which he deduced the formula—

$$Sm = 0.0500 + 0.000044 t$$

This evaluated for Regnault's temperatures gives 0.0550, over 2 per cent lower.

Kopp obtained results varying between 0.0493 and 0.0553; mean, 0.0531 (15—65°)—a result of very little value. A second set of experiments gave him results between 0.0543 and 0.0573; mean, 0.0565. The mean of the two sets of experiments is 0.0548; but the highest and lowest values he obtained were 16 per cent apart!

Person found the specific heat of molten tin to be 0.0637 (250—340°).

Bunsen found for *allotropic* tin 0.0545 (0—100°), and for cast tin 0.0559 (0—100°).

Pionchon found for molten tin up to 1000° the formula—

$$Sm \text{ (to } 0^\circ) = 0.0612931 - 0.0000104741 t + \\ + 0.0000000103448 t^2 + \frac{14.375}{t}$$

The writer has determined for Banca tin between 15° and 99°, 0.0566—a value 0.7 per cent above Regnault's.

*Latent Heat of Fusion.*—Dr. Irvine, Sen., working under Dr. Black, found that the latent heat would raise the temperature of solid tin 500° F. (at what temperature not stated). Dr. Irvine, Jun., found in a similar way 507°, the mean between 495° and 520°. In reaching these results, the heat in molten tin at its setting-point was first found. This was divided by the ordinary specific heat of tin, and the melting-point subtracted. This would be equivalent to assuming that the heat in solid tin at its melting-point is the product of that temperature into the ordinary specific heat. Since we do not know what value Irvine assumed for the latter we cannot correct his figures. If he used Crawford's value, 0.0704, his result would represent about 18.3 calories; if he had used 0.0570, his result would have been 16 calories.

Rudberg worked by the method of cooling, and assuming that the specific heat of solid tin at its melting-point is 0.0586, he obtained 13.31 calories as the latent heat of fusion. If we assume that the specific heat at this temperature is the same as Person found for molten tin (0.0637), Rudberg's results would become 14.46 calories.

Person found the amount of heat in molten tin at its setting-point to be 27.33 calories. Then, assuming that Regnault's value for the specific heat was applicable to the melting-point, he found the heat in solid tin at its melting-point to be  $232.7 \times 0.05623 = 13.08$  calories, which left 14.25 calories as the latent heat of fusion. Had he used the amount found by Bède in solid tin, at its melting-point, by direct experiment, he would have had—

$$27.33 - 13.60 = 13.73$$

calories as the latent heat.

Pionchon's formula for liquid tin evaluated for the melting-point gives 28.20 calories. Subtracting Bède's value for the heat in solid tin leaves 14.60 calories as the latent heat.

Direct experiment, by pouring liquid tin just at its melting-point into water, has given the writer 28.16 calories. This, less 13.60, would leave 14.56 calories as the latent heat of fusion. The close agreement of this result with Pionchon's is worthy of notice, especially since the heat in the molten tin was determined by two entirely different methods of procedure.

#### Titanium.

Nilson and Pettersen determined the mean specific heat as follows:—

0° to 100°	..	..	..	..	0.1125
0 to 211	..	..	..	..	0.1288
0 to 301.5	..	..	..	..	0.1485
0 to 404	..	..	..	..	0.1620

These would give the formula—

$$Sm = 0.0978 + 0.000147 t$$

This formula fits almost exactly the first, second, and last of the above observations, but gives 0.1421 for the third. A regular curve could not be found passing through all four of those values.

#### Tungsten.

Regnault gives 0.03636 (11—99°).

#### Uranium.

Blümcke found 0.02811, 0.02762, 0.02813; mean, 0.0280 (0—99°). Zimmerman found on two specimens as a mean value 0.0275 and 0.2812 (0—99°).

#### Zinc.

Wilcke found 0.102; Crawford, 0.0943; and Dalton, 0.10.

Dulong and Petit found 0.0927 (0—100°) and 0.1015 (0—300°). These results would give the formula—

$$Sm = 0.0883 + 0.000044 t$$

Neumann obtained 0.0929, at ordinary temperatures, by the method of cooling.

Regnault obtained with commercial zinc 0.09985, 0.10049, 0.100003, and with chemically pure zinc 0.09555 (14—99°).

Bède deduces from his experiments the formula—

$$Sm = 0.0865 + 0.000044 t$$

He observes that his metal contained a little lead.

Dulong and Petit's result is 3 per cent, and Bède's 4 per cent below Regnault's.

Kopp obtained results varying between 0.0899 and 0.0977; mean, 0.0932 (15—65°).

Bunsen obtained 0.0935 (0—100°).

Naccari deduces from his experiments up to 320° the formula—

$$S = 0.0907 + 0.000044 t$$

This gives 0.0932 for Regnault's temperatures.

Le Verrier states that from 0° to 110° the specific heat of zinc is constantly 0.096; between 110° and 140° it is very variable, there being an absorption of 0.8 calorie about 110°; that from this point to 300° the specific heat is constantly 0.105, and between 300° and 400° constantly 0.112. The total amount of heat is about 46 calories at about 410°—a trifle before fusion.

*Latent Heat of Fusion.*—Dr. Irvine, assuming the specific heat of zinc constant to the fusing-point (0.0943), found by experiment 62.5 calories in molten zinc, and subtracting the heat in solid zinc at its melting-point (388.9° × 0.0943), he obtained 62.5 - 35.7 = 26.8 calories as the latent heat. (I have transferred his Fahrenheit degrees to Centigrade).

Person obtained an average of 67.81 calories in molten zinc at its setting-point, and assuming Regnault's value for the specific heat true to the melting-point, he found the latent heat to be—

$$67.81 - (415.3 \times 0.09555) = 67.81 - 39.68 = 28.13$$

calories. However, we know that this latter assumption is incorrect.

Supposing we take for the mean specific heat a line which would pass through Regnault's result and be parallel to Dulong and Petit's and Bède's lines, which are parallel to each other. Such a line would be—

$$S_m = 0.09058 + 0.000044 t$$

Now, Dulong and Petit's formula would give for the heat in solid zinc at its melting-point 44.2 calories, Bède's 43.5 calories, and Naccari's 40.4 calories. The above formula gives 45.2 calories. It is noticeable that when Le Verrier gives the total heat in any metal close to its melting-point, his value is usually near to the best determinations. He says there is about 46 calories in zinc just below its melting-point. I should, therefore, take the value 45.2 given by the above equation as probably the nearest right.

Irvine's result will now become 62.5 - 45.2 = 17.3 calories. Person's results, 67.81 - 45.2 = 22.61 calories. Person's is, of course, the better determination of the two.

#### Zirconium.

Mixter and Dana have obtained 0.0662 (0-100°) with the ice calorimeter.

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## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

Ordinary Meeting, June 15th, 1893.

Dr. ARMSTRONG, President, in the Chair.

(Continued from p. 98).

40. "Sarcolactic Acid obtained by Fermentation of Inactive Lactic Acid." By PERCY FRANKLAND, F.R.S., and J. MACGREGOR, M.A.

The authors have submitted ordinary inactive calcium lactate to partial fermentation, and have recovered from the fermented liquid a lactic acid yielding levorotatory salts, which was separated from the inactive acid still present by repeated crystallisation of the zinc salts, the zinc salt of the inactive acid being less soluble than that of the active acid.

The specific rotatory power of the active zinc salt was determined in several specimens and for several different concentrations, and results were obtained showing that the rotation on the whole diminishes as the concentration increases, and agrees fairly closely with those given by Wislicenus (*Annalen*, clxvii., 332).

The identity of the two salts was further established by converting some of the zinc into the calcium salt and determining the specific rotatory power of the latter; the value found (C=5.79) was  $[\alpha]_D = -5.48$ , that given by Wislicenus (C=5.35) being  $[\alpha]_D = -5.25$ .

The authors hope to render this method available for the preparation of considerable quantities of sarcolactic acid, in the same way as has already been done by one of them in the case of active glyceric acid. In the mean-

time it is of interest to note that, as in the case of the fermentation of calcium glycerate, the bacteria attacked by preference the dextrorotatory salt. Similarly, *Linospier* (*Ber.*, xxiv., 660) has shown that *Penicillium glaucum* also first destroys the dextrorotatory lactate.

41. "Hexanitroxanilide." By A. G. PERKIN.

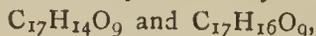
It is shown that whereas di- and tetra-nitroxanilide are converted by ammonia into the corresponding nitraniline (*cf.* *C. S. Trans.*, 1892, 458), hexanitroxanilide not only yields trinitraniline, but also trinitrophenoxamide,  $C_6H_2(NO_2)_3 \cdot NH \cdot CO \cdot CONH_2$ , a substance which crystallises from nitrobenzene in colourless glistening needles melting at  $257^\circ$ ; this compound exhibits acid properties, forming potassium, sodium, and ammonium derivatives, *e.g.*,  $C_6H_2(NO_2)_3 \cdot NR \cdot C_2O_3NH_2$ , which crystallises in red leaflets, exhibiting a magnificent golden lustre. When subjected to the action of a cold mixture of nitric and sulphuric acids, trinitrophenoxamide loses the elements of a molecule of ammonia, forming trinitroxanil. Hexanitroxanilide is converted into 1:3:5-trinitrobenzene by heating it with a mixture of nitric and sulphuric acids; tetranitroxalorthotoluidine in like manner yields 1:3:5-dinitrotoluene, but the isomeric para-derivative is converted into dinitrobenzoic acid.

Hexanitrocarbanilide has also been prepared by the author; like the corresponding nitroxanilide, it yields red potassium and sodium derivatives.

42. "The Constituents of the Indian Dye-stuff Kamala (I)." By A. G. PERKIN.

A description is given of six distinct substances extracted by ether from Kamala—Rottlerin, the principal constituent, described by Anderson, in 1855 (*Journ. Chem. Soc.*, 1855, 669); isorottlerin; two resins, one of low, the other of high melting-point; a wax, which is possibly cetylic cerotate; and a yellow crystalline colouring-matter present in a minute proportion, the composition of which is yet to be determined.

Rottlerin is best separated from the dye-stuff by means of cold carbon bisulphide, from which it crystallises in thin salmon-coloured plates melting at  $191^\circ$ ; its composition is represented by the empirical formula  $C_{11}H_{10}O_3$  already assigned to it by Anderson, but it is undoubtedly a substance of high molecular weight. It yields a diacetyl derivative. On boiling it with alkalis an odour of benzaldehyd is apparent. When oxidised by cold nitric acid it yields two acids represented by the formulæ—



while boiling nitric acid converts it into a dibasic acid of the formula  $C_{13}H_{10}O_9$ .

Isorottlerin closely resembles rottlerin in appearance, but melts at  $198-199^\circ$ , and is practically insoluble even in hot carbon bisulphide; moreover, no odour of benzaldehyd is apparent when it is boiled with alkali. It yields the acid of the formula  $C_{13}H_{10}O_9$  on oxidation.

The resin of low melting-point resembles rottlerin, with which it is evidently closely allied in most of its properties; its composition is represented by the formula  $C_{12}H_{12}O_3$ ; on oxidation it yields the acid of the formula  $C_{13}H_{10}O_2$ .

The resin of high melting-point is a light-yellow coloured substance represented by the formula  $C_{13}H_{12}O_4$ , and also resembles rottlerin in many of its properties, being converted into the acid of the formula  $C_{13}H_{10}O_9$  when boiled with nitric acid.

43. "A Quantitative Method of Separating Iodine from Chlorine and Bromine." By D. S. MACNAIR, Ph.D., B.Sc.

The method is based on the fact that when treated with potassium bichromate and concentrated sulphuric acid, silver iodide is completely converted into silver iodate, whereas silver chloride and bromide are converted into sulphate. Two portions of a solution containing the three halogens are precipitated with silver nitrate: the one precipitate is weighed, the other is heated with the oxidising mixture and the resulting iodate is then reduced

by means of sulphurous acid, and the iodide is filtered off and weighed. The silver originally present as chloride and bromide contained in the filtrate from the iodide is precipitated and weighed as chloride. The method affords very accurate results.

*Addendum.*—Since the paper was written, at the suggestion of Dr. Armstrong I have used a Gooch crucible asbestos filter, instead of paper, and have found it advantageous both as regards speed and accuracy, as it is not necessary to use two portions of the liquid when the chlorine and bromine are to be determined; the precipitate of the mixed haloids may be dried at  $120^\circ$ , weighed, and then treated with sulphuric acid and potassium bichromate as usual, along with the asbestos previously used in filtering. When the oxidation is finished, the solution is diluted and sulphurous acid is added at once, without previously filtering off the asbestos, which is collected along with the silver iodide. The weight of the asbestos used in the first filtration is necessarily deducted from that of the silver iodide. It is evident that this asbestos might be removed by filtering before adding sulphurous acid; but I do not recommend this, as silver iodate is apt to separate out during the filtration, and unless this be completely re-dissolved—no easy matter—before the addition of sulphurous acid, it will escape reduction and the results will be unreliable.

44. "Note on a form of Burette for Rapid Titration." By LLEWELLYN GARBUTT, Assistant Master at Winchester College.

The following arrangement will be found extremely convenient in volumetric operations with liquids. The liquid to be used in titrating is contained in the flask F, which may have a capacity of 300 c.c., and is delivered from a pinch-cock or stop-cock C, at the bottom of the long syphon tube T. The tube D is connected by means of rubber tube to the gas burette G. The side tube B is closed by a pinch-cock, and the graduation of G begins from the bottom. The pressure tube H, which contains water, moves freely upwards, but its downward movement is arrested by the cork A, fixed stiffly to the upper end of the tube H, and normally serving as a support to it. Before beginning the titration the pinch-cock B is opened for a moment to equalise the pressure. The quantity of water in the two tubes is adjusted once for all, so that whenever the pressure is equalised the water in G falls to zero on the scale. The titration is conducted from the cock C in the usual way, and the amount delivered is read by raising H until the liquids are at the same level in both tubes. The parallel lines drawn across the supporting-board serve as a guide to the eye. The volume of the liquid delivered can then be read off from the position of the water in G. To begin a new titration, all that is necessary is to let H slide back to its normal position, and open the pinch-cock at B for a moment; the water in G at once falls accurately to zero, and the new titration can be begun. If it is desired to use several different liquids, as many flasks, furnished with syphon and connecting tubes, should be prepared and mounted ready on stands. They can then be connected in a moment with the rubber tube E.

The advantages of this arrangement are—

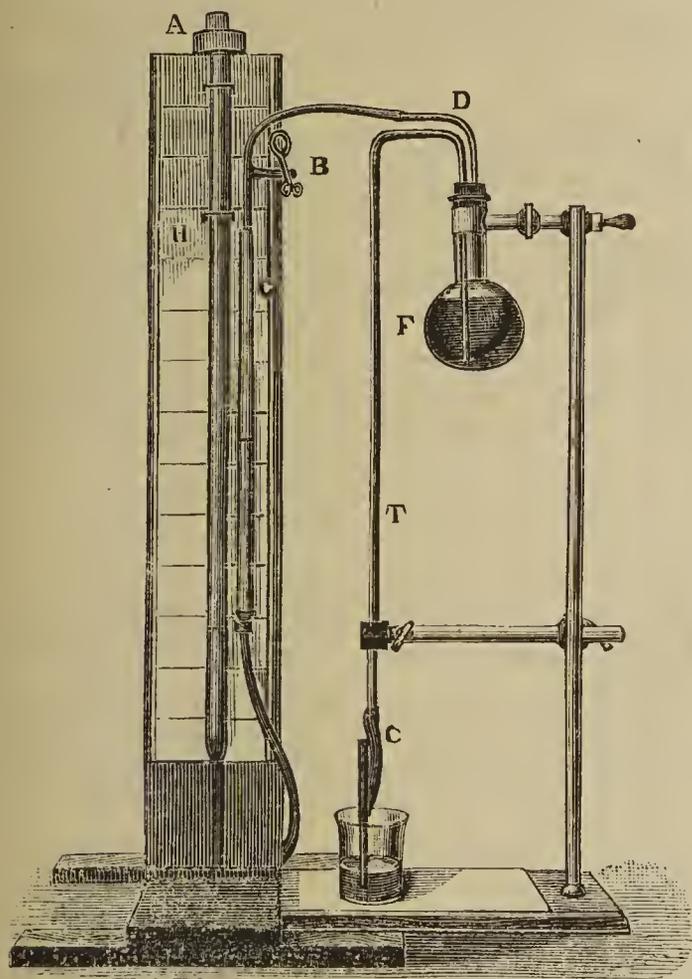
1. Extreme rapidity and simplicity of adjustment to zero.
2. As much as 300 c.c. of the liquid may be available for a series of titrations.
3. The same burette is used with all liquids, and always starting from zero, so the graduation is constant.
4. If the burette and pressure tube are thoroughly clean, there is little trouble from tears or imperfect meniscus, as only pure water is used in it.

The disadvantages are—

1. The titration must be conducted fairly rapidly (say within five or ten minutes), otherwise changes of tempera-

ture and pressure may appreciably affect the volume of the air.

2. The pressure cannot be perfectly equalised by means of the sliding tube, H. The error of reading from this cause is practically *nil* when F is full, but it might, as an extreme, amount to one-twentieth c.c. when F contains 300 c.c. of air. If it is only desired to read to one-tenth c.c. this will not matter much. For greater accuracy the flask must always be kept nearly full.



It is convenient to be able to detach H completely from the board. If the water should get out of adjustment, so that it no longer falls to zero on opening the pinch-cock at B; either a few drops of water may be added or the cork A moved a trifle along the tube H.

45. "The Use of Sodium Peroxide as an Analytical Agent." By J. CLARK, Ph.D.

Experiments are described showing that the sulphur and arsenic in minerals may be rendered soluble by cautiously heating the powdered substance with sodium peroxide, and that the peroxide may, in like manner, be used in estimating chromium in chrome ores and chromium alloys.

An ammoniacal solution of the peroxide may be used in separating manganese from zinc, nickel, and cobalt, a single precipitation sufficing in the case of zinc.

46. "Stibiotantalite: a New Mineral." By G. A. GOYDER.

The note has reference to a mineral from the alluvial tin-field at Greenbushes, Western Australia, the assay values of which varied most unaccountably. It is shown to consist, in the main, of antimony and tantalum oxides and a not inconsiderable proportion of niobic oxide; the amounts found in one sample, for example, were  $Ta_2O_5 = 51.13$ ,  $Nb_2O_5 = 7.56$ ,  $Sb_2O_3 = 40.23$ .

(To be continued.)

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 7, August 14, 1893.

**A Product of the Incomplete Oxidation of Aluminium.**—M. Pionchon.—If submitted to the action of the pointed flame of an oxyhydrogen blowpipe with a low yield of oxygen, aluminium becomes oxidised with a bright incandescence, and is converted into a substance of a blackish grey appearance, in which the proportion of the weight of oxygen to that of aluminium is close upon 0.6, and consequently very different from the value 0.888 characteristic of alumina. The product, along with free aluminium and alumina, consists of a new aluminium oxide,  $Al_6O_7 = Al_2O_3 \cdot 3Al_2O_3$ . It may be a mixture or a compound.

**New Reaction of Eserine and a Green Colouring Matter Derived from the same Alkaloid.**—Sen. S. J. Ferreira da Silva.—The author announced in 1890 that eserine was the only alkaloid of the benzenic ammoniacal group which after treatment with fuming nitric acid of specific gravity 1.4 and evaporation to dryness gave a green residue along its edges. He finds that this reaction is very suitable for the identification of very small quantities of eserine. He takes a minute fragment of eserine or of one of its salts, places it in a small capsule of porcelain, and dissolves it in one or two drops of fuming nitric acid. He thus obtains a light yellow solution, which, if heated in the water-bath, turns first to a deep yellow and then to an orange. If it is evaporated to dryness whilst stirring with a glass rod, we remark in one or two minutes after complete desiccation a change of colour to a pure green. The green colouring matter thus produced is soluble in water and still more readily in concentrated alcohol. Its green solutions are not fluorescent, and yield on evaporation the green colouring matter unaltered. The aqueous solution of the green matter, if examined with the spectroscope, is characterised by two absorption bands: one, the more distinct, situate in the red between  $\lambda 670$  and  $\lambda 688$ ; the other, broader, but having less sharply-defined edges, occupies a part of the indigo and the violet, especially between  $\lambda 400$  and  $\lambda 418$ . There is also a very faint band in the orange. The reaction shows 0.005 gm. of the alkaloid. The author proposes for the green compound the name of chlor-eserine.

**Preparation of Citric Acid by Synthesis.**—Charles Wehmer.—The author obtains citric acid by the fermentation of glucose set up by certain fungi, *Citromycetes pfefferianus* and *C. glaber*. Herr Wehmer states the spores of these fungi are abundant in the air, and can be obtained pure by cultivation.

*Bulletin de la Société Chimique de Paris.*  
Series 3, Vols. ix. and x., No. 12.

**Alleged Diffusibility of Certain Gases through a Membrane of Caoutchouc.**—A. Reychler.—The facts brought forward prove that it is not necessary to ascribe to sulphurous acid, to carbonic acid, or to a mixture of both, an abnormal speed of diffusion. We must take account of the special affinity of caoutchouc for the gases present. When a membrane of caoutchouc is interposed between sulphurous acid and the free air it becomes saturated with sulphurous acid on one of its surfaces, whilst the opposite surface allows the gas to escape into the atmosphere. Air has not a great affinity for caoutchouc, whence its component gases penetrate only to a trifling extent during the absorption of the sulphurous acid.

Acrylic Anhydride (Propenoide).

Action of Acrylchloride upon Alcohols and Phenols.

Acrylamide (Propene-amide).

Certain Substituted Acrylamides.

Acrylic Nitrile, Vinyl Cyanide, and Propene Nitrile.—These five papers, by M. Moreu, on the derivatives of nitrile, will be inserted if space allows.

Influence of Certain Organic Solvents upon Rotatory Power.—Freundler.—It is necessary to eliminate benzene, chloroform, and carbon tetrachloride if it is desired to determine the laws of the rotatory power. It is still necessary to study more closely the influence of concentration in order to see in what cases we may compare the values given by acetic or alcoholic solutions with those given by ether.

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1883 TO 1888.

**NOTICE IS HEREBY GIVEN,** that

THE ELECTROLYTIC CAUSTIC AND CHLORINE TRUST, LIMITED, of 23, Queen Victoria Street, London, have applied for leave to amend the Specification of the Letters Patent No. 2296 of 1890, granted to James Charles Richardson and Trevenen James Holland, for "Improvements in the electrolytic production of caustic soda, caustic potash, and other products from their salts."

Particulars of the proposed Amendments were set forth in the Illustrated Official Journal (Patents) issued on the 23rd August, 1893.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the Amendment within one calendar month from the date of the said Journal.

(Signed) H. READER LACK,  
Comptroller General.

The **CHEMICAL DEPARTMENT** of UNIVERSITY COLLEGE, LIVERPOOL, provides a four years' Course of Instruction in Chemistry. Classes in the departments of German, Mathematics, Physics, and Engineering are included in the Course. The Sheridan-Muspratt Chemical Scholarship of £50 per annum, for Students of the third year, will be offered in December, 1893. The Examination is not limited to University College Students. For particulars apply to the Registrar.

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Prospectuses for the Session 1893-94 will be forwarded on application.

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HENRY WM. HOLDER, M.A.,  
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Full particulars of this Course qualifying for the Victoria University Degree in Chemistry and the College Technological Chemistry Certificate will be forwarded on application.

The SESSION commences TUESDAY, OCTOBER 3rd.

H. W. HOLDER, M.A.,  
Registrar.

**MASON COLLEGE, BIRMINGHAM.**  
(With Queen's Faculty of Medicine).

**FACULTIES OF ARTS AND SCIENCE.**

PRINCIPAL—PROFESSOR R. S. HEATH, M.A., D.Sc.

SESSION 1893-94.

The SESSION will commence on MONDAY, OCTOBER 2nd. R. C. JEBB, Esq., Litt.D., M.P., Regius Professor of Greek in the University of Cambridge, will distribute the Prizes, and deliver an Inaugural Address at a Public Meeting in the College on Monday, October 9.

COMPLETE COURSES OF INSTRUCTION are provided for the various Examinations in Arts and Sciences, and the Preliminary Scientific (M.B.) Examination of the University of London, for Students of Civil, Mechanical, or Electrical Engineering, and for those who desire to obtain an acquaintance with some branch of Applied Science. Students may, however, attend any Class or combination of Classes.

(There is also a Faculty of Medicine. A Syllabus containing full particulars is published by Messrs. Cornish, New St., Birmingham. Price 6d., by Post 7d.)

A SYLLABUS of the Faculties of Arts and Science containing full information as to the various Lecture and Laboratory Courses, Lecture Days and Hours, Fees, Entrance and other Scholarships, Prizes, &c., is published by Messrs. Cornish, New Street, Birmingham. Price 6d., by Post 8d.

Further information may be obtained on application to—

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During the Session, which commences September 25th, Classes in Organic and Inorganic Chemistry will be held on Monday, Tuesday, Thursday, and Friday Evenings under the direction of Dr. MACNAIR.

Prospectus on application to Secretary.

**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.

THE CHEMICAL NEWS.

VOL. LXVII., No. 1763.

(STUDENTS' NUMBER).

ADDRESS TO STUDENTS.

In view of the re-commencement of study at our various colleges it is our duty to say once more a few words, not only to students, but to professors and teachers, and above all to examiners. We trust that these different bodies will bear with us, considering our motive, the advancement of Science in Britain and its Colonies. We can scarcely say that the prospects of our country take a notably high rank in the realms of research and discovery. The protest of Mr. Auberon Herbert and his associates let in a temporary light upon the question of higher education; but the attention created was but short-lived. The protest was never met, much less refuted; other less important topics engrossed the public mind, foremost among which must rank the political agitation of the present day. Hence, for all that appears on the surface, Mr. Herbert might as well never have written a word on the subject. The sad game of "setting papers" and preparing for "exams." still continues. Youths, as Mr. Huxley put it, study "not to know, but to pass." Heads of the higher grades of schools still boast, in their prospectuses, of the success of their pupils at this or the other competition, and the notorious examiner is still admired and envied. When a certain young lady surpassed the Cambridge senior wrangler at an examination the press was instant with loud voices in laudatory comment. But no one uttered the obvious truth that if Miss Fawcett had ascertained a novel fact in any of the sciences, or established a new generalisation, she would have deserved infinitely higher congratulations.

As we stand, the individual is nearly powerless. If the student seeks merely to *discover* he is elbowed aside as a failure. If the teacher aims at training his pupils to be successful in research, they will fail to pass and he will be pronounced incompetent. The utmost which he can effect is, whilst seeking to qualify his disciples for success at the examinations, to instil into their minds as much genuine truth as he can venture. But, as he values his "bread and butter," he must keep his attention mainly for passing. Indeed, his easiest way to emolument and reputation is to treat the examinational successes of his pupils as the one thing needful. He must be something more than an ordinary man if he acts differently. The examiner, again, is powerless. He must "set papers," devised, it is supposed, to test the proficiency of the pupils. He cannot take any method of gauging their intellectual resources, their accuracy of observation and of conclusion. He is simply a wheel in the great cram-mill, and he must act accordingly.

The only full help, as far as we can see, must come from the governing bodies of universities, medical schools, &c. But meantime much might be done by the press and by the public if it would, "unresting and unhasting," work against examinationism in all

its phases. Mr. Auberon Herbert's protest should be followed up wherever and whenever feasible.

The student, we are aware, can here do little; nor has the teacher much more power. The examiner will not, of course, be active in a movement which would lead to his own displacement. But many, less hopeful and less needed causes have been won by perseverance.

It is of course quite premature to expect any aid from the legislature. The reform which we hope for lies distinctly outside the boundaries of faction, and will therefore meet with no Parliamentary support. But opportunities may be taken of bringing the shortcomings and evil effects of the examinational system under the notice of members of either house, and inducing them to ask questions.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of Two pounds to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of one pound, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages:—Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Science:—Chemistry, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds,

their chief physical and chemical characters, their preparation, and their characteristic tests.

A Pass Certificate, signed by the Registrar, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitor declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

#### INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will be held July 16, 1894.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

#### Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

#### B.SC. EXAMINATION.

The B.Sc. Examination will be held October 15, 1894.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

#### Examination for Honours.

The examination for Honours in Chemistry will take place on Monday and Tuesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday by practical examination in Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

#### DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the

Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with this statement he shall transmit an original printed Dissertation or Thesis (at least six copies) treating scientifically some special department of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, and with especial reference to his Dissertation or Thesis.

Candidates for the Degree of D.Sc. will be expected to be so fully conversant with the branch of Science they profess as to be able, if required, to satisfy any test of their acquirements in that branch that it may be thought expedient to apply.

#### PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.\*

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examination, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

#### UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry.—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years, passing at least two examinations in Arts, and one in either Mathematics, Natural Science, Law, Modern History, or Theology, when, if he obtain a first, second, or third class, he can take his B.A. Degree; if he do not gain such honour he has to pass a third examination in *Literis Humanioribus*.

The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £75 are obtainable at Christ Church, Magdalen, and other colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the University Calendar; the Examination Statutes, 1893; the Student's Handbook to the University; and from the professors.

#### UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry.—G. D. Liveing, M.A., F.R.S.  
Jacksonian Professor of Natural and Experimental Philosophy.—J. Dewar, M.A., F.R.S.

\* Candidates who pass in all the subjects of the Preliminary Scientific (M.B.) Examination, and also pass at the same time in the Pure and Mixed Mathematics of the Intermediate Examination in Science, or who have previously passed the Intermediate Examination in Arts, are admissible to the B.Sc. Examination.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £10 a year, are chiefly given for mathematical and classical proficiency. Scholarships are given for Natural Science in Trinity, St. John's, St. Peter's, Clare, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the examinations being in December, at Easter, and in June and October.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

#### UNIVERSITY OF DUBLIN.

##### TRINITY COLLEGE.

*Professor of Chemistry*.—J. Emerson Reynolds, D.Sc., M.D., F.R.S.

*Assistant Lecturer*.—Emil A. Werner, F.C.S., F.I.C.

*Demonstrator*.—William Early, F.I.C.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 1st of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; advanced, second year.
2. *Organic Chemistry*.—General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The *Summer Course of Practical Chemistry for Medical Students* begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

#### KING'S COLLEGE.

(DEPARTMENT OF ENGINEERING AND APPLIED SCIENCE).

*Professor of Chemistry*.—J. M. Thomson, F.C.S.

*Demonstrator of Practical Chemistry*.—G. S. Johnson, F.C.S.

*Assistant Demonstrator*.—Herbert Jackson, F.C.S.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course

commences with a View of the Forces which concur to the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic elements and their principal Compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *viva voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

*Second Year*.—Students attend in the Laboratory twice a week, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis. Any Student of this Department may be admitted to this Class at any period of his study on payment of an extra fee.

*Experimental and Analytical Chemistry in the Laboratory*.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. od.; per ann., £8 8s. od.; Practical Chemistry per term, £4 4s. od.; per ann., £10 10s. od.; Experimental and Analytical Chemistry—Daily attendance: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three months, £6 6s.; Six months, £11 11s.; Nine months, £5 15s.

#### Rules as to Admission of Students.

I. The Academical Year consists of Three terms: Michaelmas Term, from beginning of October to the week before Christmas; Lent Term, from the middle of January to the week before Easter; Easter Term, from Easter to the beginning of July.

II. The days fixed for the Admission of New Students: in the Academical Year 1893-94, are Tuesday, October 3, Wednesday, January 10, and Wednesday, April 11.

#### METALLURGY.

*Professor*.—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

#### PHOTOGRAPHY.

*Lecturer*.—Prof. J. M. Thomson, F.R.S.E., F.C.S.

Arrangements are made for a complete Course of Instruction in Photography to the students of the third year. A glass house has been erected, and in connection with it a Laboratory for the preparation of Photographic Chemicals. Students entering to this department will be afforded every facility for practising the Art in all its branches.

In addition to the regular College Course in Photography occasional classes are formed, consisting each of about six gentlemen, who meet twice a week. The fee for private instruction is £5 5s. for ten lessons, or £10 10s. for three courses. There is in every case a charge of £1 each course for chemicals.

#### EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June.

#### UNIVERSITY COLLEGE.

##### FACULTY OF SCIENCE.

*Professor.*—William Ramsay, Ph.D., F.R.S.

*Assistant Professor.*—J. N. Collie, Ph.D.

*Assistants.*—James Walker, D.Sc., Ph.D., and Alexander Kellas, B.Sc.

The Session is divided into three Terms, as follows, all the dates being inclusive:—

First Term, from Tuesday, October 3rd, until Wednesday, December 20th;

Second Term, from Tuesday, January 9th, 1894, till Friday, March 16th;

Third Term, for Lectures, from Tuesday, April 10th, till Friday, June 29th. Class Examinations begin on Monday, June 18th.

#### Junior Courses.

First Term: Tuesday, Thursday, and Saturday, at 10, commencing October 5, 1893. Third Term: Tuesday and Thursday at 10, Friday at 4, beginning April 12th, 1894. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

#### Senior Course of Chemistry.

First and Second Terms: Inorganic.—The Class meets four times a week: Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises, commencing October 4th.

Fee:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

#### Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

#### Organic Chemistry.

Tuesday and Thursday, at 9, in the First Term, beginning October 5th; Tuesday, Thursday, and Saturday, at 10, in the Second Term; and Tuesday and Thursday, at 9, and Saturday, at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who in studying the subject have not a Medical Examination chiefly in view. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course during the Second and Third Terms, instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for the Second and Third Terms, £4 14s. 6d.; for a Term, £2 12s. 6d.

#### Practical Class.

First and Second Terms, Tuesday and Thursday, at 11, commencing October 4th.

Fee, including cost of materials, £5 5s.; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific and Intermediate Science Examinations.

#### Senior Practical Class.

Wednesdays from 2 to 4 and Saturdays from 10 to 12 during the Third Term; also Tuesdays and Thursdays from 11 to 12.

Fee:—(Including cost of materials) £5 5s.; for a Second Course, £3 3s.

#### Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

A Gold Medal and Certificates of Honour are competed for by first year's Students. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1893-94; also the Clothworker's Scholarship of £30.

#### Chemical Technology.

Lecturer, Watson Smith, F.I.C., F.C.S.

Courses of Lectures will be given on the following subjects:—Manufacture of Sulphuric Acid, Alkali, &c. Fuel and Gas Manufacture. Chemical Technology of Building Materials. Methods for the Technical Chemical Analysis of Raw and Manufactured Products. Coal-tar Products and Colours. Applications of Chemistry to Engineering. Methods of Technical Chemical Analysis.

Evening Lectures will be given by gentlemen qualified by practical and theoretical acquaintance with special subjects, and occasional visits to Works will be arranged.

#### ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

*Professor.*—T. E. Thorpe, Ph.D., B.Sc., F.R.S.

*Assistant Professor.*—W. P. Wynne, D.Sc., A.R.C.S.

*Demonstrators.*—H. Chapman Jones and A. E. Tutton.

*Assistants.*—G. S. Newth, J. W. Rodger, and W. Tate.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of

study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. But students who are not candidates for the Associateship are permitted to take up the course of instruction in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 4th of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and in those of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
	£	£
Chemistry .. .. .	3	13
Physics .. .. .	5	12
Biology with Botany .. .. .	5	12
Geology with Mineralogy .. .. .	4	8
Mechanics . . . . .	4	6
Metallurgy .. .. .	2	13
Mining .. .. .	4	
Astronomical Physics .. .. .	2	3

Agricultural Chemistry, per term, £13. Mathematics and Mechanical Drawing, £3 per term. Freehand Drawing, £1 per term.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half the foregoing charges.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

*Bona fide* teachers qualified to earn payments for teaching Science according to the rule of the Science Directory may attend any course of lectures on the payment of £1.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

*Summer Courses for Teachers.*—Short courses of instruction are given annually, about July, in different

branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive 3rd class railway fare to and from South Kensington, and a bonus towards their incidental expenses of £3 each. (See Science Directory.)

*Working Men's Lectures.*—Notification of these will be given in the newspapers.

THE SCHOOL OF PHARMACY  
OF THE  
PHARMACEUTICAL SOCIETY OF GREAT  
BRITAIN.

The Fifty-second Session will commence on Monday, October 2nd, 1893. Entries not previously arranged with the Dean or Secretary may be made between 10 a.m. and 1 p.m. on that day.

*Officers of the School:*—Prof. Dunstan, M.A., F.R.S., F.I.C., Chemistry (Dean); Prof. Attfield, Ph.D., F.R.S., F.I.C., Practical Chemistry; Prof. Green, M.A., B.Sc., F.L.S., Botany; Prof. Greenish, F.I.C., F.L.S., *Materia Medica*; Mr. Joseph Ince, F.L.S., Pharmacy and Practical Pharmacy.

Entries may be made for single classes. A bench in the chemical laboratories can be engaged at any time for any number of hours daily or days weekly for any period. Students are recommended to join the Lecture classes on Chemistry and Physics in October, but other convenient periods are the beginning of January or the commencement of the Second Course in April. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance on the Courses of Pharmacy also are accepted by the conjoint Board.

For Prospectuses, &c., apply to Mr. F. W. Short, B.Sc., Secretary to the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES,  
ABERYSTWYTH.

*Professor.*—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Göttingen), F.I.C.

*Demonstrator.*—A. W. Warrington, M.Sc. (Vic.), F.I.C. The College is open to male and female students above the age of sixteen years. The Session commences on Friday, September 29, on which day all Students will be expected to meet the Professors in the Library of the College.

*Lecture Courses.*—(1) Matriculation Course; three lectures weekly during the Michaelmas and two weekly during the Lent and Easter Terms. (2) Intermediate Science Pass Course; three lectures weekly during the Lent and Easter Terms. (3) Intermediate Science Honours Course; two lectures weekly during the Lent and Easter Terms. (4 and 5) B.Sc. Pass and Honours Courses; each three lectures weekly throughout the Session.

*Laboratory Courses.*—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged to suit the requirements of the individual Student.

Students intending to proceed to the M.B. or B.Sc. Degree of the University of Edinburgh may count one or two years' residence respectively spent at this College.

*Fees.*—The Fee for the whole Session, if paid in ad-

vance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 10s. per term, and for twelve hours, 20s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

*Scholarships and Exhibitions* varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 20, and exhibitions are awarded at the end of the Session on the results of the class examinations.

The Chemical Laboratories in connection with this College have been recently built, and are fitted with every convenience for the prosecution of chemical studies.

#### UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

*Chemistry.*—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Fred. Marsden, Ph.D., B.Sc. Assistant Lecturer in Agricultural Chemistry, C. F. Archibald.

*Physics.*—Professor, Andrew Gray, M.A., F.R.S.E. Assistant Lecturer and Demonstrator, R. W. Stewart, D.Sc.

The Session opens October 3rd, 1893. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

*Matriculation Course.*—Subjects: Those prescribed for the London University Matriculation Examination. Fee for the Term £2 2s. A class for revision of Matriculation Work will be held during the Summer Term. Fee for the Term, £1 1s.

*Intermediate Course.*—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Term £2 2s.

*B.Sc. Course.*—Organic Chemistry. Fee for the Session, £3 3s.

*Medical Course.*—Inorganic and Organic Chemistry. Fee for the whole Course, £4 4s.

*Agricultural Chemistry.*—Fee, £1 1s.

*Laboratory Courses.*—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

#### UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

*Professor.*—C. M. Thompson, M.A., D.Sc., F.C.S.

*Demonstrator.*—E. P. Perman, D.Sc., F.C.S.

The Session commences October 2nd, and terminates on June 22nd, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the London University Matriculation examination. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of 50 lectures held during the Lent term in continuation of the Junior Course,

and, together with laboratory practice and the course on Chemical Theory, will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £3 3s.

A course of about 20 lectures on the Theory of Chemistry will be given during the summer term.

The Senior Course consists of some 90 lectures devoted to Organic Chemistry; Fee, £3 3s.

A course of 30 lectures on Qualitative and Quantitative Analysis will also be given.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 4.30; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a conjoint College Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Female Students is attached to the College.

#### UNIVERSITY COLLEGE, BRISTOL.

*Professor of Chemistry.*—Sydney Young, D.Sc., F.R.S.

*Lecturer.*—Arthur Richardson, Ph.D.

The session 1892-93 will begin on October 5th. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratory. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articulated pupils at reduced terms. Medical education is provided by the Bristol Medical School, which is incorporated with the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

DAY LECTURES.

*Inorganic Chemistry.*

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

*Junior Course.*—Two Lectures a week will be given during the First and Second Terms.

*Senior Course.*—Three Lectures a week will be given throughout the Session.

*Organic Chemistry.*

This Course will relate to the more important groups of the Compounds of Carbon.

Lectures will be given during the Second Term on Tuesdays and Thursdays at 10 o'clock; during the Third Term on Mondays, Wednesdays, and Fridays at 10 o'clock. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session.

*Practical Chemistry.—Laboratory Instruction.*

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. The Laboratory is under the immediate supervision of the Professor and the Lecturer. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session ..	15	12½	10	7½	5
„ Two Terms ..	11	9	7½	5½	3½
„ One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

*Photographic Chemistry.*

Special arrangements can be made with regard to instruction in this subject.

*Chemical Scholarship.*—Among others, a Chemical Scholarship of £25 is offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

MASON SCIENCE COLLEGE, BIRMINGHAM.

*Professor.*—W. A. Tilden, D.Sc. Lond., F.R.S., F.I.C.

*Assistant Lecturers.*—W. W. J. Nicol, M.A., D.Sc. Edin., F.I.C., and Thomas Turner, Assoc.R.S.M., F.I.C.

*Demonstrator.*—Sidney Williamson, Ph.D., F.I.C.

The Session will be opened on Monday, October 2nd, 1893.

*Elementary Course.*

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. A Second Course of Twenty Lectures, having reference only to the subjects included in the syllabus of the Matriculation Examination of the University of London, will be given in the Summer Term. Lecture days—Wednesdays and Fridays at 11.30, Thursdays at 3.30.

Persons entirely unacquainted with Chemistry are recommended to attend the first of these Courses before entering for the General Course, which commences in October. Candidates for the Matriculation Examination of the University of London are advised to attend both these Courses.

*General Course.*

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December, and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. A Tutorial Class is held in connection with this Course once a week throughout the Session. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Tuesday, Wednesday, and Thursday at 9.30 a.m. Fee, £1 11s. 6d.

*Advanced Course.*

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet once or twice a week. Fee for the session, £3 3s.

*Laboratory Practice.*

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees:—

	All day.	Three hours per day.
One Term .. .. .	7 guineas .. ..	4½ guineas.
Two Terms .. .. .	13 „ .. ..	8½ „
Three Terms .. .. .	18 „ .. ..	12 „

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

*Metallurgy.*

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each course. A more advanced course upon selected subjects is also given by Mr. Turner, the Lecturer in Metallurgy.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

*Evening Classes.*

Several Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

*Excursions.*

During previous Sessions permission has been obtained

to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor.

BRADFORD TECHNICAL COLLEGE.  
CHEMISTRY AND DYEING DEPARTMENT.

*Professor.*—Mr. Arthur Duffon, B.A. (Cantab.), B.Sc. (Lond.).

*Lecturer on Botany and Materia Medica.*—William West, F.L.S.

The school year is divided into three terms. The Session commences on September 18th and terminates on July 22nd. The course of instruction extends over two years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Inclusive fee, £4 4s. per term.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day and for pharmaceutical students.

ROYAL AGRICULTURAL COLLEGE,  
CIRENCESTER.

CHEMICAL DEPARTMENT.

*Professor.*—Prof. E. Kinch, F.C.S., F.I.C.

*Assistants.*—Cecil C. Duncan and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY.  
THE YORKSHIRE COLLEGE, LEEDS.

*Professor of Chemistry.*—Arthur Smithells, B.Sc. Lond., F.I.C.

*Lecturer in Organic Chemistry.*—Julius B. Cohen, Ph.D., F.I.C.

*Assistant Lecturer in Agricultural Chemistry.*—Herbert Ingle, F.I.C.

*Demonstrators.*—C. F. Baker, Ph.D., B.Sc., and A. C. Wright, B.A.

The Session begins October 10, 1892.

*Lecture Courses.*

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m., from October to the end of the second term, and during part of the third term. Fee for the Course, £4 4s.

2. Inorganic Chemistry.—First year Honours Course, Non-metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Inorganic Chemistry.—Second year Honours Course, Metals. Tuesday, Thursday, and Saturday at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 11.30 p.m. Fee £3 13s. 6d.

5. Organic Chemistry Honours Course.—Wednesday and Friday at 9.30 a.m. Fee, £2 12s. 6d.

6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.

7. Chemistry as Applied to Coal Mining.—Tuesday during the First Term, at 4 p.m.

8. Agricultural Chemistry.—Monday, Tuesday, and Friday, at 3 p.m., during first and second terms.

*Laboratory Courses.*

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session.—Students working six days per week, £18 18s.; five, £16 16s.; four, £14 14s.; three, £12 12s.

*Class in Practical Chemistry,* Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

*Practical Chemistry for Medical Students.*—October to end of March, at times to be arranged.

*Practical Course in Sanitary Chemistry.*—At times to be arranged.

*Practical Organic Chemistry for Medical Students.*—On Mondays, from 11 to 1, from April to July.

*Evening Class.*

A Course of twenty Lectures by Mr. Ingle, on the Elements of Inorganic Chemistry (the Non-Metals) will begin during the first and second Terms, on Wednesdays, at 7.30 p.m., beginning October 14. Fee, 10s. 6d.

*Dyeing Department.*

*Professor.*—J. J. Hummel, F.I.C.

*Lecturer and Research Assistant.*—A. G. Perkin, F.R.S.E.

*Assistant Lecturers.*—W. M. Gardner and J. B. Shaw.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

*Leather Industries Department.*

*Lecturer.*—H. R. Procter, F.I.C.

The full Course, which extends over a period of three years, is suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and is recommended to sons of tanners. The Course includes instruction in chemistry, engineering, microscopy, leather manufacture, and practical work in the Leather Industries Laboratory.

*Agricultural Department.*

*Professor.*—James Muir.

The full Course occupies two years, and includes instruction in chemistry, physics, botany, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, Emsley, Craven, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition, and one of the new 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

*Professor.*—J. Campbell Brown, D.Sc.

*Lecturer on Organic Chemistry.*—C. A. Kohn, B.Sc., Ph.D.

*Demonstrators and Assistant Lecturers.*—C. A. Kohn, B.Sc., Ph.D., T. L. Bailey, Ph.D., and S. B. Schryver, B.Sc., Ph.D.

*Assistant.*—H. H. Froyssell.

The Session commences October 2nd.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

*Lecture Courses.*

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, £4.

Course A.—Non-metals. Fee, £3 10s.

Course B.—Metals. Fee, £3 10s.

Course C.—Organic Chemistry. Fee, £3.

Course D.—Physical Chemistry. One Term. Fee, £1.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Course F.—Technological Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) Copper, Iron, and Steel. (3) Lead, Silver and Gold, Aluminium, and other Metals. (4) Distillation of Coal and Tar Industries. (5) Fuel. (6) Chemistry Applied to Sanitation. (7) Technical Gas Analysis. (8) Spectroscopy.

*Practical Classes.*

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Revision Class. (4) Senior: Practical Organic (Advanced Medical Class). (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Adulterations of Drugs and of Food, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class: Course arranged to suit the requirements of the London University B.Sc. Examinations, Pass and Honours, and for Intermediate M.B. Honours.

*Chemical Laboratory.*

The Chemical Laboratories provide accommodation for every kind of chemical work.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day . . . .	£4	£8
Two days . . . .	6	10
Three days . . . .	8	12
Four days . . . .	9	15
Whole week . . . .	10 10s.	20

*Technological Curriculum.*

*Preliminary Year.*—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, or Physics. Elementary Engineering, Drawing, and Design (in this or one of the following years). French or German. Or the Course for the Preliminary Examination, Victoria University, may be taken.

*First Year.*—Chemistry—Courses A and B; Chemical Laboratory three days per week; Practical Organic Class during the Summer Term; Technological Chemistry, Course F. Physics, with laboratory work, one

day per week. Mathematics (intermediate). German; Intermediate B.Sc. Examination may be passed. Engineering, First Year Course, Autumn and Lent Terms.

*Second Year.*—Chemistry, Lecture Course on Organic Chemistry, C, Lecture Course E or D, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

*Third Year.*—Courses D, F, and C. Any other Courses omitted in a previous year. Laboratory, five days per week. Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry of Great Britain and Ireland may be taken. Three years study after passing the Preliminary Examination of Victoria University are required for the B.Sc. Degree in the Honours School of Chemistry.

*Evening Classes.*

Lectures will be given on Chemistry in relation to every-day Industries.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1893, on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

LIVERPOOL COLLEGE OF CHEMISTRY.

*Principal.*—George Tate, Ph.D., F.I.C., F.C.S.

The Laboratories are open daily from 10 to 5, excepting Saturdays, when they close at 1 p.m. The course of instruction is adapted to the requirements of students of Chemistry as a science, and in its applications to chemical and metallurgical industries. The fee for a three years' course of study is eighty guineas, or per session of three months eight guineas.

Prospectuses, containing full particulars of the day and evening classes, may be had on application at the College.

DURHAM COLLEGE OF SCIENCE,  
NEWCASTLE-ON-TYNE.

*Professor of Chemistry.*—P. Phillips Bedson, D.Sc., F.I.C., F.C.S.

*Lecturer in Chemistry.*—Saville Shaw, F.C.S.

*Lecturer in Agricultural Chemistry.*—R. Greig Smith, B.Sc. (Edin.), F.C.S.

*Assistant Lecturer and Demonstrator.*—F. C. Garrett, M.Sc. (Vit.), F.C.S.

The Session will commence on September 25th, 1893.

1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11.15 a.m., and will commence on Wednesday, October 4th. Fee, £3 10s. for the Session.

2. *Advanced Course.*—Inorganic Chemistry, Tuesdays and Fridays, 3 to 4 p.m., during Michaelmas and Epiphany Terms.

3. *Organic Chemistry*.—A Course of about ninety Lectures will be given throughout the Session, the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a.m., and will commence on Thursday, October 5th. Fee, £3 10s. for the Session.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for each course, £2 2s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m., commencing October 10th. Fee, £1 1s.

*Metallurgy and Assaying*.—Lecturer, Saville Shaw, F.C.S. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry-Assaying, and in the preparation and analysis of Alloys, &c. Fee as for Chemical Laboratory.

*Agricultural Chemistry*.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

A Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, Two Guineas.

*Practical Chemistry*.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees*.—Students working six days per week, £5 5s. per term; three days, £3 3s. per term, £8 8s. per session; two days, £2 2s. per term, £5 5s. per session; one day per week, £1 11s. 6d. per term, £3 3s. per session.

*Courses of Study*.—Students will be divided into two classes:—(1) Regular, or Matriculated Students; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.

2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

*Associateship in Physical Science*.—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year. Associates in Science are admissible one year after obtaining the title of Associate to examination for the degree of Bachelor of Science of the University of Durham.

*Exhibitions*.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 25th.

*Evening Lectures*.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable [Scholarships are available for students.

## OWENS COLLEGE,

## VICTORIA UNIVERSITY, MANCHESTER.

*Professor and Director of the Chemical Laboratory*.—Harold B. Dixon, M.A., F.R.S.

*Professor of Organic Chemistry*.—W. H. Perkin, Ph.D., F.R.S.

*Demonstrators and Assistant Lecturers*.—George H. Bailey, D.Sc., Ph.D.; Arthur Harden, M.Sc., Ph.D.; P. J. Hartog, B.Sc.; and S. H. Davies, B.Sc.

*Lecturer in Dyeing and Printing*.—Ernest Bentz.

*Assistant Lecturer in Metallurgy*.—Gilbert J. Fowler, M.Sc.

The Session begins on October 4, 1892, and ends on June 23, 1893.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

*General Chemistry*.

*General Chemistry Course*.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

*Introduction to Organic Chemistry*.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

*First Year Honours Course*.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

*Second Year Honours Course*.—Mondays, Wednesdays, Fridays, 3.30 p.m., during the two Winter Terms. The Metals.

*Third Year Honours Course*.—At times to be arranged. Physical Chemistry.

*Organic Chemistry (General)*.—Tuesdays and Thursdays, 9.30, during two Winter Terms.

*Organic Chemistry (Honours)*.—Mondays and Fridays, 9.30, during the two Winter Terms.

*History of Chemistry and Chemical Philosophy*.—Wednesdays, 10.30, during the Session.

**METALLURGY**.—*Lectures*: The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical*: Saturdays, 9.30. The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

An ordinary degree of B.Sc. in Chemistry, Victoria University, may be taken at the College in three years. The Degree of B.Sc. with Honours in Chemistry can also be taken in three years, and the College Certificate in Technological Chemistry may be taken in the same time.

A number of important Scholarships, &c., are available to students.

*Technological Chemistry*.

*First Course*.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

*Second Course*.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

*Third Course*.—The Chemistry of Coal Tar.

*Fourth Course*.—Natural and Artificial Dye-stuffs.

*Fifth Course*.—Calico-printing.

*Certificates in Applied Chemistry*.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third

year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

A combined Lecture and Laboratory Course on the Bleaching, Dyeing, and Printing of Cotton Fabrics is given on Saturdays, at 3, by Mr. Bentz.

#### UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENT OF CHEMISTRY, METALLURGY,  
AND AGRICULTURE.

*Professor of Chemistry.*—Frank Clowes, D.Sc. Lond., F.I.C.

*Demonstrators of Chemistry.*—J. B. Coleman, A.R.C.Sc. Dublin, F.I.C., and R. L. Whiteley, F.I.C.

*Lecturers.*—J. B. Coleman, F.I.C.; R. L. Whiteley, F.I.C.; C. Haydon White, M.R.C.S.; J. W. Carr, M.A.; F. R. Sargeant; M. J. R. Dunstan, M.A., F.R.S.E.; and F. T. Addyman, B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The dates of commencement and end of Terms in the Session 1892-93 will be as follows:—First Term, October 9th to December 23rd; Second Term, January 15th to March 31st; Third Term, April 16th to June 30th.

*Lecture Courses.*—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Non-Metals for the first two terms and for Elementary Organic Chemistry in the third term. In his second year he takes the course on Metals for the first two terms, and Advanced Organic Chemistry. In his third year he attends a course on Applied Chemistry during the first two terms. Fee for Day Lectures and Classes: Non-Metals or Metals 42s.; Organic Chemistry (one term) 21s.; Applied Chemistry, 30s.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 2s. 6d.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

*Practical Chemistry.*—The chemical laboratory is open every day except Saturday from 10 to 5, on Saturday from 10 to 12, and on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation and in Qualitative and Quantitative Analysis; and students are enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees: For one term, £7; for the session, £18; for day students for six hours weekly, 40s., and 5s. extra for each additional hour per

week. For evening students, 10s. for one evening per week, and 20s. for two evenings per week, per term.

*Courses of Technical Chemistry Lectures* are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

*A Pharmaceutical Curriculum* extending over three Winter Sessions, includes Pharmaceutical Chemistry (lectures and laboratory work), Pharmaceutical Botany (lectures and class work on specimens), Materia Medica (lectures and use of specimens), Practical Dispensing, taught by demonstrations and practical work in the laboratory, and Lecture and Laboratory Instruction in Physics.

*Government Lectures and Classes.*—Evening Lectures and Laboratory instruction will be given by the Demonstrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in October. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

*An Agricultural Course* of instruction, extending over two years, is now organised under the general direction of Mr. M. J. R. Dunstan, M.A., F.R.S.E. It includes instruction in chemistry, botany, agriculture, with practical work on experimental fields, dairy work, fariery, land surveying, &c. The instruction is designed for those who intend to become farmers, bailiffs, land agents, or colonists, and may be extended to a third year if desired. Fee, £15 per annum for residents in Notts, £20 to residents in other counties.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

#### FIRTH COLLEGE, SHEFFIELD.

*Professor of Chemistry.*—W. Carleton Williams, B.Sc., F.C.S.

*Demonstrators and Assistant Lecturers.*—G. Young, Ph.D., and L. T. O'Shea, B.Sc., F.C.S.,

The Session will commence on October 1st.

*First Year's Course.*—Chemistry of the Non-Metallic Elements. Monday, Wednesday, Thursday, from 10 to 11 a.m. Fee, £3 3s.

*Second Year's Course.*—Chemistry of Metals. Tuesday, Wednesday, and Thursday, from 10 to 11 a.m. £3 3s.; or for the First and Second Courses, £5 5s.

*Third Year's Course.*—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 2s.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

*Laboratory.*—Working hours to be arranged between Professor and Students.

*Sessional Fees for Day Students:*—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Students who have worked for three sessions in the Chemical Laboratory are eligible for election to a scholarship value £150 for two years.

*Evening Classes.*—Lectures, Wednesday, 8 to 9. Labo-

ratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s.

### UNIVERSITY COLLEGE, DUNDEE.

(UNIVERSITY OF ST. ANDREWS).

*Professor.*—Percy Frankland, Ph.D., B.Sc., F.R.S., &c.

*Assistant Lecturers and Demonstrators.*—F. J. Hambly, F.I.C., J. R. Appleyard, F.C.S., and John Foggie, F.C.S.

The tenth session of the College will be opened on October 10th, 1893.

The Lectures and Laboratory practice in this University are recognised by the Royal College of Physicians and Royal College of Surgeons, London, and by the Royal College of Surgeons, Edinburgh, and for degrees in Science and Medicine by the Universities of Edinburgh, Glasgow, and Aberdeen.

The courses are suitable for the Degrees of the London University and for the Civil Service appointments, and will also satisfy the requirements of students in Pharmacy, and of students who intend to become candidates for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

#### Lecture Courses.

The object of these courses will be (1) to give systematic instruction in the general principles of the science, and information regarding the elements and their more important compounds; (2) to show how this knowledge may be usefully applied in the Arts and Manufactures.

A course of instruction in Practical Chemistry in the Laboratory is recommended to all who wish to obtain a sound knowledge of the science, and the methods of applying it to useful purposes—the duration of such course depending upon the special wants of the student.—The Professor will be glad to give any information to intending students.

First year's lecture course: General Chemistry (Non-Metals, Metals, and Elements of Organic Chemistry) (100 lectures), Monday, Tuesday, Wednesday, Thursday, and Friday, from 10 to 11 a.m.; fee, £3 3s.

Second year's lecture course: 1. Advanced Inorganic Chemistry, including modern Chemical Theory (50 lectures). 2. Organic Chemistry (50 lectures). Fee for the whole course, £3 3s.

A Lecture Course on Analytical Chemistry will be given on Saturdays, from 9 to 10. Fee, £1 1s.

Courses of lectures will be given on Dyeing, Bleaching, and the Chemistry of the Textile Fibres, with practical instruction in the Laboratory and Dyehouse. In connection with this Department there is an extensive Technical Museum, containing a large collection of specimens illustrating many branches of Applied Chemistry, and particularly the local industries.

#### Practical Chemistry (Laboratory).

The aim of the Laboratory Courses is to make the student practically acquainted with the science, so that he may conduct chemical analysis and original research, and generally to fit him for applying the science to the Arts, Manufactures, Agriculture, and Public Health. The courses are also arranged for students preparing for their medical and pharmaceutical examinations. A three months' course of practical instruction in Sanitary Chemistry for the B.Sc. Edinburgh, in the department of Public Health, may be taken in the College Laboratory.

The Laboratory will be open for students daily from 9 a.m. to 4 p.m., except on Saturdays, when it will be closed at 2 p.m. Each student on entering will be allowed to arrange his working hours to suit his own convenience, but will be required to keep the hours when once fixed.

*Sessional Fees for Day Students.*—The fees for both sessions are—for six hours per week, £3 3s.; each ad-

ditional hour per week, 10s. 6d. Day students may not enter for less than six hours a week. Students joining the Laboratory during the second term will be charged two-thirds, and during the third term one-third of the above fees. Students may also enter for short periods, working every day in the week at the following fees:—For one month, £2 12s. 6d.; for two months, £5 5s.; for three months, £7 7s.

*Evening Classes.*—Courses of Lectures and Practical Laboratory instruction are given in Chemistry, Dyeing, and Bleaching.

#### Forster Research Scholarship.

This scholarship, of the value of £30, is awarded annually to the best student on the condition that he devotes himself during the ensuing year to original research in the College Laboratory.

### UNIVERSITY OF EDINBURGH.

#### DEPARTMENT OF CHEMISTRY.

*Professor.*—Alex. Crum Brown, M.D., D.Sc., F.R.S., Pres. C.S.

*Assistants.*—L. Dobbin, Ph.D.; H. Marshall, D.Sc.; W. W. Taylor, M.A.; and A. F. Watson, B.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to end of July.

*Lecture Courses.*—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. A class for advanced students is held in summer: it meets thrice weekly; fee £2 2s.

In addition to the above, Lecture Courses are given by the Assistants on special subjects, such as Chemical Theory, Physical Chemistry, or some particular branch of Organic and Inorganic Chemistry. These lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

*Laboratories.*—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 10 till 4. (Fees: Winter Session, £10 10s.; Summer Session, £6 6s.) Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

*Graduation.*—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Second B.Sc. Examination includes any three or more of the following subjects:—1. Mathematics. 2. Natural Philosophy. 3. Astronomy. 4. Chemistry. 5. Human Anatomy, including Anthropology. 6. Physiology. 7. Geology, including Mineralogy. 8. Zoology, including Comparative Anatomy. 9. Botany, including Vegetable Physiology. Chemistry in this

examination includes Inorganic Chemistry, Organic Chemistry, Relation between Chemical and Physical Properties, Complex Qualitative Analysis (practical), and Simple Quantitative Determinations (practical).

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination: The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

#### HERIOT-WATT COLLEGE, EDINBURGH.

*Professor.*—John Gibson, Ph.D., F.R.S.E.

*Assistant Professor.*—Arthur W. Bishop, Ph.D.

*Demonstrator.*—Bertram Prentice.

The Session begins October 1st, 1891.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Lecture Course to day students in Chemistry is mainly devoted to Inorganic Chemistry. In the Laboratory course each student is required to prepare and study the properties of the principal elementary and compound gases; to perform the more important experiments shown by the Professor in the Lecture Room; to make himself thoroughly acquainted with the preparation and purification of a number of salts. After a careful study of the reactions of the principal metals and acids, he passes on to a full course of the systematic qualitative analysis, and may then, if attending a second year, take up an extensive course of quantitative analysis (gravimetric, volumetric, and electrolytic), ultimately making a speciality of any branch of the subject which may be most necessary for his future work. Great attention has been paid to the thorough equipment of the Advanced Laboratories, and special facilities are given to advanced students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely chemical or of a technical nature.

The teaching in the Evening Classes is based on the Syllabus of the Science and Art Department, and includes Elementary, Advanced, and Honours Courses in Theoretical and Practical Inorganic and Organic Chemistry.

#### GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following any industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Mr. L. H. Cooke, A.R.S.M., formerly Assistant in the Mining Department of the Royal School of Mines, London, has been appointed Lecturer on Mining and Geology at this College. Complete courses of instruction in Metallurgy and Mining will now be given in both Day and Evening Classes.

Copies of the Calendar for 1893-94 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

#### UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

*Professor of Chemistry.*—T. Purdie, B.Sc., Ph.D., Assoc. R.S.M.

The Session begins on October 10th. A Competitive Examination, open to intending Students of Arts or Science, for a number of Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held in the beginning of October. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

#### *Lecture Courses.*

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

*First Year's Course.*—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment. The Lectures are supplemented by a Course of Laboratory Practice of two hours per week, to which Members of the Class are admitted without additional fee.

These courses of instruction are intended to meet the requirements of the Arts' Curriculum; also of candidates for the First B.Sc. Examination, and of students of medicine, so far as Theoretical Chemistry is concerned.

*Second Year's Course.*—The first part of the Course is devoted to Organic Chemistry, and the second part treats of the General Principles and Theory of Chemistry, the instruction in general being such as is required for the Second B.Sc. Examination.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £13 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

#### *Practical Chemistry.*

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the First and Second B.Sc. Examinations, and for Students of Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly.

#### QUEEN'S COLLEGE, BELFAST.

*Professor.*—E. A. Letts, Ph.D., F.R.S.E., F.C.S.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week until the beginning of April, and on three days of each week after May 1st,

at 2 p.m. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry.

II.—*Advanced and Organic Chemistry*.—Lectures on these subjects are given during the first or second terms, or from May 1st until the middle of July, as may suit the convenience of the class.

III.—*Practical Chemistry*.—In this course the Students are instructed in the general methods of conducting Chemical Analyses.

IV.—*Laboratory Pupils*.—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

#### QUEEN'S COLLEGE, CORK.

*Professor*.—Augustus E. Dixon, M.D.

*Assistant*.—D. J. O'Mahony, F.C.S.

The College Session begins on October 17th, 1893, and ends on June 9th, 1894. The classes are open to male and female students.

*Systematic Chemistry*.—(1) Inorganic Chemistry; Elementary Organic Chemistry; Chemical Philosophy. (2) Advanced Organic Chemistry, and Chemical Philosophy.

Fee.—For each Sessional Course, £2. Each subsequent Course, £1.

*Practical Chemistry*.—(1) The General Course of Practical Chemistry, consisting of about forty Lectures of two hours each, begins on January 8th, 1894. (2) A Course for Pharmaceutical Students. (3) Special Courses.—Fee for each Sessional Course, £3.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

#### QUEEN'S COLLEGE, GALWAY.

*Professor*.—Alfred Senier, Ph.D., M.D., F.I.C.

The College Session is divided into three terms. The First Term extends from October 17 to December 23, the Second Term from January 8 to March 17, and the Third Term from March 31 to June 12.

The study of Chemistry is pursued throughout the Session by means of experimental lectures and by practice in the laboratory, where each student works independently. Attention is also directed to those technical applications of the science which the wants of the students or the special needs of the West of Ireland appear to demand.

*Theory of Chemistry*.—(1) A General Course of about seventy lectures is given in the First and Second Terms, embracing inorganic and organic chemistry, the non-metallic elements, the atomic theory, the metals, and the synthesis and properties of the more important fatty and aromatic compounds and their probable constitution. (2) A Special Honour Course of about twenty lectures is given in the Third Term. This course is devoted chiefly to organic synthesis, and includes a review of some of the latest researches.

*Experimental Work*.—(1) A General Course of about forty lessons of two hours each is given in the laboratory in the First and Second Terms, embracing the elements of qualitative analysis and the chemical examination of urine. (2) Special Courses of experiments in volumetric and gravimetric analysis, in inorganic and organic preparations, and in the applications of chemistry to medicine and the arts are arranged to meet the requirements of the students.

For prospectuses and further particulars apply to the Registrar.

ROYAL COLLEGE OF SCIENCE FOR IRELAND,  
STEPHEN'S GREEN, DUBLIN.  
(SCIENCE AND ART DEPARTMENT).

*Professor of Chemistry*.—W. N. Hartley, F.R.S.

*Assistant Chemist*.—Hugh Ramage, F.I.C., Associate of the Royal College of Science, Dublin.

*Demonstrator of Chemistry and Assaying*.—E. V. Clark, Associate of the Royal College of Science, London.

The Session commences on Monday, October 2nd, 1893, and ends on June 21st, 1894.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures. The Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Chemical Manufactures and Metallurgy; (3) Analytical and Experimental Chemistry; (4) Instructions in Chemical Research.

Fees payable by Associate Students in the Faculty of Manufactures:—For the entire Course—first year, £19; second year, £25; third year, £12.

Fees payable by Non-Associates:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month; £5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months; £12 for the entire session.

NOTE.—Important changes have been made in the Curriculum by which the First Year's Course of study has been simplified. Full particulars are contained in the Directory of the College, which may be had on application to the Secretary.

The following are supplementary courses of instruction arranged for those who are attending a Course of Lectures:—

- (1) Laboratory Instruction in the Theory of Chemistry.
- (2) An Analytical Course for Students in Engineering.
- (3) A Course of Practical Chemistry for Medical Students.
- (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health.
- (5) Assaying.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Examinations of the Department of Science and Art.

### CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—*City and Guilds Central Institution, Exhibition Road*.—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of industry, whether Manufactures or Arts. The main purpose of the instruction

given is to point out the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations will begin on Tuesday, Sept. 19th, and the Winter Session opens on Wednesday, October 4th. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. The College embraces the following departments:—1. Mechanical Engineering and Applied Mathematics; 2. Electrical Engineering and Applied Physics; 3. Industrial and Technical Chemistry; 4. Applied Art; 5. the Building Trades. The College is under the general direction of the Principal. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College at 10 o'clock on Tuesday, September 26th, 1893.

ADDEY'S SCIENCE AND ART SCHOOL, Church Street, Deptford.—Head Master, William Ping, F.C.S.—Day and Evening Classes in Theoretical and Practical Chemistry, &c. The Classes are approved by the County Council.

BIRKBECK LITERARY AND SCIENTIFIC INSTITUTION, BREAM'S BUILDINGS, CHANCERY LANE.—*Chemistry*: Courses will be conducted, commencing October 2nd, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University. *Inorganic Chemistry*: Mr. G. Chaloner, F.C.S. Lectures—Elementary, Tuesdays, 8.30 p.m.; Advanced, Thursdays, 7 p.m.; Practical, Tuesdays, 6—8 p.m.; Thursdays, 8—10 p.m.; Saturdays, 7—9 p.m. *Organic Chemistry*: Mr. F. Gossling, B.Sc. Lectures—Elementary, Wednesdays, 6.30 p.m.; Practical, Wednesdays, 7.30 p.m., Fridays, 6 p.m.

THE CENTRAL SCHOOL OF CHEMISTRY AND PHARMACY, 173, Marylebone Rd., London.—Mr. J. Woodland, F.C.S., Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c., and Mr. Lionel Cooper. Lectures are given on Chemistry, Botany, Materia Medica, Pharmacy, Latin, and Physics. Laboratory instruction.

MIDDLESEX COLLEGE OF CHEMISTRY AND PHARMACY, 40, Charlotte Street, Portland Place.—Principal, F. H. Painter. Day and Evening Classes and Laboratory Instruction in Chemistry, Pharmacy, Materia Medica, &c.

PENYVERN HOUSE MILITARY AND ENGINEERING COLLEGE, Penyvern Road, Earl's Court, S.W.

SOUTH LONDON SCHOOL OF PHARMACY, 325, Kennington Road, S.E.—Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., Daily, at 9 a.m. (Organic) and 10 a.m. (Inorganic). Lectures on Botany daily at 12 noon, and at 2 p.m. on Materia Medica and

Pharmacy, by Mr. Dodd, F.C.S. The Laboratories for Qualitative and Quantitative Analysis open daily from 9 till 5, under the direction of Mr. de Koningh, F.I.C., F.C.S. The Students' Laboratory of this Institution is specially designed to accommodate 40 Students. The Technical Laboratory is open daily from 9 till 4, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees for the first three months £12 12s.; afterwards £3 3s. per month respectively, inclusive of all departments.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Head of the Chemical Department, Mr. A. G. Bloxam, F.I.C.; Assistant, Mr. H. C. L. Bloxam. Lectures and Practical Classes, also special classes in Chemistry as applied to various arts and industries, are held in the evenings from 7.30—10.0, and are open to both sexes.

PEOPLE'S PALACE, Mile End Road, E. (Draper's Company's Institute).—Lecturer, Mr. D. S. Macnair, B.Sc., F.C.S.; Assistant, Mr. F. G. Pope. The classes are open to both sexes without limit of age. Evening classes in Theoretical and Practical Chemistry. The Session commences on Monday, September 25th.

POLYTECHNIC INSTITUTE, 309, Regent Street, London, W.—Mr. R. A. Ward and Assistants.—Evening Classes in Theoretical and Practical Chemistry, &c.. The Classes are open to both sexes. The next term commences on October 2nd, 1893.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C. (Science Department of the Univ. Corr. Coll.).—The large Chemical, Biological, and Physical laboratories opened last Session have been found admirably suited to their purpose, and the proportion of passes in the London University Science Lists has increased rapidly. Students may work either for long or short periods. The Session commences October 2nd, 1893.

WESTMINSTER COLLEGE OF CHEMISTRY AND PHARMACY, Trinity Square, Borough, S.E.—Messrs. Wills and Wootton. Day and Evening Classes.

BRISTOL MEDICAL SCHOOL.—Mr. T. Coomber, F.C.S.

THE CLIFTON LABORATORY, Berkeley Square, Bristol.—Principal, Mr. Ernest H. Cook, D.Sc.Lond., F.I.C., F.C.S.; Assistants, Messrs. H. J. Palmer, F.C.S., S. B. Froude, and J. M. Vaughan. Students are received either as Private Pupils or Members of a Class. Instruction is given to those requiring to use science or scientific methods in Commercial and Industrial pursuits, or in preparing for Examinations. Every effort is made to produce thorough chemists rather than successful examinees.

LEEDS SCHOOL OF SCIENCE AND TECHNOLOGY, (Mechanics' Institution, Leeds).—Lecturer on Chemistry, Mr. S. J. Harris, M.Sc., F.C.S. Lecturer on Metallurgy, Mr. B. A. Burrell, F.I.C., F.C.S. Lecturer on Physics, Mr. A. Wheatley, B.Sc. Practical Physics and Demonstrator in Chemistry, Mr. H. Holbeche, A.R.C.S. The Chemical Laboratory is open for five evenings, and the Metallurgical Laboratory for two evenings per week. There is a three years' course of lectures in Inorganic Chemistry, and a two years' course in Organic Chemistry and Metallurgy.

INSTITUTE OF CHEMICAL TECHNOLOGY, Hackins Hey, Liverpool (A. Norman Tate and Co.).—Principal, Mr. F. H. Tate, F.I.C. The course of instruction is intended more especially for students who wish to gain a knowledge of chemistry and the allied sciences in their relation to industrial and commercial pursuits, and embraces a thorough preliminary course of theoretical chemistry and practical laboratory work, followed by instruction in chemical technology fitted to the requirements of each pupil. In addition to these chemical studies, students

who desire it can enter upon a special course calculated to afford them knowledge useful in the erection and arrangement of manufactories and plant, and construction of apparatus.

THE MUNICIPAL TECHNICAL SCHOOL, Princess Street, Manchester.—Mr. J. H. Reynolds. Day and Evening Classes.

SHEFFIELD BOROUGH ANALYSTS' LABORATORY, 1, Surrey Street.—Mr. A. H. Allen, F.C.S. Day and Evening Classes.

STOCKPORT TECHNICAL SCHOOL.—Department of Chemistry and Dyeing.—Principal: Mr. R. J. Brown, M.Sc. A syllabus with full particulars of the courses of instruction, hours, fees, &c., is obtainable on application.

TECHNICAL INSTITUTE, SWANSEA.—Classes in Theoretical and Practical Inorganic Chemistry and Metallurgy, Electricity, Mathematics, &c., from October to May. Principal, W. Morgan, Ph.D., F.C.S., F.I.C.

ABERDEEN UNIVERSITY.—Prof. Japp.

SCHOOL OF MEDICINE (NEW VETERINARY COLLEGE, EDINBURGH).—Mr. Ivison Macadam.

SCHOOL OF MEDICINE, Edinburgh.—Dr. S. Macadam, Mr. King, Mr. I. Macadam, Mr. Paterson, and Drs. Aitken and Readman.

SURGEON'S HALL, Nicolson Street, Edinburgh.—Mr. Ivison Macadam. Laboratory work and demonstrations in Agricultural Chemistry. Chemistry Class for Women.

ST. MUNGO'S COLLEGE AND SCHOOL OF MEDICINE, EDINBURGH.—Dr. Milne.

GLASGOW UNIVERSITY.—Prof. J. Ferguson.

GLASGOW VETERINARY COLLEGE.—Professor Cooke.

ANDERSON'S COLLEGE, GLASGOW.—Mr. J. R. Watson.

LABORATORY OF SCIENCE, Painters' Hall, Paisley.—Mr. J. M. B. Taylor. Practical Agricultural Chemistry, October to February inclusive. Practical Botany, Geology, and Mineralogy from March to September.

ROYAL COLLEGE OF SURGEONS IN IRELAND, DUBLIN.—Professor of Chemistry and Hygiene: Sir Charles A. Cameron, M.D., F.R.C.S.I. Instruction is given in the College Laboratory in General, Practical, and Analytical Chemistry, and in the subjects (Physical, Chemical, and Microscopical) required for Examinations in Public Health and to educate for the position of Public Analyst.

DUBLIN, CATHOLIC UNIVERSITY.—Dr. Campbell.

## CORRESPONDENCE.

### SECTION B.

#### BRITISH ASSOCIATION, NOTTINGHAM MEETING.

To the Editor of the *Chemical News*.

SIR,—I have had several requests from brother chemists to furnish some outline of the Programme for the Chemical Section at the approaching Nottingham Meeting. As far as the order of some of the leading events can be stated, before the meeting of the Sectional Committee, it will be as follows:—President's Address, treating mainly of the "Comparative Chemistry of the Elements," at 12, on Thursday, Sept. 14th; M. Moissan's demonstration of the preparation and properties of Fluorine, Friday, 15th; Bacteriology in its chemical aspects, discussion introduced by Dr. Percy Frankland, Monday, 18th; "Colliery Explosions," discussion introduced by Prof. Harold B. Dixon, Tuesday, 19th. The Sectional proceedings commence at 11 o'clock.—I am, &c.,

FRANK CLOWES, Hon. Local Sec.

## 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. cxvii., No. 8, August 21, 1893.

This number contains no chemical matter.

*Bulletin de la Société Chimique de Paris.*  
Series 3, Vols. ix. and x., No. 12.

**A New Method of Preparing Urea.**—A. Reychler.—The author obtains urea in the wet way by acting upon potassium or ammonium cyanide with an alkaline hypochlorite, and finds the actual yield 89.4 per cent. By Volhard's method, which is very tedious, the yield is only 68 per cent.

**Essential Oil of Eucalyptus.**—G. Bouchardat and Oliveiro.—The oil in question, obtained from specimens of eucalyptus grown in the South of France, appears to be a mixture of various products.

**Chemical Composition of Oil of Niaouli.**—G. Bertrand.—Already inserted.

WILLIAM F. CLAY,  
CHEMICAL AND TECHNICAL BOOKSELLER,  
18, Teviot Place, Edinburgh.

### SPECIALITIES.

SECOND-HAND CHEMICAL LITERATURE (*English and Foreign*).  
The most extensive Stock in Great Britain, including New Publications.

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CHEMICAL LITERATURE IN ANY QUANTITY PURCHASED FOR CASH  
OR EXCHANGED AT THE HIGHEST MARKET VALUE.  
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## THE CHEMICAL NEWS.

VOL. LXVII., No. 1764.

BRITISH ASSOCIATION  
FOR THE  
ADVANCEMENT OF SCIENCE.

NOTTINGHAM, 1893.

INAUGURAL ADDRESS OF THE PRESIDENT,  
J. C. BURDON-SANDERSON, M.A., M.D., LL.D., D.C.L.,  
F.R.S., F.R.S.E.,

Professor of Physiology in the University of Oxford.

We are assembled this evening as representatives of the sciences—men and women who seek to advance knowledge by scientific methods. The common ground on which we stand is that of belief in the paramount value of the end for which we are striving, of its inherent power to make men wiser, happier, and better; and our common purpose is to strengthen and encourage one another in our efforts for its attainment. We have come to learn what progress has been made in departments of knowledge which lie outside of our own special scientific interests and occupations, to widen our views, and to correct whatever misconceptions may have arisen from the necessity which limits each of us to his own field of study; and, above all, we are here for the purpose of bringing our divided energies into effectual and combined action.

Probably few of the members of the Association are fully aware of the influence which it has exercised during the last half-century and more in furthering the scientific development of this country. Wide as is the range of its activity, there has been no great question in the field of scientific inquiry which it has failed to discuss; no important line of investigation which it has not promoted; no great discovery which it has not welcomed. After more than sixty years of existence it still finds itself in the energy of middle life, looking back with satisfaction to what it has accomplished in its youth, and forward to an even more efficient future. One of the first of the national associations which exist in different countries for the advancement of science, its influence has been more felt than that of its successors because it is more wanted. The wealthiest country in the world, which has profited more—vastly more—by science than any other, England stands alone in the discredit of refusing the necessary expenditure for its development, and cares not that other nations should reap the harvest for which her own sons have laboured.

It is surely our duty not to rest satisfied with the reflection that England in the past has accomplished so much, but rather to unite and agitate in the confidence of eventual success. It is not the fault of governments, but of the nation, that the claims of science are not recognised. We have against us an overwhelming majority of the community, not merely of the ignorant, but of those who regard themselves as educated, who value science only in so far as it can be turned into money; for we are still in great measure—in greater measure than any other—a nation of shopkeepers. Let us who are of the minority—the remnant who believe that truth is in itself of supreme value, and the knowledge of it of supreme utility—do all that we can to bring public opinion to our side, so that the century which has given Young, Faraday, Lyell, Darwin, Maxwell, and Thomson to England, may before it closes see us prepared to take our part with other countries in combined action for the full development of natural knowledge.

Last year the necessity of an imperial observatory for physical science was, as no doubt many are aware, the subject of a discussion in Section A, which derived its interest from the number of leading physicists who took part in it, and especially from the presence and active participation of the distinguished man who is at the head of the National Physical Laboratory at Berlin. The equally pressing necessity for a central institution for chemistry, on a scale commensurate with the practical importance of that science, has been insisted upon in this Association and elsewhere by distinguished chemists. As regards biology I shall have a word to say in the same direction this evening. Of these three requirements it may be that the first is the most pressing. If so, let us all, whatever branch of science we represent, unite our efforts to realise it, in the assurance that if once the claim of science to liberal public support is admitted, the rest will follow.

In selecting a subject on which to address you this evening I have followed the example of my predecessors in limiting myself to matters more or less connected with my own scientific occupations, believing that in discussing what most interests myself I should have the best chance of interesting you. The circumstance that at the last meeting of the British Association in this town, Section D assumed for the first time the title which it has since held, that of the Section of Biology, suggested to me that I might take the word "Biology" as my starting-point, giving you some account of its origin and first use, and of the relations which subsist between biology and other branches of natural science.

*Origin and Meaning of the Term "Biology."*

The word "biology," which is now so familiar as comprising the sum of the knowledge which has as yet been acquired concerning living nature, was unknown until after the beginning of the present century. The term was first employed by Treviranus, who proposed to himself as a life-task the development of a new science, the aim of which should be to study the forms and phenomena of life, its origin and the conditions and laws of its existence, and embodied what was known on these subjects in a book of seven volumes, which he entitled "Biology, or the Philosophy of Living Nature." For its construction the material was very scanty, and was chiefly derived from the anatomists and physiologists. For botanists were entirely occupied in completing the work which Linnæus had begun, and the scope of zoology was in like manner limited to the description and classification of animals. It was a new thing to regard the study of living nature as a science by itself, worthy to occupy a place by the side of natural philosophy, and it was therefore necessary to vindicate its claim to such a position. Treviranus declined to found this claim on its useful applications to the arts of agriculture and medicine, considering that to regard any subject of study in relation to our bodily wants—in other words to utility—was to narrow it, but dwelt rather on its value as a discipline and on its surpassing interest. He commends biology to his readers as a study which, above all others, "nourishes and maintains the taste for simplicity and nobleness; which affords to the intellect ever new material for reflection, and to the imagination an inexhaustible source of attractive images."

Being himself a mathematician as well as a naturalist, he approaches the subject both from the side of natural philosophy and from that of natural history, and desires to found the new science on the fundamental distinction between living and non-living material. In discussing this distinction, he takes as his point of departure the constancy with which the activities which manifest themselves in the universe are balanced, emphasising the impossibility of excluding from that balance the vital activities of plants and animals. The difference between vital and physical processes he accordingly finds, not in the nature of the processes themselves, but in their co-

ordination; that is, in their adaptedness to a given purpose, and to the peculiar and special relation in which the organism stands to the external world. All of this is expressed in a proposition difficult to translate into English, in which he defines life as consisting in the reaction of the organism to external influences, and contrasts the uniformity of vital reactions with the variety of their exciting causes.\*

The purpose which I have in view in taking you back as I have done to the beginning of the century is not merely to commemorate the work done by the wonderfully acute writer to whom we owe the first scientific conception of the science of life as a whole, but to show that this conception, as expressed in the definition I have given you as its foundation, can still be accepted as true. It suggests the *idea of organism* as that to which all other biological ideas must relate. It also suggests, although perhaps it does not express it, that *action* is not an attribute of the organism but of its essence—that if, on the one hand, protoplasm is the basis of life, life is the basis of protoplasm. Their relations to each other are reciprocal. We think of the visible structure only in connection with the invisible process. The definition is also of value as indicating at once the two lines of inquiry into which the science has divided by the natural evolution of knowledge. These two lines may be easily educed from the general principle from which Treviranus started, according to which it is the fundamental characteristic of the organism that all that goes on in it is to the advantage of the whole. I need scarcely say that this fundamental conception of organism has at all times presented itself to the minds of those who have sought to understand the distinction between living and non-living. Without going back to the true father and founder of biology, Aristotle, we may recall with interest the language employed in relation to it by the physiologists of three hundred years ago. It was at that time expressed by the term *consensus partium*—which was defined as the concurrence of parts in action, of such a nature that each does *quod suum est*, all combining to bring about one effect “as if they had been in secret council,” but at the same time *constantiquadam naturæ lege*.† Professor Huxley has made familiar to us how a century later Descartes imagined to himself a mechanism to carry out this *consensus*, based on such scanty knowledge as was then available of the structure of the nervous system. The discoveries of the early part of the present century relating to reflex action and the functions of sensory and motor nerves, served to realise in a wonderful way his anticipations as to the channels of influence, afferent and efferent, by which the *consensus* is maintained; and in recent times (as we hope to learn from Professor Horsley's lecture on the physiology of the nervous system) these channels have been investigated with extraordinary minuteness and success.

Whether with the old writers we speak about *consensus*, with Treviranus about *adaptation*, or are content to take *organism* as our point of departure, it means that, regarding a plant or an animal as an organism, we concern ourselves primarily with its activities, or, to use the word which best expresses it, its energies. Now the first thing that strikes us in beginning to think about the activities of an organism is that they are naturally distinguishable into two kinds, according as we consider the action of the whole organism in its relation to the external world or to other organisms, or the action of the parts or organs in their relation to each other. The distinction to which we are thus led between the *internal* and *external* relations of plants and animals has of course always existed, but has only lately come into such prominence that it divides

biologists more or less completely into two camps,—on the one hand those who make it their aim to investigate the actions of the organism and its parts by the accepted methods of physics and chemistry, carrying this investigation as far as the conditions under which each process manifests itself will permit; on the other, those who interest themselves rather in considering the place which each organism occupies, and the part which it plays in the economy of Nature. It is apparent that the two lines of inquiry, although they equally relate to what the organism *does*, rather than to what it *is*, and therefore both have equal right to be included in the one great science of life, or biology, yet lead in directions which are scarcely even parallel. So marked, indeed, is the distinction that Prof. Haeckel some twenty years ago proposed to separate the study of organisms with reference to their place in Nature under the designation of “*Œcology*,” defining it as comprising “the relations of the animal to its organic as well as to its inorganic environment, particularly its friendly or hostile relations to those animals or plants with which it comes into direct contact.” Whether this term expresses it or not, the distinction is a fundamental one. Whether with the *œcologist* we regard the organism in relation to the world, or with the *physiologist* as a wonderful complex of vital energies, the two branches have this in common, that both studies fix their attention, not on stuffed animals, butterflies in cases, or even microscopical sections of the animal or plant body,—all of which relate to the framework of life,—but on life itself.

The conception of biology which was developed by Treviranus as far as the knowledge of plants and animals which then existed rendered possible, seems to me still to express the scope of the science. I should have liked, had it been within my power, to present to you both aspects of the subject in equal fulness; but I feel that I shall best profit by the present opportunity if I derive my illustrations chiefly from the division of biology to which I am attached—that which concerns the *internal* relations of the organism, it being my object not to specialise in either direction, but, as Treviranus desired to do, to regard it as part—surely a very important part—of the great science of Nature.

The origin of life, the first transition from non-living to living, is a riddle which lies outside of our scope. No seriously-minded person, however, doubts that organised nature, as it now presents itself to us, has become what it is by a process of gradual perfecting or advancement, brought about by the elimination of those organisms which failed to obey the fundamental principle of adaptation which Treviranus indicated. Each step, therefore, in this evolution is a reaction to external influences, the motive of which is essentially the same as that by which from moment to moment the organism governs itself. And the whole process is a necessary outcome of the fact that those organisms are most prosperous which look best after their own welfare. As in that part of biology which deals with the internal relations of the organism, the interest of the individual is in like manner the sole motive by which every energy is guided. We may take what Treviranus called *selfish* adaptation—*Zweckmässigkeit für sich selber*—as a connecting link between the two branches of biological study. Out of this relation springs another which I need not say was not recognised until after the Darwinian epoch—that, I mean, which subsists between the two evolutions, that of the race and that of the individual. Treviranus, no less distinctly than his great contemporary Lamarck, was well aware that the affinities of plants and animals must be estimated according to their developmental value, and consequently that classifi-

\* “Leben besteht in der Gleichförmigkeit der Reaktionen bei ungleichförmigen Einwirkungen der Aussenwelt.”—Treviranus, “*Biologie oder Philosophie der lebenden Natur*,” Göttingen, 1802, vol. i., p. 83.

† Bausner, “*De Consensu Partium Humani Corporis*,” Amst., 1556, Præf. ad lectorem, p. 4.

\* These he identifies with “those complicated mutual relations which Darwin designates as conditions of the struggle for existence.” Along with chorology—the distribution of animals—*œcology* constitutes what he calls *Relations physiologie*. Haeckel, “*Entwicklungsgang n. Aufgaben der Zoologie*,” *Jenaische Zeitsch.*, vol. v., 1869, p. 353.

cation must be founded on development; but it occurred to no one what the real link was between descent and development; nor was it, indeed, until several years after the publication of the "Origin" that Haeckel enunciated that "biogenetic law" according to which the development of any individual organism is but a memory, a recapitulation by the individual of the development of the race—of the process for which Fritz Müller had coined the excellent word "phylogenesis"; and that each stage of the former is but a transitory reappearance of a bygone epoch in its ancestral history. If, therefore, we are right in regarding ontogenesis as dependent on phylogenesis, the origin of the former must correspond with that of the latter; that is, on the power which the race or the organism at every stage of its existence possesses of profiting by every condition or circumstance for its own advancement.

From the short summary of the connection between different parts of our science you will see that biology naturally falls into three divisions, and these are even more sharply distinguished by their methods than by their subjects; namely, *Physiology*, of which the methods are entirely experimental; *Morphology*, the science which deals with the forms and structure of plants and animals, and of which it may be said that the body is anatomy,—the soul, development; and finally *Ecology*, which uses all the knowledge it can obtain from the other two, but chiefly rests on the exploration of the endless varied phenomena of animal and plant life as they manifest themselves under natural conditions. This last branch of biology—the science which concerns itself with the external relations of plants and animals to each other, and to the past and present conditions of their existence—is by far the most attractive. In it those qualities of mind which especially distinguish the naturalist find their highest exercise, and it represents more than any other branch of the subject what Treviranus termed the "philosophy of living nature." Notwithstanding the very general interest which several of its problems excite at the present moment, I do not propose to discuss any of them, but rather to limit myself to the humbler task of showing that the fundamental idea which finds one form of expression in the world of living beings regarded as a whole—the prevalence of the best—manifests itself with equal distinctness, and plays an equally essential part in the internal relations of the organism in the great science which treats of them—Physiology.

#### *Origin and Scope of Modern Physiology.*

Just as there was no true philosophy of living nature until Darwin, we may with almost equal truth say that physiology did not exist as a science before Johannes Müller. For although the sum of his numerous achievements in comparative anatomy and physiology, notwithstanding their extraordinary number and importance, could not be compared for merit and fruitfulness with the one discovery which furnished the key to so many riddles, he, no less than Darwin, by his influence on his successors was the beginner of a new era.

Müller taught in Berlin from 1833 to 1857. During that time a gradual change was in progress in the way in which biologists regarded the fundamental problem of life. Müller himself, in common with Treviranus and all the biological teachers of his time, was a vitalist, *i. e.*, he regarded what was then called the *vis vitalis*—the *Lebenskraft*—as something capable of being correlated with the physical forces; and as a necessary consequence held that phenomena should be classified or distinguished, according to the forces which produced them, as vital or physical, and that all those processes—that is, groups or series of phenomena in living organisms—for which, in the then very imperfect knowledge which existed, no obvious physical explanation could be found, were sufficiently explained when they were stated to be dependent on so-called vital laws. But during the period of Müller's greatest activity times were changing, and he

was changing with them. During his long career as Professor at Berlin he became more and more objective in his tendencies, and exercised an influence in the same direction on the men of the next generation, teaching them that it was better and more useful to observe than to philosophise; so that, although he himself is truly regarded as the last of the vitalists,—for he was a vitalist to the last,—his successors were adherents of what has been very inadequately designated the mechanistic view of the phenomena of life. The change thus brought about just before the middle of this century was a revolution. It was not a substitution of one point of view for another, but simply a frank abandonment of theory for fact, of speculation for experiment. Physiologists ceased to theorise because they found something better to do. May I try to give you a sketch of this era of progress?

Great discoveries as to the structure of plants and animals had been made in the course of the previous decade, those especially which had resulted from the introduction of the microscope as an instrument of research. By its aid Swann had been able to show that all organised structures are built up of those particles of living substance which we now call cells, and recognise as the seats and sources of every kind of vital activity. Hugo Mohl, working in another direction, had given the name "protoplasm" to a certain hyaline substance which forms the lining of the cells of plants, though no one as yet knew that it was the essential constituent of all living structures—the basis of life no less in animals than in plants. And, finally, a new branch of study—histology—founded on observations which the microscope had for the first time rendered possible, had come into existence. Bowman, one of the earliest and most successful cultivators of this new science, called it physiological anatomy,\* and justified the title by the very important inferences as to the secreting function of epithelial cells and as to the nature of muscular contraction, which he deduced from his admirable anatomical researches. From structure to function, from microscopical observation to physiological experiment, the transition was natural. Anatomy was able to answer some questions, but asked many more. Fifty years ago physiologists had microscopes, but had no laboratories. English physiologists—Bowman, Paget, Sharpey—were at the same time anatomists; and in Berlin Johannes Müller, along with anatomy and physiology, taught comparative anatomy and pathology. But soon that specialisation which, however much we may regret its necessity, is an essential concomitant of progress, became more and more inevitable. The structural conditions on which the processes of life depend had become, if not known, at least accessible to investigation; but very little indeed had been ascertained of the nature of the processes themselves,—so little indeed that if at this moment we could blot from the records of physiology the whole of the information which had been acquired, say in 1840, the loss would be difficult to trace,—not that the previously-known facts were of little value, but because every fact of moment has since been subjected to experimental verification. It is for this reason that, without any hesitation, we accord to Müller, and to his successors Brücke, du Bois-Reymond, Helmholtz, who were his pupils, and Ludwig in Germany, and to Claude Bernard† in France, the title of founders of our science. For it is the work which they began at that remarkable time (1845—55), and which is now being carried on by their pupils or their pupils' pupils in England, America, France, Germany, Denmark, Sweden, Italy, and even in that youngest contributor to the advancement of science, Japan, that physiology has been gradually built up to whatever completeness it has at present attained.

\* The first part of the *Physiological Anatomy* appeared in 1843. It was concluded in 1856.

† It is worthy of note that these five distinguished men were nearly contemporaneous! Ludwig graduated in 1839, Bernard in 1843, the other three between those dates. Three survive—Helmholtz, Ludwig, du Bois-Reymond.

What were the conditions which brought about this great advance which coincided with the middle of the century? There is but little difficulty in answering the question. I have already said that the change was not one of doctrine, but of method. There was, however, a leading idea in the minds of those who were chiefly concerned in bringing it about. That leading notion was that, however complicated may be the conditions under which vital energies manifest themselves, they can be split into processes which are identical in nature with those of the non-living world, and, as a corollary to this, that the analysing of a vital process into its physical and chemical constituents, so as to bring these constituents into measurable relation with physical or chemical standards, is the only mode of investigating them which can lead to satisfactory results.

There were several circumstances which at that time tended to make the younger physiologists (and all of the men to whom I have just referred were then young) sanguine, perhaps too sanguine, in the hope that the application of experimental methods derived from the exact sciences would afford solutions of many physiological problems. One of these was the progress which had been made in the science of chemistry, and particularly the discovery that many of the compounds which before had been regarded as special products of vital processes could be produced in the laboratory, and the more complete knowledge which had been thereby acquired of their chemical constitutions and relations. In like manner the new school profited by the advances which had been made in physics, partly by borrowing from the physical laboratory various improved methods of observing the phenomena of living beings, but chiefly in consequence of the direct bearing of the crowning discovery of that epoch (that of the conservation of energy) on the discussions which then took place as to the relations between vital and physical forces; in connection with which it may be noted that two of those who (along with Mr. Joule and your President at the last Nottingham meeting) took a prominent part in that discovery—Helmholtz and J. R. Mayer—were physiologists as much as they were physicists. I will not attempt even to enumerate the achievements of that epoch of progress. I may, however, without risk of wearying you, indicate the lines along which research at first proceeded, and draw your attention to the contrast between then and now. At present a young observer who is zealous to engage in research finds himself provided with the most elaborate means of investigation, the chief obstacle to his success being that the problems which have been left over by his predecessors are of extreme difficulty, all of the easier questions having been worked out. There were then also difficulties, but of an entirely different kind. The work to be done was in itself easier, but the means for doing it were wanting, and every investigator had to depend on his own resources. Consequently the successful men were those who, in addition to scientific training, possessed the ingenuity to devise and the skill to carry out methods for themselves. The work by which du Bois-Reymond laid the foundation of animal electricity would not have been possible had not its author, besides being a trained physicist, knows how to do as good work in a small room in the upper floor of the old University Building at Berlin as any which is now done in his splendid laboratory. Had Ludwig not possessed mechanical aptitude, in addition to scientific knowledge, he would have been unable to devise the apparatus by which he measured and recorded the variations of arterial pressure (1848), and verified the principles which Young had laid down thirty years before as to the mechanics of the circulation. Nor, lastly, could Helmholtz, had he not been a great deal more than a mere physiologist, have made those measurements of the time-relations of muscular and nervous responses to stimulation, which not only afford a solid foundation for all that has been done since in the same direction, but have served as models of physiological experiment, and as evidence

that perfect work was possible and was done by capable men, even when there were no physiological laboratories.

Each of these examples relates to work done within a year or two of the middle of the century.\* If it were possible to enter more fully on the scientific history of the time, we should, I think, find the clearest evidence, first, that the foundation was laid in anatomical discoveries, in which it is gratifying to remember that English anatomists (Allen Thomson, Bowman, Goodsir, Sharpey) took considerable share; secondly, that progress was rendered possible by the rapid advances which, during the previous decade, had been made in physics and chemistry, and the participation of physiology in the general awakening of the scientific spirit which these discoveries produced. I venture, however, to think that, notwithstanding the operation of these two causes, or rather combinations of causes, the development of our science would have been delayed had it not been for the exceptional endowments of the four or five young experimenters whose names I have mentioned, each of whom was capable of becoming a master in his own branch, and of guiding the future progress of inquiry.

Just as the affinities of an organism can be best learned from its development, so the scope of a science may be most easily judged of by the tendencies which it exhibits in its origin. I wish now to complete the sketch I have endeavoured to give of the way in which physiology entered on the career it has since followed for the last half-century, by a few words as to the influence exercised on general physiological theory by the progress of research. We have seen that no real advance was made until it became possible to investigate the phenomena of life by methods which approached more or less closely to those of the physicist, in exactitude. The methods of investigation being physical or chemical, the organism itself naturally came to be considered as a complex of such processes, and nothing more. And in particular the idea of adaptation, which, as I have endeavoured to show, is not a consequence of organism, but its essence, was in great measure lost sight of. Not, I think, because it was any more possible than before to conceive of the organism otherwise than as a working together of parts for the good of the whole, but rather that, if I may so express it, the minds of men were so occupied with new facts that they had not time to elaborate theories. The old meaning of the term "adaptation" as the equivalent of "design" had been abandoned, and no new meaning had yet been given to it, and consequently the word "mechanism" came to be employed as the equivalent of "process," as if the constant concomitance or sequence of two events was in itself a sufficient reason for assuming a mechanical relation between them. As in daily life so also in science, the misuse of words leads to misconceptions. To assert that the link between *a* and *b* is mechanical, for no better reason than that *b* always follows *a*, is an error of statement, which is apt to lead the incautious reader or hearer to imagine that the relation between *a* and *b* is understood, when in fact its nature may be wholly unknown. Whether or not at the time which we are considering, some physiological writers showed a tendency to commit this error, I do not think that it found expression in any generally accepted theory of life. It may, however, be admitted that the rapid progress of experimental investigation led to too confident anticipations, and that to some enthusiastic minds it appeared as if we were approaching within measurable distance of the end of knowledge. Such a tendency is, I think, a natural result of every signal advance. In an eloquent Harveian oration, delivered last autumn by Dr. Bridges, it was indicated how, after Harvey's great discovery of the circulation, men were too apt to found upon it explanations of all phenomena

\* The *Untersuchungen über thierische Electricität* appeared in 1848; Ludwig's researches on the circulation, which included the first description of the "kymograph" and served as the foundation of the "graphic method" in 1847; Helmholtz's research on the propagation in motor nerves in 1851.

whether of health or disease, to such an extent that the practice of medicine was even prejudicially affected by it. In respect of its scientific importance the epoch we are considering may well be compared with that of Harvey, and may have been followed by an undue preference of the new as compared with the old, but no more permanent unfavourable results have shown themselves. As regards the science of medicine, we need only remember that it was during the years between 1845 and 1860 that Virchow made those researches by which he brought the processes of disease into immediate relation with the normal processes of cell development and growth, and so, by making pathology a part of physiology, secured its subsequent progress and its influence on practical medicine. Similarly in physiology, the achievements of those years led on without any interruption or drawback to those of the following generation; while in general biology, the revolution in the mode of regarding the internal processes of the animal or plant organism which resulted from these achievements, prepared the way for the acceptance of the still greater revolution which the Darwinian epoch brought about in the views entertained by naturalists of the relations of plants and animals to each other and to their surroundings.

It has been said that every science of observation begins by going out botanising, by which, I suppose, is meant that collecting and recording observations is the first thing to be done in entering on a new field of inquiry. The remark would scarcely be true of physiology, even at the earliest stage of its development, for the most elementary of its facts could scarcely be picked up as one gathers flowers in a wood. Each of the processes which go to make up the complex of life requires separate investigation, and in each case the investigation must consist in first splitting up the process into its constituent phenomena, and then determining their relation to each other, to the process of which they form part, and to the conditions under which they manifest themselves. It will, I think, be found that even in the simplest inquiry into the nature of vital processes some such order as this is followed. Thus, for example, if muscular contraction be the subject on which we seek information, it is obvious that, in order to measure its duration, the mechanical work it accomplishes, the heat wasted in doing it, the electromotive forces which it develops, and the changes of form associated with these phenomena, special modes of observation must be used for each of them, that each measurement must be in the first instance separately made, under special conditions, and by methods specially adapted to the required purpose. In the synthetic part of the inquiry the guidance of experiment must again be sought for the purpose of discriminating between apparent and real causes, and of determining the order in which the phenomena occur. Even the simplest experimental investigations of vital processes are beset with difficulties. For, in addition to the extreme complexity of the phenomena to be examined and the uncertainties which arise from the relative inconstancy of the conditions of all that goes on in the living organism, there is this additional drawback, that, whereas in the exact sciences experiment is guided by well-ascertained laws, here the only principle of universal application is that of adaptation, and that even this cannot, like a law of physics, be taken as a basis for deductions, but only as a summary expression of that relation between external exciting causes and the reactions to which they give rise, which, in accordance with Treviranus's definition, is the essential character of vital activity.

(To be continued).

**Rapid Determination of Extract in Wine.**—Medicus evaporates 5 c.c. of wine in a tared watch-glass, and dries it for thirty minutes in a water drying stove. Sweet wines must first be diluted to ten times their volume.—*Zeit. Anal. Chem.*, xxxii., Part 3.

ON THE  
ACTION OF IODINE ON SOME  
PHENOLS AND ALLIED COMPOUNDS IN  
PRESENCE OF FREE ALKALI, AND  
A NEW CLASS OF DERIVATIVES  
RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 100).

*Products Obtained in Presence of a Large Excess of  
Caustic Alkali (60° C.).*

SOLUTIONS were set up exactly of the same strength as those used in the preparation of the red-violet precipitate, excepting that the quantity of alkali was increased four times; and the process followed was precisely the same, excepting that the quantity of iodine solution added was lessened by a half.

In this case no precipitate was formed until after acidification, when a white precipitate was obtained, which consisted of soft satiny needle-shaped crystals having a low melting-point and constituted for the most part of true substituted phenols. The melting-point of a similarly prepared precipitate was before given as 65° C.

Total iodine of the whole precipitate:—

Quantity taken = 0.2852 gm.

Silver iodide found = 0.3753 „ = 71.10 p.c. iodine.

A quantity of the precipitate was dissolved in chloroform and allowed to evaporate slowly in a flat dish, when the precipitate was found to be deposited in two pretty distinct circles. The inner constituted only a very small portion, was definitely crystallised in somewhat tabular form, and melted at a fairly high temperature; whilst the outer circle crystallised much less distinctly in the needle-shaped form, and melted about 66° C. This outer portion was re-deposited from ether, and the outer circle again taken. When this is deposited from solution in ether, a little free iodine becomes apparent at the moment of deposition, but it may be crystallised colourless from alcohol.

Total iodine of this portion:—

Quantity taken = 0.1769 gm.

Silver iodide found = 0.2401 „ = 73.33 p.c. iodine.

Melting-point 66° C.

This was therefore taken to be a di-iodophenol, the theoretical iodine percentage being 73.41. The melting-point given for a di-iodophenol in "Watts' Dictionary" is 68° C., but no other evidence is given which could be used for identification or criticism. However, the above method of preparation is simpler, and the product less liable to contamination with disturbing isomers and products of different substitution degree than any of the published methods of preparing the di-iodophenols. It may be remarked here, however, that throughout the classes of compounds dealt with in this paper, the presence of a mere trace of free iodine greatly disturbs the melting-point of any individual member. This is the more conspicuous in the oxidised class, of which this paper more particularly treats, in that they combine with iodine which is not free in the ordinary sense, but which is free relative to the true state of substitution.

*Products Obtained at the Ordinary Temperature.*

The process and quantities used were the same as those employed in the preparation of the red-violet precipitate, excepting that no heat was applied (temperature 14° C.). No precipitate was formed until after acidification, when a white pulverulent precipitate was obtained. This precipitate was distilled in a current of steam. A considerable portion passed over and remained soluble in the hot water, slowly crystallising out as the water cooled.

This was collected and dried, when it appeared in the form of white satiny needles, quite similar to the white compound examined in the last case when slowly crystallised, with odour less pronounced. Melting-point  $72^{\circ}$  C.

Total iodine of this distillate:—

Quantity taken = 0.0977 gm.  
Silver iodide found = 0.1330 „ = 73.55 p.c. iodine.

This, therefore, was also a di-iodophenol. The melting-point agrees with that given in "Watts' Dictionary" for a di-iodophenol.

The residue which remained from the distillate was dissolved out by ether, from which it was recovered in the form of a caked mass, partly crystalline and of a slightly reddish colour, due to liberation of iodine. It was fairly soluble in alcohol, from which it crystallised in brittle white needles, which on exposure to air showed free iodine.

Total iodine of this residue:—

Quantity taken = 0.1658 gm.  
Silver iodide found = 0.2405 „ = 78.37 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1491 gm.  
Water found = 0.0126 „ = 0.94 p.c. hydrogen.  
Carbon dioxide found = 0.0813 „ = 14.87 p.c. carbon.

The melting-point was taken, when it was observed that a portion melted about  $135^{\circ}$  C., in which the remainder seemed to dissolve. A small portion was therefore heated over this temperature in an open basin until volatilisation was scarcely perceptible, and the remaining portion was then allowed to solidify. Heat was again applied, when it was observed to melt about  $145^{\circ}$  C. The remainder of the residue was therefore treated similarly, and the less volatile portion remaining was then taken for analysis.

Total iodine:—

Quantity taken = 0.1898 gm.  
Silver iodide found = 0.2785 „ = 79.27 p.c. iodine.

The remainder was then still further heated until only a very small portion remained, which was taken for analysis.

Total iodine:—

Quantity taken = 0.0816 gm.  
Silver iodide found = 0.1176 „ = 77.86 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1550 gm.  
Water found = 0.0124 „ = 0.88 p.c. hydrogen.  
Carbon dioxide found = 0.0818 „ = 14.39 p.c. carbon.

This is sufficient to show that the residue from the distillation was not a mere mixture of a tri-derivative with others of lower substitution, but that oxidation had also taken place in this case. What was volatilised must have been a mixture of di- and tri-substituted phenols.

*Relative to Messinger and Vortman's Paper on the Red-Violet Compounds.*

It would be somewhat uncharitable to criticise the remarks occurring in their paper regarding the composition and constitution of the red phenol compounds obtained by them, since they are given very provisionally. Nevertheless it must be remembered that three years have elapsed since its publication. The criticism might indeed be put into a nutshell by simply stating that they failed to recognise that the precipitate was a complex one, and contained iodine other than that of substitution. However, the following abstract will be of service, and is needful in order to show their train of thought and experimental evidence adduced:—

It is described as violet-coloured, insoluble in water and dilute acids, soluble with red colour in alcohol, readily soluble in ether, benzol, and chloroform. When distilled in a current of steam it loses its red colour, the distillate contains free iodine, and, on standing, deposits a small quantity of a body in white needles melting at from  $138^{\circ}$  to  $140^{\circ}$  C. They think probably this is a di-iodophenol. When the red iodophenol is boiled with caustic potash it is changed to a bright reddish white colour, and loses a large part. When the alkaline filtrate is acidified the solution deposits a white substance melting at  $154^{\circ}$  to  $156^{\circ}$  C., corresponding to a tri-iodophenol. The filtrate from the latter is free from iodine. Total iodine found in this white precipitate = 80.8 per cent. This they take to be the tri-iodophenol already known, whilst the red compound they consider to be an isomer. They would represent the red compound as di-iodophenol-iodide,  $C_6H_3I_2.OI$ , having regard to its conversion into tri-iodophenol by potash as above, as also its splitting into iodine and di-iodophenol.

(To be continued.)

ON THE DETERMINATION OF VANADIC ACID.\*

By Herren A. DITTE, CARNOT, MANASSE, and ERICSHEIM.

(Concluded from p. 102.)

THE solution is placed in a weighed platinum capsule, evaporated, the residue 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 on the air-bath at  $120^{\circ}$ , and then heated in the oxidising flame with access of air, at first avoiding fusion, and the mass when ultimately fused is distributed as much as possible over the sides of the crucible by shaking round. When cold it appears (except in a few dark spots) reddish-brown, coarsely crystalline, with the characteristic structure of pure melted vanadic acid, and contains only traces of tungstic acid (1-10th to 2 10ths per cent of  $WO_3$  in the total quantity). To determine it the contents of the crucible, after weighing, are treated with a gentle heat with dilute sulphuric acid and sulphurous acid, when all the vanadium is dissolved as vanadyl sulphate. The trifling residue of tungstic acid which is left is washed with dilute sulphuric acid after filtration, and weighed. The solution of vanadium is evaporated, the sulphuric acid is driven off, and the residue ignited as above, when vanadic acid is obtained which becomes quite homogeneous on fusion. Vanadic acid must *not* be melted in porcelain vessels; otherwise, on dissolving in sulphuric or sulphurous acids, there is left a yellow residue, formed by the action of vanadic acid upon the glaze, and probably containing silico-vanadic acid.

The fixed alkalies present may be determined in a simple manner in the solution filtered off from the mercurial salts of the acids. The mercury is removed by means of sulphuretted hydrogen, and the alkali determined as sulphate, converting the acid sulphates into normal salts by heating in a current of air charged with ammonia, as indicated by G. Krüss (*Berichte*, xx., 1682).

If this method of analysis is to be applied to metatungstates they must first be converted into normal tungstates by boiling and repeated evaporation with ammonia. The solution, freed from excess of ammonia, is then precipitated as already explained. Salts of lead and silver are best decomposed with extremely dilute solution of sodium chloride; the remaining metallic and earthy alkaline salts are decomposed by repeated fusion with sodium-potassium carbonate; the united alkaline solutions are to be neutralised at a gentle heat with acetic acid, and precipitated as above directed.

It must be especially pointed out that the reagents used

\* *Zeitschrift für Analytische Chemie.*

must be purified with the utmost care. All fixed residues from the mercurial salt, the hydrochloric acid, the nitric acid, and the ammonia would be found in the vanadic acid, in which case it melts either with great difficulty or not at all.

G. Krüss and K. Ohnmais used Friedheim's method in the analysis of the various vanadium sulpho-salts, and obtained very satisfactory results (*Liebig's Annalen*, 263, 39), both in the determination of the vanadic acid and of the fixed alkalies.

For the detection and determination of vanadium in rocks and ores L. l'Hôte utilises the volatility of vanadium oxychloride (*Comptes Rendus*, civ., 990).

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 101.)

### B. With Especial Apparatus.

THE leading idea in the design of the new spectral apparatus which my next photographs required was the utmost possible reduction of the resistance of the air. My reflections had led me to three different constructions, according to which the stratum of air was to be reduced either diminishing the focal distance or by exhausting the tubes of the collimator and the camera, whilst retaining the original focal distance, or by exhausting the entire spectrum apparatus.

The entire removal of the air from the track of the rays in the apparatus would certainly ensure the most favourable result conceivable, if the desired object is attainable in this manner. But the difficulties of obtaining such a spectrum apparatus, exhausted of air in the manner of Geissler tubes, seemed so considerable that I even renounced the less serious project of partial exhaustion, and decided on the diminution of the focal distance.

A very short focal distance yields, if a single quartz prism is employed, spectra of a minute length. Spectra rich in lines, such as that of the sun, are then no longer capable of resolution. For such photographs the apparatus is almost useless. This applies more to the visible spectrum than to the ultra-violet; and in the most refrangible part of the ultra-violet, where the lines, according to their wave-length, are relatively much more remote from each other than in the less refrangible part, the conditions are still more favourable. Here therefore, as I show below, the resolution of densely crowded lines, which in such cases are decisive, can be effected with microscopical minuteness, even with a very small apparatus.

An increase of dispersion by means of a greater number of prisms cannot be admitted, on account of the loss of light involved. The result of the experiment depends in the first place upon preserving the energy of the rays.

In order that the proofs, in spite of their smallness, might meet the most severe demands, everything was done which could promote the sharpness and distinctness of the image, both in the construction of the apparatus and in the selection and arrangement of the auxiliary apparatus required for taking the photograph.

Concerning the measurement of the focal distance I have remained for a long time undecided, as all the data for the effects of a greater or less reduction of the length of the tube were wanting. The numerical values which Cornu has established for the absorption of the most refrangible rays in the air were here unsuitable, from the reason mentioned. So much only seemed certain that a moderate decrease of the length of the tube would scarcely lead to a decisive result. Proceeding from the assumption that the greater energy of the rays, and in like man-

ner the complete sharpness of the image, were connected with a smaller length of the tube, and that a small but sharply defined image was preferable to one large but less clear, I selected a lens of only 150 m.m. focal distance.

### The Photographic Spectrum Apparatus.

Its optical part consists of a double prism of 60°, with a square aperture of 30 m.m., and of two plano-convex quartz lenses of 150 m.m. focal distance (D, 589) and 26 m.m. diameter.

The optician Herr B. Halle, to whose kindness I am indebted for these lenses, has used the greatest care in the selection of the material and in its elaboration. How greatly this circumstance favoured the sharpness of the proofs I did not learn until I compared proofs taken with another pair of lenses of a different origin.

The two halves of the prism are joined together with a very thin layer of glycerine.

The mechanical part of the apparatus consists of a strong tripod fitted with levelling screws, which supports on a strong pillar a disc of 18 c.m. in diameter, capable of revolving on its centre, upon which are fixed the collimator, the support of the prism, and the camera, so as to be capable of adjustment. The slide of the slit has cast-steel cheeks and a micrometer screw, the drum of which allows of readings down to 0.002 m.m. It is connected with the collimator by means of a very accurately-executed draw-tube, with which also the plate is focussed. That this is effected with the collimator, and not also with the camera, is because the entire camera is built of glass, and is not adapted for drawing out. The support of the prism has adjustments necessary for levelling the prism (the Gauss eyepiece), and for adjustment to the minimum of deflection. A piece of velvet is suspended over the prism to exclude extraneous light.

The camera is the only peculiar feature in the apparatus. Except the case, it is built of mirror-glass, and—with the exception of a small metal screw-clamp, serving to secure the track of the case—there is in the entire camera not a single screw-joint. The case can revolve on the medium line of the photographic plate, so that the plate can take any desired angle with the axis of the lens between 20 and 32°. The lens is secured directly to the glass body of the camera. Two openings, which the case in consequence of its mobility forms with the body of the camera, are closed with velvet. A glass junction, which I would here have used in preference, was impracticable. The oblique position of the plate can be read off on a roughly-graduated arc. The body of the camera is of a parallel-pipedal shape, and is supported by an arm of strong mirror-glass, prolonged at right angles on its long side. The prolongation of the arm effects the connection of the camera with the rotatory disc of the apparatus, for which purpose the latter bears two powerful clamps.

(To be continued.)

The Chemical Laboratory of Wiesbaden.—In the Summer Term, 1893, there were fifty-seven students on the books. Of these, thirty-six were from Germany, five from Austro-Hungary, four from Russia, four from North America, three from Sweden and Norway, one from Holland, one from Belgium, one from France, one from Spain, and one from Batavia. Besides the director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged as teachers in the establishment Prof. Dr. H. Fresenius, Prof. Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, Dr. W. Lenz, and architect J. Brahm. The assistants in the instruction laboratory were three in number, in the private laboratory eighteen, and in the Versuchsstation two. The next Winter Term begins the 16th of October. During the last term, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory and the Versuchsstation, on behalf of manufacture, trade, mining, agriculture, and hygiene.

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

## PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

Ordinary Meeting, June 15th, 1893.

Dr. ARMSTRONG, President, in the Chair.

(Concluded from p. 109).

47. "The Colouring-matter of *Drosera Whittakeri*." (II.). By E. RENNIE, M.A., D.Sc.

In a previous communication (*C. S. Trans.*, 1889, 371), the author has described two colouring-matters separated from *D. Whittakeri*, which he believed to be derivatives of methyl-naphthaquinone. He now confirms the formula  $C_{11}H_8O_5$  previously assigned to the less soluble and more abundant constituent; a determination of its molecular weight, by Raoult's cryoscopic method, gave the value 223, the calculated value being 220. When boiled with a solution of sodium carbonate, this substance yields reddish brown crystals of a mono-sodium derivative,  $C_{11}H_7O_5Na \cdot 2H_2O$ , from which the corresponding calcium derivative was prepared; it also yields a disodium derivative. Two yellow crystalline acetyl derivatives were obtained from it, one melting at  $154^\circ$ , the other at  $138^\circ$ , the former being a triacetate, and the latter a compound of the triacetate with acetic acid.

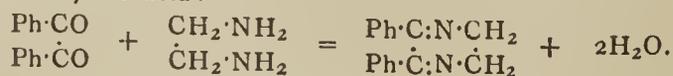
The formula  $C_{11}H_8O_4$  previously assigned to the more soluble substance is confirmed; it yields a diacetate. Hitherto this substance has always been obtained in red crystals; in an experiment in which a small quantity was incompletely oxidised, a portion was recovered in the form of yellow crystals melting at  $178^\circ$ , and the author is therefore inclined to think that the pure substance is yellow.

## 48. "Preparation of Mono-, Di-, and Tri-Benzylamine." By ARTHUR T. MASON, Ph.D.

No good method having as yet been published for the preparation of the benzylamine bases, the author has carefully examined the interaction of ammonia and benzyl chloride in alcoholic solution, and finds that it takes place without application of heat and is complete in four or five days. If the theoretical quantity of ammonia be used, tribenzylamine is the principal product, the primary and secondary amines being formed in very small quantity; whereas when a large excess of ammonia (20 mols. to 1 mol. of chloride) is used, mono- and dibenzylamine form the chief products, tribenzylamine appearing in small quantity. The details of the process have been worked out, as also an easy method for the separation of the three amines based on the difference in solubility in water of the chlorhydrides. Dibenzylamine has been prepared for the first time by distillation under reduced pressure: it is a colourless liquid distilling without undergoing the slightest decomposition at  $188-189^\circ$  under 35 m.m. pressure.

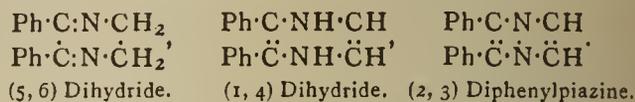
## 49. "Piazine (Pyrazine) Derivatives." (II.) By ARTHUR T. MASON, Ph.D.

A continuation of previous researches (*C. S. Trans.*, 1889, 97; *Ber.*, xx., 267), having reference to the constitution of the compounds resulting from the interaction of ethylene diamine and orthodiketones. The first product from benzil and ethylenediamine is not a true piazine, being easily re-converted into its generators by dilute chlorhydric acid:—

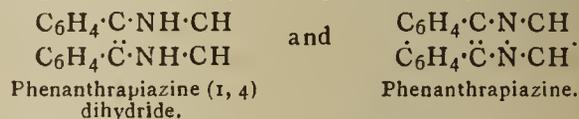


When heated above its melting-point, this compound (so-called) (2, 3) diphenylpiazine (5, 6) dihydride yields two true piazine derivatives, which are not resolved into their generators by dilute chlorhydric acid; one of these compounds is isomeric with the (5, 6) dihydride, and is formed by a molecular transformation of that substance: it contains two imide (NH) groups, and is a strong base,

being very soluble in dilute chlorhydric acid; it is very easily oxidised, and even when dissolved in chlorhydric acid saturated with carbon dioxide changes spontaneously into the final product of interaction—(2, 3) diphenylpiazine. In the author's opinion, these facts can only be explained by assuming that the true piazines contain a para-band, thus—



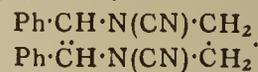
By the interaction of phenanthraquinone and ethylenediamine, only two compounds are obtained, neither of which, however, is re-converted into its generators by chlorhydric acid; they are represented by the formulæ—



A series of analogous compounds prepared from other ketones of the phenanthrene (tene and chrysene quinones) series and ethylene- and propylene-diamine are described; their general properties are shown to be similar to those of phenanthrapiazine (1, 4) dihydride and phenanthrapiazine.

## 50. "Piazine Derivatives." (III.) By ARTHUR T. MASON, Ph.D., and L. A. DRYFOOS, Ph.D.

Details are given of the mode of preparing (2, 3) diphenylpiazine (1, 4) dihydride and of its dibenzoyl and its diacetyl derivatives. An addition product obtained by the interaction of the (5, 6) dihydride and hydrogen cyanide in alcoholic solution is described; as this is converted into diphenylpiazine by alcoholic potash, it is to be supposed that the cyanogen radicles are attached to the nitrogen atoms. The constitutional formula of the compound is very probably—



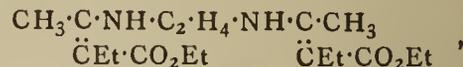
An account is given of a new method of preparing (2, 3) diphenylpiazine, which consists in heating the (5, 6) dihydride with alcoholic potash; a small quantity of a complicated compound—tetraphenyldipiazine—is also formed, which is distinguished by its sparing solubility in the ordinary solvents.

The products of the interaction of dimethoxybenzil or anisil and ethylenediamine, viz., (2, 3) dimethoxyphenylpiazine (5, 6) dihydride and (2, 3) dimethoxyphenylpiazine, are described.

It is shown that, when submitted to the action of potassium cyanide, (2, 3) diphenylpiazine (5, 6) dihydride yields the amide of (2, 3) diphenylpiazinecarboxylic acid, and that the corresponding compound is formed from dimethoxyphenylpiazine dihydride when it is similarly treated.

## 51. "Condensation Products from Ethylenediamine and Derivatives of Acetoacetic Acid." (IV.) By ARTHUR T. MASON, Ph.D., and L. A. DRYFOOS, Ph.D.

The authors describe ethylic ethylene- $\beta$ -amidomethylcrotonate,—



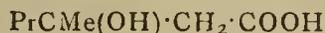
obtained by the interaction of ethylic methylacetoacetate and ethylenediamine; and also the corresponding compounds from ethylic ethylacetoacetate and methylic acetoacetate.

## 52. "Studies of the Oxidation Products of Turpentine." By S. B. SCHRYVER, Ph.D., B.Sc.

The author finds that on oxidising turpentine with chromic mixture, besides terebic and terpenylic acids, a third acid is obtained having the same composition as camphoronic acid,  $C_9H_{14}O_6$ , but differing from it in electric conductivity (0.0102 instead of 0.0175): it is con-

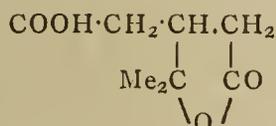
tained in the mother-liquors from which the other acids have been separated, and is isolated through the agency of an insoluble lead salt. The crude acid fused at 125—160°, but after repeated crystallisation from nitric acid at 135—137°.

With the object of determining the constitution of terpenylic acid, attempts were made to synthesise various heptolactones; eventually that prepared from the methylisopropylactic acid of the formula—



was found to be identical with the lactone prepared from teracrylic acid.

On reducing terpenylic acid with iodhydric acid an acid was obtained which is shown to be identical with  $\beta$ -isopropylglutaric acid prepared synthetically by condensing isobutaldehyde and ethylic malonate, combining the product with ethylic sodiomalonate, and hydrolysing the resulting tetrethylic salt. The conclusion is arrived at that terpenylic acid is to be represented by the formula—



53. "Addendum to Note on the Nature of Depolarisers." By HENRY E. ARMSTRONG.

I am induced to somewhat extend my recent note on depolarisers in order that the argument there made use of in considering the dissolution of metals such as magnesium in nitric acid may be clearly understood and its consequences more fully realised.

It is one of the most noteworthy features of such interactions that when reduction is carried beyond the nitric oxide stage, it invariably proceeds to ammonia, and gives rise to a variety of products; so that whereas neither nitrous oxide nor nitrogen is evolved when metals such as silver and mercury are dissolved, these two gases are always obtained when more active metals are the agents. From this it would appear that there is a limit of (?) electromotive force which must be exceeded if it be desired to extend the reduction beyond the stage involving the formation merely of nitrogen dioxide and monoxide.

A somewhat similar case is presented by the behaviour of sulphuric acid solutions on electrolysis. Whereas, besides hydrogen, only oxygen is obtained under certain conditions, under others ozone, persulphuric acid, and hydrogen peroxide are also produced. This apparently is a phenomenon of the same order, but in a measure the converse of that presented by nitric acid, as oxygen—not hydrogen—is the active substance. Judging from McLeod's observations (*C. S. Trans.*, 1886, 591), it is clear that "current density" is an all-important factor in determining "peroxidation," but it remains to be determined whether it is the sole factor: the individual influence of electromotive force, of current strength, and of current density, in fact, all require careful study in this as in many other cases of electrolysis; undoubtedly much depends on the concentration of the acid. The peroxidation may be regarded as the outcome of oxygen depolarisation, effected apparently in two ways: part of the oxygen becoming affixed to sulphuric acid, persulphuric acid is formed, which in part gradually undergoes hydrolysis, affording hydrogen peroxide—a non-electrolytic change; while another part serves as oxygen depolariser, affording ozone. On this assumption, ozone is not the product of the fortuitous concurrence of three oxygen atoms, but of the interaction of oxygen atoms in circuit with persulphuric acid; and if this be the origin of electrolytic ozone, it appears not improbable that the oxidation of phosphorus, which is attended by the formation of ozone, will also be found to involve the formation of a peroxide hitherto undiscovered.

In the case of a metal such as magnesium dissolving in considerable excess of nitric acid, if a plate be imagined to be undergoing attack and conversion into nitrate at

any one point, the displaced hydrogen may, it would seem, "travel along" a very large number of paths to other points on the plate capable of acting as negative pole and of there meeting with nitric acid in sufficient amount to oxidise it, and it is scarcely conceivable, therefore, that it should escape if the nitric acid act directly as depolariser. It is also difficult to understand why one substance, an electrolyte, should act in two ways in the same circuit, and the difficulty appears to be equally great whether any form of Grothus' hypothesis, or a dissociation hypothesis, be adopted in explanation of electrolysis. But these difficulties seemingly disappear if—as previously suggested—the active depolariser be a nitrous compound or derivative; perhaps, at all events, at the initial stage, nitrogen dioxide. Moreover, it would appear to be possible in this manner to account also for the extension of the reduction to ammonia: in the case of a metal like silver the amount of depolariser must always tend to reach a maximum value depending on the extent to which the reversible interchange expressed by the equation  $\text{NO} + 2\text{HNO}_3 = 3\text{NO}_2 + \text{OH}_2$  is limited by the concentration and temperature; but it is limited by these conditions alone. In the case of more active metals, it appears probable that the nitric oxide also functions as depolariser and is reduced to hydroxylamine and ultimately to ammonia. If such an action take place, it follows (from Ohm's law) that the more active the metal the more rapidly will hydrogen be displaced by it, giving greater opportunity therefore for nitric oxide to undergo reduction and leading to the production of an increased proportion of products of extended reduction. Any circumstance which would tend to diminish the proportion of nitrogen dioxide relatively to monoxide present in solution would, therefore, promote the formation of such products, and, in point of fact, Acworth and I have noticed, even in the case of copper, that when the metal is dissolved in diluted nitric acid, it appears to be more "active," *i.e.*, to furnish a larger proportion of products of extended reduction, than when more concentrated acid is used: as the presence of water must obviously favour the reversal of the interchange expressed by the equation  $\text{NO} + 2\text{HNO}_3 = 3\text{NO}_2 + \text{H}_2\text{O}$ , so that weaker would potentially contain a larger proportion of monoxide than stronger solutions of nitric acid, these observations would appear to be in harmony with the hypothesis here advocated. There is no evidence, be it remarked, that hypobitrous acid can be formed in acid solution, *i.e.*, by direct reduction of nitric or even of nitrous acid, and the whole of the nitrous oxide which is evolved when metals are dissolved in nitric acid may result from the interaction of nitrous acid and hydroxylamine. That reduction invariably extends to ammonia whenever hydroxylamine is formed is probably a consequence of the extreme readiness with which hydroxylamine is itself reduced, so that, in fact, when reduction once proceeds beyond the nitric oxide stage, it is to be supposed that there are necessarily a number of competing depolarisers present in solution—nitrogen dioxide and monoxide and hydroxylamine (and perhaps others), none of which, however, are electrolytes in the sense in which the term is ordinarily understood. And here it may be pointed out that the fact that a nitrate may be reduced in alkaline solution by sodium amalgam, or aluminium, or zinc, is no argument against the conclusion above arrived at that probably nitric acid does not directly act as depolariser, as in these cases the alkaline solution appears to be the electrolyte and the nitrate merely the depolariser—so that the nitrate does not act in two ways. As nitrates may be wholly converted into ammonia by reducing an alkaline solution, it would seem probable that in such cases hydroxylamine is not an intermediate product, as nitrogen is obtained on boiling an alkaline solution of this substance.

The argument here made use of would appear also to afford an explanation of the effect produced by varying the electromotive force, *i.e.*, by metals of different degrees of "activity": as increase of electromotive force, other con-

ditions remaining unchanged, would increase the current strength, and consequently the rate of change; and, as indicated above, an increase in the rate of change would doubtless involve an increase in the amount of products of extended reduction.

It remains to be pointed out that the objection made to the assumption that nitric acid can act in two ways is equally applicable to the case of sulphuric acid; in other words, that it is not likely that sulphuric acid would act as electrolyte and as oxygen depolariser. It becomes necessary, therefore, to reconsider the manner in which solutions of this acid undergo electrolysis. On the one hand it is conceivable that the water molecule alone suffers partition, not the sulphuric acid ( $\text{H}_2\text{SO}_4$ ) molecule, as commonly supposed, and that under certain conditions the latter takes a direct part in the change, becoming oxidised; but this does not appear to be probable, especially as there is reason to believe that the acid in conjunction with water actually functions as electrolyte. An alternative assumption would be that the immediate product has been overlooked, and it can scarcely be gainsaid that there is much evidence in favour of this view. It is not improbable that the first products of electrolysis are hydrogen and persulphuric acid; it may be supposed that under "ordinary" circumstances this latter substance is resolved at the electrode surface into oxygen and sulphuric acid, but when the electrode surface is small much escapes unchanged, this being especially the case when the electrolyte is a somewhat concentrated acid—a condition which in itself favours the survival of persulphuric acid. Not only do recent observations on the electrolysis of various sulphates support this contention, but it would seemingly also serve to explain the extraordinary character of the curve representing the change in conductivity of solutions of sulphuric acid on dilution.

54. "The Molecular Complexity of Liquids." By WILLIAM RAMSAY, Ph.D., F.R.S., and JOHN SHIELDS, Ph.D., D.Sc.

From the ascent of a liquid in a capillary tube of known diameter and its relative density, the surface tension of the liquid may be calculated. The molecular volume of a liquid, at any temperature, is proportional to the number of molecules contained in unit volume at that temperature; and the two-thirds root of the number representing the molecular volume is proportional to the number of molecules distributed in unit surface, with the proviso that the mean distance between 2 mols. at the surface is equal to that between any 2 mols. in the interior. Multiplying the number representing surface tension by that representing molecular surface, the product may be termed "molecular surface energy." By stating surface tension in degrees, and molecular surface in square centimetres, the product is expressed in ergs, and may be defined as the work required to produce or to extend a surface on which equal numbers of molecules lie.

This energy is *nil* at the critical temperature of the liquid, for there is no surface. It increases with fall of temperature, and after about  $20^\circ$  below the critical temperature, the rate of increase is practically a linear function of the temperature. The equation which exhibits this relation is—

$$\gamma(Mv)^{\frac{2}{3}} = k(\tau - d),$$

where the letters have the following definitions:—

$\gamma$ , surface tension,  $k$ , a numerical constant,  
 $M$ , molecular weight,  $\tau$ , temperature measured downwards from the critical temperature,  
 $v$ , specific volume,

$d$ , being a numerical constant equal to about 6.

This equation is analogous to that which expresses volume energy in its relation to heat, viz.,  $p v = RT$ .

As a gas is said to be normal if, when  $v$  expresses the volume of its molecular weight taken in grms., and  $p$  is measured in atmospheres,  $R$  is constant between various

limits of temperature, so a liquid may be said to be normal, *i.e.*, to be composed of molecules of no greater degree of complexity than those which form its gas, if the value of  $k$  is constant between various limits of temperature. This affords a means, therefore of investigating the molecular weights of liquids as such, and it is the first colligative property of liquids which has been discovered.

In all fifty-seven liquids have been investigated. They divide themselves into two groups: those of which the molecules are simple (thirty six in number), and those which, in the liquid state, consist of molecules composed of several gaseous molecules coalesced to form a complex. To the latter class belong the alcohols, the acids, water, phenol, and three others, nitroethane, acetonitrile, and acetone.

It is remarkable that, so far as our experiments have gone, no liquid shows a greater molecular complexity than that in which the molecular weight of the gas is multiplied by the factor 4. Water at  $0^\circ$  has approximately the formula  $\text{H}_8\text{O}_4$ , *i.e.*,  $(\text{H}_2\text{O})_4$ ; the degree of complexity, however, is altered by rise of temperature, and the complex molecules gradually dissociate into more simple groups.

A determination of molecular surface energy also permits of a close estimate of the critical temperatures of "normal" liquids. The numbers representing these important data are given in the complete memoir.

55. "The Preparation of Active Amyl Alcohol and Active Valeric Acid from Fusel Oil." By W. A. C. ROGERS.

The author has prepared the alcohol by a modification of Le Bel's method communicated to him by Professor Odling and Mr. Marsh, which consists in heating the alcohol with a fuming aqueous solution of hydrogen chloride in closed tubes at  $100^\circ$ , the treatment being repeated until the rotatory power of the product reached a maximum. Finally, from 16.2 litres of purified fusel oil, he obtained 250 c.c. of an alcohol rotating  $-8^\circ 30'$  per 200 m.m. at  $22^\circ$  (or  $[\alpha]_D = -5.2^\circ$ ). By oxidising this alcohol, a valeric acid was obtained rotating  $26^\circ$  per 200 m.m. at  $22^\circ$  ( $[\alpha]_D = 13.9^\circ$ ). The values thus obtained are practically identical with those given by Guye and Chavanne in a recent paper.

#### Research Fund.

A donation of £100 to the Research Fund has been received from Mr. L. Mond, F.R.S., by the Treasurer since the meeting of the Society.

## CORRESPONDENCE.

### SODIUM PEROXIDE.

To the Editor of the Chemical News.

SIR,—I notice in the *Transactions of the Chemical Society* for September, 1893, a paper by Dr. J. Clark on the "Use of Sodium Peroxide as an Analytical Agent." I think it only fair to myself to state that the usefulness of this substance as a reagent in analysis and as a source of hydrogen peroxide occurred to me nearly two years ago, and I suggested its use to Mr. Alfred Allen, F.I.C., &c., in a letter dated October, 1891, that is, prior to the patent of the Aluminium Company, and therefore before this substance had attracted my attention. I made some experiments with the substance, but not on a very extended scale, and not in any way comparable in point of thoroughness with those described in Dr. Clark's paper, which I have no desire to undervalue. I found it difficult to make solutions of hydrogen peroxide of greater than one-volume strength without great loss of oxygen, and as my idea was to use the sodium peroxide to make solutions of hydrogen peroxide, this militated against its

apparent chance of success. I noticed its power of converting manganese salts into the green manganate, and suggested its use to Mr. Allen for oxidising sulphuretted hydrogen into sulphuric acid in the well-known estimation of sulphur in steel by evolution of sulphuretted hydrogen.

On looking through the literature of the subject I found only two papers, viz., the original paper by Davy and an exhaustive one by Vernon Harcourt (*Chem. Soc. Journ.*, xiv., 276). There was also a paper by Fairley (*Chem. Soc. Journ.*, 1877, i., 125), in which hydrated peroxides are produced by adding hydrogen peroxide to caustic soda in alcoholic solution.

No doubt Mr. Allen will be able to corroborate the statements with which I have associated his name.—I am, &c.,

H. K. TOMPKINS.

Gipsy Hill, London, S.W.,  
September 7, 1893.

## 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. cxvii., No. 9, August 28, 1893.

This issue contains no chemical matter.

*Bulletin de la Société Chimique de Paris.*  
Series 3, Vols. ix. and x., No. 12.

**Titration of Morphine in Opium.**—Cannepin and Van Eyk.—The author operates as follows:—He weighs 10 grms. of opium, 4 grms. of slaked lime, and grinds them carefully in a mortar, adding by portions 100 c.c. of the solution of morphine hydrochlorate indicated (0.805 gm. per litre), and digests for half an hour, stirring from time to time. He throws the mixture upon a filter, and evaporates rapidly the 20 c.c. filtrate upon a water-bath at 100°. He weighs off of the filtrate a weight equal to 50 grms. plus the weight of the fixed soluble matters yielded by 5 grms. of opium, which makes about 52 grms. He adds to the liquid 10 c.c. of ether, and agitates so as to saturate the aqueous solution. He adds further one-half gm. ammonium hydrochlorate (free from carbonate), agitates until the precipitate appears, and allows to settle for two hours. He decants the ether and throws it upon a tared filter, through which all the liquid is filtered. The precipitate of morphine is collected, and washed with morphine water (0.42 gm. morphine per litre) until the filter and the precipitate are decolourised. The filter and its contents are then dried in the stove at a temperature not exceeding 98° and weighed. The solution of morphine hydrochlorate indicated contains 0.805 gm. of crystalline morphine hydrochlorate per litre. The author adds it to compensate an error.

**A New Method for the Detection of Alkaloids, Saccharine, and Salicylic Acid.**—MM. Lindeman and Motten.—This paper will be inserted in full.

**Volumetric Determination of Pyrophosphoric Acid and the Alkaline Pyrophosphates.**—G. Farrel.—The author adds to the solution of pyrophosphate a tincture of cochineal, and runs into the mixture decinormal acid until the colour turns to a yellow; each c.c. then represents 0.0089 gm. of pyrophosphoric acid. No free alkali must be present along with the alkaline pyrophosphate. In such a case the free alkali is first determined, using soluble blue as indicator. A second determination is then made, using cochineal as an indicator. The difference in the number of c.c. used in the second and first titration, multiplied by 0.0089, will give the pyrophos-

phoric acid. If there is an alkaline carbonate in presence of the pyrophosphate, the author first determines the total alkali, using cochineal; in an equal volume of the liquid he adds the same number of c.c. of decinormal acid as that employed in the first operation, and then decinormal soda until the colour turns in presence of soluble blue. The number of c.c. used multiplied by 0.0089 will again give the quantity of pyrophosphoric acid. The author's results authorised him to conclude that pyrophosphoric acid is monobasic in presence of cochineal, but bibasic with soluble blue (Poirrier's C<sub>4</sub>B) if we operate at the ordinary temperature.

**Volumetric Determination of Alkalies in Alkaline Arsenites.**—G. Farrel.—The author has studied the action of alkalies with arsenious acid in presence of some indicators. He first prepared a solution of 1-10th equiv. arsenious acid (9.9 grms.) in 2-10ths equiv. of soda (6.2 grms.) so as to obtain a litre of liquid with distilled water. If to 10 c.c. of this decinormal solution we add 20 c.c. of decinormal acid, all the alkali is saturated, the liquid remaining clear and the arsenious acid subsiding only after a very long time. The 10 c.c. of arsenious acid thus set at liberty, after the addition of a few drops of tincture of cochineal, always require for the change of colour one or at most two drops of decinormal soda; arsenious acid seems therefore indifferent to cochineal. In presence of phthalein it is necessary under the same conditions to add 2 to 3 c.c. of decinormal soda to effect the change; with soluble blue (C<sub>4</sub>B Poirrier) we have to use 12 or 13 c.c. Hence it results that if to a solution of an alkaline arsenite we add decinormal acid and a few drops of tincture of cochineal, the alkalinity will remain as long as we do not add a quantity of acid equivalent to that of the base combined with the arsenious acid. Hence we can easily determine the alkali in arsenites if we use exclusively cochineal as the indicator. It will not be the same if we use phenolphthalein or soluble blue. We determine, in the ordinary manner, the arsenious acid by means of decinormal iodine (Mohr's method), and the alkali combined with it by means of a decinormal acid with cochineal as the indicator.

**Amidonaphtholsulphonic Acids.**—F. Reverdin and Ch. de la Harpe.—This lengthy memoir does not admit of convenient abstraction.

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## THE CHEMICAL NEWS.

VOL. LXVII., No. 1765.

BRITISH ASSOCIATION  
FOR THE  
ADVANCEMENT OF SCIENCE.

NOTTINGHAM, 1893.

INAUGURAL ADDRESS OF THE PRESIDENT,  
J. C. BURDON-SANDERSON, M.A., M.D., LL.D., D.C.L.,  
F.R.S., F.R.S.E.,  
Professor of Physiology in the University of Oxford.

(Concluded from p. 131.)

*The Specific Energies of the Organism.*

WHEN in 1826 J. Müller was engaged in investigating the physiology of vision and hearing he introduced into the discussion a term "specific energy," the use of which by Helmholtz\* in his physiological writings has rendered it familiar to all students. Both writers mean by the word energy, not the "capacity of doing work," but simply *activity*, using it in its old-fashioned meaning, that of the Greek word from which it is derived. With the qualification "specific" it serves, perhaps, better than any other expression to indicate the way in which adaptation manifests itself. In this more extended sense the "specific energy" of a part or organ—whether that part be a secreting cell, a motor cell of the brain or spinal cord, or one of the photogenous cells which produce the light of the glow-worm, or the protoplasmic plate which generates the discharge of the torpedo—is simply the special action which it normally performs, its norma or rule of action being in each instance the *interest of the organism* as a whole of which it forms part, and the exciting cause some influence outside of the excited structure, technically called a stimulus. It thus stands for a characteristic of living structures which seem to be universal. The apparent exceptions are to be found in those bodily activities which, following Bichat, we call vegetative, because they go on, so to speak, as a matter of course; but the more closely we look into them the more does it appear that they form no exception to the general rule, that every link in the chain of living action, however uniform that action may be, is a response to an antecedent influence. Nor can it well be doubted that, as every living cell or tissue is called upon to act in the interest of the whole, the organism must be capable of influencing every part so as to regulate its action. For, although there are some instances in which the channels of this influence are as yet unknown, the tendency of recent investigations has been to diminish the number of such instances. In general there is no difficulty in determining both the nature of the central influence exercised, and the relation between it and the normal function. It may help to illustrate this relation to refer to the expressive word *Auslösung* by which it has for many years been designated by German writers. This word stands for the performance of function by the "letting off" of "specific energies." Carrying out the notion of "letting off" as expressing the link between action and reaction, we might compare the whole process to the mode of working of a repeating clock (or other similar mechanism), in which case the pressure of the finger on the button would represent the external influence or stimulus, the striking of the clock the normal

reaction. And now may I ask you to consider in detail one or two illustrations of physiological reaction—of the *letting off of specific energy?*

The repeater may serve as a good example, inasmuch as it is, in biological language, a highly differentiated structure, to which a single function is assigned. So also in the living organism, we find the best examples of specific energy where Müller found them, namely, in the most differentiated, or, as we are apt to call them, the *highest* structures. The retina, with the part of the brain which belongs to it, together constitute such a structure, and will afford us therefore the illustration we want, with this advantage for our present purpose, that the phenomena are such as we all have it in our power to observe in ourselves. In the visual apparatus the principle of *normality* of reaction is fully exemplified. In the physical sense the word "light" stands for ether vibrations, but in the sensuous or subjective sense for sensations. The swings are the stimulus, the sensations are the reaction. Between the two comes the link, the "letting off," which it is our business to understand. Here let us remember that the man who first recognised this distinction between the physical and the physiological was not a biologist, but a physicist. It was Young who first made clear (though his doctrine fell on unappreciative ears) that, although in vision the external influences which give rise to the sensation of light are infinitely varied, the responses need not be more than three in number, each being, in Müller's language, a "specific energy" of some part of the visual apparatus. We speak of the organ of vision as *highly differentiated*, an expression which carries with it the suggestion of a distinction of rank between different vital processes. The suggestion is a true one; for it would be possible to arrange all those parts or organs of which the bodies of the *higher* animals consist in a series, placing at the lower end of the series those of which the functions are continuous, and therefore called vegetative; at the other, those highly specialised structures, as, *e.g.*, those in the brain, which in response to physical light produce physiological, that is subjective, light; or, to take another instance, the so-called motor cells of the surface of the brain, which, in response to a stimulus of much greater complexity, produce voluntary motion. And just as in civilised society an individual is valued according to his power of doing one thing well, so the high rank which is assigned to the structure, or rather to the "specific energy" which it represents, belong to it by virtue of its specialisation. And if it be asked how this conformity is manifested, the answer is, by the quality, intensity, duration, and extension of the response, in all which respects vision serves as so good an example, that we can readily understand how it happened that it was in this field that the relation between response and stimulus was first clearly recognised. I need scarcely say that, however interesting it might be to follow out the lines of inquiry thus indicated, we cannot attempt it this evening. All that I can do is to mention one or two recent observations which, while they serve as illustrations, may perhaps be sufficiently novel to interest even those who are at home in the subject.

Probably everyone is acquainted with some of the familiar proofs that an object is seen for a much longer period than it is actually exposed to view; that the visual reaction lasts much longer than its cause. More precise observations teach us that this response is regulated according to laws which it has in common with all the higher functions of an organism. If, for example, the cells in the brain of the torpedo are "let off"—that is, awakened by an external stimulus—the electrical discharge, which, as in the case of vision, follows after a certain interval, lasts a certain time, first rapidly increasing to a maximum of intensity, then more slowly diminishing. In like manner, as regards the visual apparatus, we have, in the response to a sudden invasion of the eye by light, a rise and fall of a similar character. In the case of the electrical organ, and in many analogous instances, it is

\* "Handb. der Physiologischen Optik," 1886, p. 233. Helmholtz uses the word in the plural—the "energies of the nerves of special sense."

easy to investigate the time relations of the successive phenomena, so as to represent them graphically. Again, it is found that in many physiological reactions, the period of rising "energy" (as Helmholtz called it) is followed by a period during which the responding structure is not only inactive, but its capacity for energising is so completely lost that the same exciting cause which a moment before "let off" the characteristic response is now without effect. As regards vision, it has long been believed that these general characteristics of physiological reaction have their counterpart in the visual process, the most striking evidence being that in the contemplation of a lightning flash—or, better, of an instantaneously illuminated white disc\*—the eye seems to receive a double stroke, indicating that, although the stimulus is single and instantaneous, the response is reduplicated. The most precise of the methods we until lately possessed for investigating the wax and wane of the visual reaction, were not only difficult to carry out but left a large margin of uncertainty. It was therefore particularly satisfactory when M. Charpentier, of Nancy, whose merits as an investigator are perhaps less known than they deserve to be, devised an experiment of extreme simplicity which enables us, not only to observe, but to measure with great facility both phases of the reaction. It is difficult to explain even the simplest apparatus without diagrams; you will, however, understand the experiment if you will imagine that you are contemplating a disc, like those ordinarily used for colour mixing; that it is divided by two radial lines which diverge from each other at an angle of 60°; that the sector which these lines enclose is white, the rest black; that the disc revolves slowly, about once in two seconds. You then see, close to the front edge of the advancing sector, a black bar, followed by a second at the same distance from itself but much fainter. Now the scientific value of the experiment consists in this, that the angular distance of the bar from the black border is in proportion to the frequency of the revolutions—the faster, the wider. If, for example, when the disc makes half a revolution in a second the distance is ten degrees, this obviously means that when light bursts into the eye, the extinction happens one-eighteenth of a second after the excitation.†

The fact thus demonstrated, that the visual reaction, consequent on an instantaneous illumination, exhibits the alterations I have described, has enabled M. Charpentier to make out another fact in relation to the visual reaction which is, I think, of equal importance. In all the instances, excepting the retina, in which the physiological response to stimulus has a definite time-limitation, and in so far resembles an explosion—in other words, in all the higher forms of specific energy—it can be shown experimentally that the process is propagated from the part first directly acted on to other contiguous parts of similar endowment. Thus in the simplest of all known phenomena of this kind, the electrical change, by which the leaf of the *Dionæa* plant responds to the slightest touch of its sensitive hairs, is propagated from one side of the leaf to the other, so that in the opposite lobe the response occurs after a delay which is proportional to the distance between the spot excited and the spot observed. That in the retina there is also such propagation has not only been surmised from analogy, but inferred from certain observed facts. M. Charpentier has now been able by a method which, although simple, I must not attempt to describe, not only to prove its existence, but to measure its rate of progress over the visual field.

There is another aspect of the visual response to the stimulus of light which, if I am not trespassing too long on your patience, may, I think, be interesting to consider.

\* The phenomenon is best seen when, in a dark room, the light of a luminous spark is thrown on to a white screen with the aid of a suitable lens.

† Charpentier, "Réaction oscillatoire de la Rétine sous l'influence des excitations lumineuses," *Archives des Physiol.*, vol. xxiv., p. 541; and "Propagation de l'action oscillatoire, &c," p. 362.

As the relations between the sensations of colour and the physical properties of the light which excites them, are among the most certain and invariable in the whole range of vital reactions, it is obvious that they afford as fruitful a field for physiological investigation as those in which white light is concerned. We have on one side physical facts, that is, wave-lengths or vibration-rates; on the other, facts in consciousness—namely, sensations of colour—so simple that notwithstanding their subjective character there is no difficulty in measuring either their intensity or their duration. Between these there are *lines of influence*, neither physical nor psychological, which pass from the former to the latter through the visual apparatus (retina, nerve, brain). It is these lines of influence which interest the physiologist. The structure of the visual apparatus affords us no clues to trace them by. The most important fact we know about them is that they must be at least three in number.

It has been lately assumed by some that vision, like every other specific energy having been developed progressively, objects were seen by the most elementary forms of eye only in *chiaroscuro*, that afterwards some colours were distinguished, eventually all. As regards hearing it is so. The organ which, on structural grounds, we consider to represent that of hearing in animals low in the scale of organisation—as, *e.g.*, in the *Ctenophora*—has nothing to do with sound,\* but confers on its possessor the power of judging of the direction of its own movements in the water in which it swims, and of guiding these movements accordingly. In the lowest vertebrates, as, *e.g.*, in the dogfish, although the auditory apparatus is much more complicated in structure, and plainly corresponds with our own, we still find the particular part which is concerned in hearing scarcely traceable. All that is provided for is that sixth sense, which the higher animals also possess, and which enables them to judge of the direction of their own movements. But a stage higher in the vertebrate series we find the special mechanism by which we ourselves appreciate sounds beginning to appear—not supplanting or taking the place of the imperfect organ, but added to it. As regards hearing, therefore, a new function is acquired without any transformation or fusion of the old into it. We ourselves possess the sixth sense, by which we keep our balance and which serves as the guide to our bodily movements. It resides in the part of the internal ear which is called the labyrinth. At the same time we enjoy along with it the possession of the cochlea, that more complicated apparatus by which we are able to hear sounds and to discriminate their vibration rates.

As regards vision, evidence of this kind is wanting. There is, so far as I know, no proof that visual organs which are so imperfect as to be incapable of distinguishing the forms of objects, may not be affected differently by their colours. Even if it could be shown that the least perfect forms of eye possess only the power of discriminating between light and darkness, the question whether in our own such a faculty exists separately from that of distinguishing colours is one which can only be settled by experiment. As in all sensations of colour the sensation of brightness is mixed, it is obvious that one of the first points to be determined is whether the latter represents a "specific energy" or merely a certain combination of specific energies which are excited by colours. The question is not whether there is such a thing as white light, but whether we possess a separate faculty by which we judge of light and shade—a question which, although we have derived our knowledge of it chiefly from physical experiment, is one of eye and brain, not of wave-lengths or vibration-rates, and is therefore essentially physiological.

There is a German proverb which says, "Bei Nacht

\* Verworn, "Gleichgewicht u. Otolithenorgan," *Pflüger's Archiv.*, vol. 1., p. 423; also Ewald's "Researches on the Labyrinth as a Sense-organ" ("Ueber das Endorgan des Nervus octavus," Wiesbaden, 1892).

sind alle Katzen grau." The fact which this proverb expresses presents itself experimentally when a spectrum projected on a white surface is watched, while the intensity of the light is gradually diminished. As the colours fade away they become indistinguishable as such, the last seen being the primary red and green.\* Without entering into details, let us consider what this tells us of the specific energy of the visual apparatus. Whether or not the faculty by which we see grey in the dark is one which we possess in common with animals of imperfectly developed vision, there seems little doubt that there are individuals of our own species, who in the fullest sense of the expression have no eye for colour; in whom all colour sense is absent; persons who inhabit a world of grey, seeing all things as they might have done had they and their ancestors always lived nocturnal lives. In the theory of colour vision, as it is commonly stated, no reference is made to such a faculty as we are now discussing.

Professor Hering, whose observations as to the diminished spectrum I referred to just now, who was among the first to subject the vision of the *totally* colour-blind to accurate examination, is of opinion, on that and on other grounds, that the sensation of light and shade is a specific faculty. Very recently the same view has been advocated on a wide basis by a distinguished psychologist, Professor Ebbinghaus.† Happily, as regards the actual experimental results relating to both these main subjects, there seems to be a complete coincidence of observation between observers who interpret them differently. Thus the recent elaborate investigations of Captain Abney‡ (with General Festing), representing graphically the results of his measurements of the subjective values of the different parts of the diminished spectrum, as well as those of the fully illuminated spectrum as seen by the totally colour-blind, are in the closest accord with the observations of Hering, and have, moreover, been substantially confirmed in both points by the measurements of Dr. König in Helmholtz's laboratory at Berlin.§ That observers of such eminence as the three persons whom I have mentioned, employing different methods and with a different purpose in view, and without reference to each other's work, should arrive in so complicated an inquiry at coincident results, augurs well for the speedy settlement of this long-debated question. At present the inference seems to be that such a specific energy as Hering's theory of vision postulates actually exists, and that it has for associates the colour-perceiving activities of the visual apparatus, provided that these are present; but that whenever the intensity of the illumination is below the chromatic threshold—that is, too feeble to awaken these activities—or when, as in the totally colour-blind, they are wanting, it manifests itself independently; all of which can be most easily understood on such a hypothesis as has lately been suggested in an ingenious paper by Mrs. Ladd Franklin,|| that each of the elements of the visual apparatus is made up of a central structure for the sensation of light and darkness, with collateral appendages for the sensations of colour—it being, of course, understood that this is a mere diagrammatic representation, which serves no purpose beyond that of facilitating the conception of the relation between the several "specific energies."

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*Phototaxis and Chemiotaxis.*

Considering that every organism must have sprung from a unicellular ancestor, some have thought that unless we

\* Hering, "Untersuch. eines total Farbenblinden," *Pflüger's Arch.*, vol. xlix., 1891, p. 563.

† Ebbinghaus, "Theorie des Farbensehens," *Zeit. f. Psychol.*, v., 1893, p. 145.

‡ Abney and Festing, "Colour Photometry," Part III. *Phil. Trans.*, clxxxiii.A, 1891, p. 513.

§ König, "Ueber den Helligkeitwerth der Spectralfarben bei verschiedener absoluter Intensität," *Beiträge zur Psychologie, &c.*, "Festschrift zu H. von Helmholtz, 70. Geburtstag," 1891, p. 309.

|| Christine Ladd Franklin, "Eine neue Theorie der Lichtempfindungen," *Zeit. f. Psychologie*, vol. iv., 1893, p. 211; see also the *Proceedings of the last Psychological Congress in London, 1892.*

are prepared to admit a deferred epigenesis of mind, we must look for psychical manifestations even among the lowest animals, and that as in the protozoon all the vital activities are blended together, mind should be present among them not merely potentially but actually, though in diminished degree.

Such a hypothesis involves ultimate questions which it is unnecessary to enter upon: it will, however, be of interest in connection with our present subject to discuss the phenomena which served as a basis for it—those which relate to what may be termed the behaviour of unicellular organisms and of individual cells, in so far as these last are capable of reacting to external influences. The observations which afford us most information are those in which the stimuli employed can be easily measured, such as electrical currents, light, or chemical agents in solution.

A single instance, or at most two, must suffice to illustrate the influence of light in directing the movements of freely-moving cells, or, as it is termed, phototaxis. The rod-like purple organism called by Engelmann *Bacterium photometricum*,\* is such a light-lover that if you place a drop of water containing these organisms under the microscope, and focus the smallest possible beam of light on a particular spot in the field, the spot acts as a light trap and becomes so crowded with the little rodlets as to acquire a deep port wine colour. If instead of making his trap of white light, he projected on the field a microscopic spectrum, Engelmann found that the rodlets showed their preference for a spectral colour which is absorbed when transmitted through their bodies. By the aid of a light trap of the same kind, the very well-known spindle-shaped and flagellate cell of *Euglena* can be shown to have a similar power of discriminating colour, but its preference is different. This familiar organism advances with its flagellum forwards, the sharp end of the spindle having a red or orange eye point. Accordingly, the light it loves is again that which is most absorbed—viz., the blue of the spectrum (line F).

These examples may serve as an introduction to a similar one in which the directing cause of movement is not physical but chemical. The spectral light trap is used in the way already described; the organisms to be observed are not coloured, but bacteria of that common sort which twenty years ago we used to call *Bacterium termo*, and which is recognised as the ordinary determining cause of putrefaction. These organisms do not care for light, but are great oxygen-lovers. Consequently, if you illuminate with your spectrum a filament of a confervoid alga, placed in water containing bacteria, the assimilation of carbon and consequent disengagement of oxygen is most active in the part of the filament which receives the red rays (B to C). To this part, therefore, where there is a dark band of absorption, the bacteria which want oxygen are attracted in crowds. The motive which brings them together is their desire for oxygen. Let us compare other instances in which the source of attraction is food.

The plasmodia of the myxomycetes, particularly one which has been recently investigated by Mr. Arthur Lister,† may be taken as a typical instance of what may be called the chemical allurements of living protoplasm. In this organism, which in the active state is an expansion of labile living material, the delicacy of the reaction is comparable to that of the sense of smell in those animals in which the olfactory organs are adapted to an aquatic life. Just as, for example, the dogfish is attracted by food which it cannot see, so the plasmodium of *Badhamia* becomes aware, as if it smelled it, of the presence of its food—a particular kind of fungus. I have no diagram to

\* Engelmann, "Bacterium Photometricum," *Onderzoek. Physiol. Lab. Utrecht*, vol. vii., p. 200; also "Ueber Licht- u. Farbenperception niederster Organismen," *Pflüger's Arch.*, vol. xxix., p. 387.

† Lister, "On the Plasmodium of *Badhamia utricularis*, &c." *Annals of Botany*, No. 5, June, 1888.

explain this, but will ask you to imagine an expansion of living material, quite structureless, spreading itself along a wet surface; that this expansion of transparent material is bounded by an irregular coast-line; and that somewhere near the coast there has been placed a fragment of the material on which the *Badhamia* feeds. The presence of this bit of *Stereum* produces an excitement at the part of the plasmodium next to it. Towards this centre of activity streams of living material converge. Soon the afflux leads to an outgrowth of the plasmodium, which in a few minutes advances towards the desired fragment, envelopes, and incorporates it.

May I give you another example also derived from the physiology of plants? Very shortly after the publication of Engelmann's observations of the attraction of bacteria by oxygen, Pfeffer made the remarkable discovery that the movements of the antherozoids of ferns and of mosses are guided by impressions derived from chemical sources, by the allurements exercised upon them by certain chemical substances in solution—in one of the instances mentioned by sugar, in the other by an organic acid. The method consisted in introducing the substance to be tested, in any required strength, into a minute capillary tube, closed at one end, and placing it under the microscope in water inhabited by antherozoids, which thereupon showed their predilection for the substance, or the contrary, by its effect on their movements. In accordance with the principle followed in experimental psychology, Pfeffer\* made it his object to determine, not the relative effects of different doses, but the smallest perceptible increase of dose which the organism was able to detect, with this result,—that, just as in measurements of the relation between stimulus and reaction in ourselves we find that the sensational value of a stimulus depends, not on its absolute intensity, but on the ratio between that intensity and the previous excitation, so in this simplest of vital reagents the same so-called psycho-physical law manifests itself. It is not, however, with a view to this interesting relation that I have referred to Pfeffer's discovery, but because it serves as a centre around which other phenomena, observed alike in plants and animals, have been grouped. As a general designation of reactions of this kind Pfeffer devised the term Chemotaxis, or, as we in England prefer to call it, Chemiotaxis. Pfeffer's contrivance for chemiotactic testing was borrowed from the pathologists, who have long used it for the purpose of determining the relation between a great variety of chemical compounds or products, and the colourless corpuscles of the blood. I need, I am sure, make no apology for referring to a question which, although purely pathological, is of very great biological interest—the theory of the process by which, not only in man, but also, as Metschnikoff has strikingly shown, in animals far down in the scale of development, the organism protects itself against such harmful things as, whether articulate or not, are able to penetrate its framework. Since Cohnheim's great discovery in 1867 we have known that the central phenomenon of what is termed by pathologists *inflammation* is what would now be called a chemiotactic one; for it consists in the gathering together, like that of vultures to a carcase, of those migratory cells which have their home in the blood stream and in the lymphatic system, to any point where the living tissue of the body has been injured or damaged, as if the products of disintegration which are set free where such damage occurs were attractive to them.

The fact of chemiotaxis, therefore, as a constituent phenomenon in the process of inflammation, was familiar in pathology long before it was understood. Cohnheim himself attributed it to changes in the channels along which the cells moved, and this explanation was generally accepted, though some writers, at all events, recognised its incompleteness. But no sooner was Pfeffer's discovery

known than Leber,\* who for years had been working at the subject from the pathological side, at once saw that the two processes were of similar nature. Then followed a variety of researches of great interest, by which the importance of chemiotaxis in relation to the destruction of disease-producing microphytes was proved, by that of Buchner† on the chemical excitability of leucocytes being among the most important. Much discussion has taken place, as many present are aware, as to the kind of wandering cells, or leucocytes, which in the first instance attack morbid microbes, and how they deal with them. The question is not by any means decided. It has, however, I venture to think, been conclusively shown that the process of destruction is a chemical one, that the destructive agent has its source in the chemiotactic cells—that is, cells which act under the orders of chemical stimuli. Two Cambridge observers, Messrs. Kanthack and Hardy,‡ have lately shown that, in the particular instance which they have investigated, the cells which are most directly concerned in the destruction of morbid bacilli, although chemiotactic, do not possess the power of incorporating either bacilli or particles of any other kind. While, therefore, we must regard the relation between the process of devitalising and that of incorporating as not yet sufficiently determined, it is now no longer possible to regard the latter as essential to the former.

There seems, therefore, to be very little doubt that chemiotactic cells are among the agents by which the human or animal organism protects itself against infection. There are, however, many questions connected with this action which have not yet been answered. The first of these are chemical ones—that of the nature of the attractive substance and that of the process by which the living carriers of infection are destroyed. Another point to be determined is how far the process admits of adaptation to the particular infection which is present in each case, and to the state of liability or immunity of the infected individual. The subject is therefore of great complication. None of the points I have suggested can be settled by experiments in glass tubes such as I have described to you. These serve only as indications of the course to be followed in much more complicated and difficult investigations—when we have to do with acute diseases as they actually affect ourselves or animals of similar liabilities to ourselves, and find ourselves face to face with the question of their causes.

It is possible that many members of the Association are not aware of the unfavourable—I will not say discreditable—position that this country at present occupies in relation to the scientific study of this great subject—the causes and mode of prevention of infectious diseases. As regards administrative efficiency in matters relating to public health, England was at one time far ahead of all other countries, and still retains its superiority; but as regards scientific knowledge we are, in this subject as in others, content to borrow from our neighbours. Those who desire either to learn the methods of research or to carry out scientific inquiries have to go to Berlin, to Munich, to Breslau, or to the Pasteur Institute in Paris, to obtain what England ought long ago to have provided. For to us, from the spread of our race all over the world, the prevention of acute infectious diseases is more important than to any other nation. At the beginning of this address I urged the claims of pure science. If I could, I should feel inclined to speak even more strongly of the application of science to the discovery of the causes of acute diseases. May I express the hope that the effort which is now being made to establish in England an

\* Leber, "Die Anhäufung der Leucocyten am Orte des Entzündungsreizes," &c., *Die Entstehung der Entzündung*, &c., pp. 423–464, Leipzig, 1891.

† Buchner, "Die Chem. Reizbarkeit der Leucocyten," &c., *Berliner klin. Woch.*, 1890, No. 17.

‡ Kanthack and Hardy, "On the Characters and Behaviour of the Wandering Cells of the Frog," *Proceedings of the Royal Society*, vol. lii., p. 267.

\* Pfeffer, *Untersuch. a. d. botan. Institute z. Tübingen*, vol. i. part 3, 1884.

Institution for this purpose not inferior in inefficiency to those of other countries may have the sympathy of all present? And now may I ask your attention for a few moments more to the subject that more immediately concerns us?

#### Conclusion.

The purpose which I have had in view has been to show that there is one principle—that of adaptation—which separates biology from the exact sciences, and that in the vast field of biological inquiry the end we have is not merely, as in natural philosophy, to investigate the relation between a phenomenon and the antecedent and concomitant conditions on which it depends, but to possess this knowledge in constant reference to the interest of the organism. It may perhaps be thought that this way of putting it is too teleological, and that in taking, as it were, as my text this evening so old-fashioned a biologist as Treviranus, I am yielding to a retrogressive tendency. It is not so. What I have desired to insist on is that *organism* is a fact which encounters the biologist at every step in his investigations; that in referring it to any general biological principle, such as adaptation, we are only referring it to itself, not explaining it; that no explanation will be attainable until the conditions of its coming into existence can be subjected to experimental investigation so as to correlate them with those of processes in the non-living world.

Those who were present at the meeting of the British Association at Liverpool will remember that then, as well as at some subsequent meetings, the question whether the conditions necessary for such an inquiry could be realised was a burning one. This is no longer the case. The patient endeavours which were made about that time to obtain experimental proof of what was called *abiogenesis*, although they conduced materially to that better knowledge which we now possess of the conditions of life of bacteria, failed in the accomplishment of their purpose. The question still remains undetermined; it has, so to speak, been adjourned *sine die*. The only approach to it lies at present in the investigation of those rare instances in which, although the relations between a living organism and its environment ceases as a watch stops when it has not been wound, these relations can be re-established—the process of life re-awakening—by the application of the required stimulus.

I was also desirous to illustrate the relation between physiology and its two neighbours on either side, natural philosophy (including chemistry) and psychology. As regards the latter I need add nothing to what has already been said. As regards the former, it may be well to notice that although physiology can never become a mere branch of applied physics or chemistry, there are parts of physiology wherein the principles of these sciences may be applied directly. Thus, in the beginning of the century, Young applied his investigations as to the movements of liquids in a system of elastic tubes, directly to the phenomena of the circulation; and a century before, Borelli successfully examined the mechanisms of locomotion and the action of muscles, without reference to any, excepting mechanical principles. Similarly, the foundation of our present knowledge of the process of nutrition was laid in the researches of Bidder and Schmidt, in 1851, by determinations of the weight and composition of the body, the daily gain of weight by food or oxygen, the daily loss by the respiratory and other discharges, all of which could be accomplished by chemical means. But in by far the greater number of physiological investigations, both methods (the physical or chemical and the physiological) must be brought to bear on the same question—to co-operate for the elucidation of the same problem. In the researches, for example, which during several years have occupied Professor Bohr, of Copenhagen, relating to the exchange of gases in respiration, he has shown that factors purely physical—namely, the partial pressures of oxygen and carbon dioxide in the

blood which flows through the pulmonary capillaries—are, so to speak, interfered with in their action by the “specific energy” of the pulmonary tissue, in such a way as to render this fundamental process, which, since Lavoisier, has justly been regarded as one of the most important in physiology, much more complicated than we for a long time supposed it to be. In like manner Heidenhain has proved that the process of lymphatic absorption, which before we regarded as dependent on purely mechanical causes—*i.e.*, differences of pressure—is in great measure due to the specific energy of cells, and that in various processes of secretion the principal part is not, as we were inclined not many years ago to believe, attributable to liquid diffusion, but to the same agency. I wish that there had been time to have told you something of the discoveries which have been made in this particular field by Mr. Langley, who has made the subject of “specific energy” of secreting cells his own. It is in investigations of this kind, of which any number of examples could be given, in which vital reactions mix themselves up with physical and chemical ones so intimately that it is difficult to draw the line between them, that the physiologist derives most aid from whatever chemical and physical training he may be fortunate enough to possess.

There is, therefore, no doubt as to the advantages which physiology derives from the exact sciences. It could scarcely be averred that they would benefit in anything like the same degree from closer association with the science of life. Nevertheless, there are some points in respect of which that science may have usefully contributed to the advancement of physics or of chemistry. The discovery of Graham as to the characters of colloid substances, and as to the diffusion of bodies in solution through membranes, would never have been made had not Graham “ploughed,” so to speak, “with our heifer.” The relations of certain colouring-matters to oxygen and carbon dioxide would have been unknown, had no experiments been made on the respiration of animals and the assimilative process in plants; and, similarly, the vast amount of knowledge which relates to the chemical action of ferments must be claimed as of physiological origin. So also there are methods, both physical and chemical, which were originally devised for physiological purposes. Thus the method by which meteorological phenomena are continuously recorded graphically originated from that used by Ludwig (1847) in his “Researches on the Circulation”; the mercurial pump, invented by Lothar Meyer, was perfected in the physiological laboratories of Bonn and Leipzig; the rendering the galvanometer needle aperiodic by damping was first realised by du Bois-Reymond—in all of which cases invention was prompted by the requirements of physiological research.

Let me conclude with one more instance of a different kind, which may serve to show how, perhaps, the wonderful ingenuity of contrivance which is displayed in certain organised structures—the eye, the ear, or the organ of voice—may be of no less interest to the physicist than to the physiologist. Johannes Müller, as is well known, explained the compound eye of insects on the theory that an erect picture is formed on the convex retina by the combination of pencils of light, received from different parts of the visual field through the eyelets (*ommatidia*) directed to them. Years afterwards it was shown that in each eyelet an image is formed which is reversed. Consequently, the mosaic theory of Müller was for a long period discredited on the ground that an erect picture could not be made up of “upside-down” images. Lately the subject has been re-investigated, with the result that the mosaic theory has regained its authority. Professor Exner,\* has proved photographically that behind each part of the insect's eye an erect picture is formed of the objects towards which it is directed. There is, therefore, no longer any difficulty in understanding how the

\* Exner, “Die Physiologie der facettirten Augen von Krebsen u. Insecten,” Leipzig, 1891.

whole field of vision is mapped out as consistently as it is imaged on our own retina, with the difference, of course, that the picture is erect. But behind this fact lies a physical question—that of the relation between the erect picture which is photographed and the optical structure of the crystal cones which produce it—a question which, although we cannot now enter upon it, is quite as interesting as the physiological one.

With this history of a theory which, after having been for thirty years disbelieved, has been reinstated by the fortunate combination of methods derived from the two sciences, I will conclude. It may serve to show how, though physiology can never become a part of natural philosophy, the questions we have to deal with are cognate. Without forgetting that every phenomenon has to be regarded with reference to its useful purpose in the organism, the aim of the physiologist is not to inquire into final causes, but to investigate processes. His question is ever *How*, rather than *Why*.

May I illustrate this by a simple, perhaps too trivial, story, which derives its interest from its having been told of the childhood of one of the greatest natural philosophers of the present century? He was even then possessed by that insatiable curiosity which is the first quality of the investigator; and it is related of him that his habitual question was "What is the *go* of it?" and if the answer was unsatisfactory, "What is the particular *go* of it?" That North Country boy became Professor Clerk Maxwell. The questions he asked are those which in our various ways we are all trying to answer.

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ADDRESS TO THE CHEMICAL SECTION  
OF THE  
BRITISH ASSOCIATION.  
NOTTINGHAM, 1893.

By Professor EMERSON REYNOLDS, M.D., Sc.D., F.R.S.,  
President of the Section.

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At the Nottingham Meeting of the British Association in 1866, Dr. H. Bence Jones addressed the Section over which I have now the honour to preside on the place of Chemical Science in Medical Education. Without dwelling on this topic to-day, it is an agreeable duty to acknowledge the foresight of my predecessor as to the direction of medical progress. Twenty-seven years ago the methods of inquiry and instruction in medicine were essentially based on the formal lines of the last generation. Dr. Bence Jones saw that modern methods of research in chemistry—and in the experimental sciences generally—must profoundly influence medicine, and he urged the need of fuller training of medical students in those sciences.

The anticipated influence is now operative as a powerful factor in the general progress of medicine and medical education; but much remains to be desired in regard to the chemical portion of that education. In the later stages of it, undue importance is still attached to the knowledge of substances rather than of principles; of products instead of the broad characters of the chemical changes in which they are formed. Without this higher class of instruction it is unreasonable to expect an intelligent perception of complex physiological and pathological processes which are chemical in character, or much real appreciation of modern pharmacological research. I have little doubt, however, that the need for this fuller chemical education will soon be so strongly felt that the necessary reform will come from within a profession which has given ample proof in recent years of its zeal in the cause of scientific progress.

In our own branch of science the work of the year has been substantial in character, if almost unmarked by discoveries of popular interest. We may probably place in the latter category the measure of success which the skill of Moissan has enabled him to attain in the artificial production of the diamond form of carbon, apparently in minute crystals similar to those recognised by Koenig, Mallard, Daubrée, and by Friedel in the supposed meteorite of Cañon de Diablo in Arizona. Members of the Section will probably have the opportunity of examining some of these artificial diamonds through the courtesy of M. Moissan, who has also, at my request, been so good as to arrange for us a demonstration of the properties of the element fluorine, which he succeeded in isolating in 1887.

Not less interesting or valuable are the studies of Dr. Perkins, on electro-magnetic rotation; of Lord Rayleigh, on the relative densities of gases; of Dewar, on chemical relations at extremely low temperatures; of Clowes, on exact measurements of flame-cap indications afforded by Miner's testing lamps; of Horace Brown and Morris, on the chemistry and physiology of foliage leaves, by which they have been led to the startling conclusion that cane-sugar is the first sugar produced during the assimilation of carbon, and that starch is formed at its expense as a more stable reserve material for subsequent use of the plant; or of Cross, Bevan, and Beadle, on the interaction of alkali cellulose and carbon bisulphide, in the course of which they have proved that a cellulose residue can act like an alcohol radical in the formation of thiocarbonates, and thus have added another to the authors' valuable contributions to our knowledge of members of the complex group of celluloses.

But it is now an idle task for a President of this Section to attempt a slight sketch of the works of chemical philosophers even during the short space of twelve months; they are too numerous and generally too important to be lightly treated, hence we can but apply to them a paraphrase of the ancient formula—Are they not written in the books of the chronicles we term "Jahresberichte," "Annales," or "Transactions and Abstracts," according to our nationality?

I would, however, in this connection ask your consideration for a question relating to the utilisation of the vast stores of facts laid up—some might even say buried—in the records to which reference has just been made. The need exists, and almost daily becomes greater, for facile reference to this accumulated wealth, and of such a kind that an investigator, commencing a line of inquiry with whose previous history he is not familiar, can be certain to learn *all* the facts known on the subject up to a particular date, instead of having only the partial record to be found in even the best edited of the dictionaries now available. The best and most obvious method of attaining this end is the publication of a subject-matter index of an ideally complete character. I am glad to know that the Chemical Society of London will probably provide us in the years to come with a compilation which will doubtless aim at a high standard of value as a work of reference to memoirs, and in some degree to their contents, so far as the existing indexes of the volumes of the Society's Journal supply the information. Whether this subject-matter index is published or not, the time has certainly arrived for adopting the immediately useful course of publishing monographs, analogous to those now usual in Natural Science, which shall contain all the information gained up to a particular date in the branch of chemistry with which the author is specially familiar by reason of his own work in the subject. Such monographs should include much more than any mere compilation, and would form the best material from which a complete subject-matter index might ultimately be evolved.

My attention was forcibly drawn to the need of such special records by noting the comparatively numerous cases of re-discovery and imperfect identification of derivatives of thiourea. In my laboratory, where this

\* "Life of Clerk Maxwell" (Campbell and Garnett), p. 28.

substance was isolated, we naturally follow with interest all work connected with it, and therefore readily detect lapses of the kind just mentioned. But when it is remembered that the distinct derivatives of thiourea now known number considerably over six hundred substances, and that their descriptions are scattered through numerous British and foreign journals, considerable excuse can be found for workers overlooking former results. The difficulty which exists in this one small department of the science I hope shortly to remove, and trust that others may be induced to provide similar works of reference to the particular branches of chemistry with which they are personally most familiar.

When we consider the drift of investigation in recent years, it is easy to recognise a distinct reaction from extreme specialisation in the prominence now given to general physico-chemical problems, and to those broad questions concerning the relations of the elements which I would venture to group under the head of "Comparative Chemistry." Together these lines of inquiry afford promise of definite information about the real nature of the seventy or more entities we term "elements," and about the mechanism of that mysterious yet definite change in matter which we call "chemical action." Now and again one or other class of investigation enables us to get some glimpse beyond the known which stimulates the imaginative faculty.

For example, a curious side-light seems to be thrown on the nature of the elements by the chemico-physical discussion of the connection existing between the constitution of certain organic compounds and the colours they exhibit. Without attempting to intervene in the interesting controversy in which Armstrong and Hartley are engaged as to the nature of the connection, we may take it as an established fact that a relation exists between the power which a dissolved chemical compound possesses of producing the colour impression within our comparatively small visual range, and the particular mode of grouping of its constituent radicals in its molecule: Further, the reality of this connection will be most freely admitted in the class of aromatic compounds—that is, in derivatives of benzene—whose constituents are so closely linked together as to exhibit quasi-elemental persistence. If, then, the possession of what we call colour by a compound be connected with its constitution, may we not infer that "elements" which exhibit distinct colour, such as gold and copper, in thin layers and in their soluble compounds are at least complexes analogous to definitely decomposable substances? This inference, while legitimate as it stands, would obviously acquire strength if we could show that anything like isomerism exists among the elements; for identity of atomic weight of any two chemically distinct elements must, by all analogy with compounds, imply dissimilarity in constitution, and therefore definite structure, independently of any argument derived from colour. Now, nickel and cobalt are perfectly distinct elements, as we all know, but, so far as existing evidence goes, the observed differences in their atomic weights (nickel 58.6, cobalt 58.7) are so small as to be within the range of the experimental errors to which the determinations were liable. Here, then, we seem to have the required example of something like isomerism among elements, and consequently some evidence that these substances are complexes of different orders; but in the cases of cobalt and nickel we also know that in transparent solutions of their salts, if not in thin layers of the metals themselves, they exhibit strong and distinct colours; compare the beautiful rosy tint of cobalt sulphate with the brilliant green of the corresponding salt of nickel. Therefore, in exhibiting characteristically different colours, these substances afford us some further evidence of structural differences between the matter of which they consist, and support the conclusion to which their apparent identity in atomic weight would lead us. By means of such side-lights we may gradually acquire some idea of the nature of the elements, even if we are

unable to get any clue to their origin other than such as may be found in Crookes's interesting speculations.

Again, while our knowledge of the genesis of the chemical elements is as small as astronomers possess of the origin of the heavenly bodies, much suggestive work has recently been accomplished in the attempt to apply the principle of gravitation, which simply explains the relative motions of the planets, to account for the interactions of the molecules of the elements. The first step in this direction was suggested by Mendeleeff in his Royal Institution lecture (May 31, 1889), wherein he proposed to apply Newton's third law of motion to chemical molecules, regarded as systems of atoms analogous to double stars. The Rev. Dr. Haughton has followed up this idea with his well-known mathematical skill, and, in a series of papers just published, has shown that the three Newtonian laws are applicable to explain the interactions of chemical molecules, "with this difference, that whereas the specific coefficient of gravity is the same for all bodies, independent of the particular kind of matter of which they are composed, the atoms have specific coefficients of attraction which vary with the nature of the atoms concerned." The laws of gravitation, with this proviso, were found to apply to all the definite cases examined, and it was shown that a chemical change of combination is equivalent to a planetary catastrophe. So far the fundamental hypothesis of "Newtonian Chemistry" has led to conclusions which are not at variance with the facts of the science, while it gives promise of help in obtaining a solution of the great problem of the nature of chemical action.

Passing from considerations of the kind to which I have just referred, permit me to occupy the rest of the time at my disposal with a short account of a line of study in what I have already termed "comparative chemistry," which is not only of inherent interest, but seems to give us the means of filling in some details of a hitherto rather neglected chapter in the early chemical history of this earth.

The most remarkable outcome of "comparative chemistry" is the periodic law of the elements, which asserts that the properties of the elements are connected in the form of a periodic function with the masses of their atoms. Concurrently with the recognition of this principle, other investigations have been in progress, aiming at more exact definitions of the characters of the relations of the elements, and ultimately of their respective offices in nature. Among inquiries of this kind the comparative study of the elements carbon and silicon appears to me to possess the highest interest. Carbon, whether combined with hydrogen, oxygen, or nitrogen, or with all three, is the great element of organic nature, while silicon, in union with oxygen and various metals, not only forms about one-third of the solid crust of the earth, but is unquestionably the most important element of inorganic nature. The chief functions of carbon are those which are performed at comparatively low temperatures; hence carbon is essentially the element of the present epoch. On the other hand, the activities of silicon are most marked at very high temperatures; hence it is the element whose chief work in nature was performed in the distant past, when the temperature of this earth was far beyond that at which the carbon compounds of organic life could exist. Yet between these dominant elements of widely different epochs remarkably close analogies are traceable, and the characteristic differences observed in their relations with other elements are just those which enable each to play its part effectively under the conditions which promote its greatest activity.

The chemical analogies of the two tetrad elements carbon and silicon are most easily recognised in compounds which either do not contain oxygen or which are oxygen compounds of a very simple order, and the following Table will recall a few of the most important of these, as well as some which have resulted from the fine researches of Friedel, Crafts, and Ladenburg:—

## Some Silicon Analogues of Carbon Compounds.

SiH <sub>4</sub> .. ..	Hydrides .. ..	CH <sub>4</sub> .
SiCl <sub>4</sub> } .. ..	Chlorides .. ..	{ CCl <sub>4</sub> .
Si <sub>2</sub> Cl <sub>6</sub> }		{ C <sub>2</sub> Cl <sub>6</sub> .
SiO <sub>2</sub> .. ..	Oxides .. ..	CO <sub>2</sub> .
H <sub>2</sub> SiO <sub>3</sub> .. ..	Meta acids.. ..	H <sub>2</sub> CO <sub>3</sub> .
HSiHO <sub>2</sub> .. ..	Formic acids .. ..	HCHO <sub>2</sub> .
(SiHO) <sub>2</sub> O .. ..	Formic anhydrides .. ..	(CHO) <sub>2</sub> O ?
H <sub>2</sub> Si <sub>2</sub> O <sub>4</sub> .. ..	Oxalic acids .. ..	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .
HSi(CH <sub>3</sub> )O <sub>2</sub> .. ..	Acetic acids .. ..	HC(CH <sub>3</sub> )O <sub>2</sub> .
HSi(C <sub>6</sub> H <sub>5</sub> )O <sub>2</sub> .. ..	Benzoic acids .. ..	HC(C <sub>6</sub> H <sub>5</sub> )O <sub>2</sub> .
SiC <sub>8</sub> H <sub>19</sub> H .. ..	Nonyl hydrides.. ..	C <sub>9</sub> H <sub>19</sub> H.
SiC <sub>8</sub> H <sub>19</sub> OH .. ..	Nonyl alcohols .. ..	C <sub>9</sub> H <sub>19</sub> OH.

But these silicon analogues of carbon compounds are generally, very different from the latter in reactive power, especially in presence of oxygen and water. For example, hydride of silicon, even when pure, is very easily decomposed, and, if slightly warmed, is spontaneously inflammable in air; whereas the analogous marsh gas does not take fire in air below a red heat. Again, the chlorides of silicon are rapidly attacked by water, affording silicon hydroxides and hydrochloric acid; but the analogous carbon chlorides are little affected by water even at comparative high temperatures. Similarly, silicon chloroform and water quickly produce silico-formic acid and anhydride along with hydrochloric acid, while ordinary chloroform can be kept in contact with water for a considerable time without material change.

Until recently no well-defined compounds of silicon were known including nitrogen; but we are now acquainted with a number of significant substances of this class.

Chemists have long been familiar with the fact that a violent reaction takes place when silicon chloride and ammonia are allowed to interact. Persoz, in 1830, assumed that the resulting white powder was an addition compound, and assigned to it the formula SiCl<sub>4</sub>.6NH<sub>3</sub>, while Besson, as lately as 1892, gave SiCl<sub>4</sub>.5NH<sub>3</sub>. These formulæ only express the proportions in which ammonia reacts with the chloride under different conditions, and give us no information as to the real nature of the product; hence they are almost useless. Other chemists have, however, carefully examined the product of this reaction, but owing to peculiar difficulties in the way have not obtained results of a very conclusive kind. It is known that the product when strongly heated in a current of ammonia gas affords ammonium chloride which volatilises and a residue, to which Schutzenberger and Colson have assigned the formula Si<sub>2</sub>N<sub>3</sub>H. This body they regard as a definite hydride of Si<sub>2</sub>N<sub>3</sub>, which latter they produced by acting on silicon at a white heat with pure nitrogen. Gattermann suggests that a nearer approach to the silicon analogue of cyanogen, Si<sub>2</sub>N<sub>2</sub>, should be obtained from the product of the action of ammonia on silicon chloroform; but it does not appear that this suggestion has yet borne fruit. It was scarcely probable that the above-mentioned rather indefinite compounds of silicon with nitrogen were the only ones of the class obtainable, since bodies including carbon combined with nitrogen are not only numerous, but are among the most important carbon compounds known. Further investigation was therefore necessary in the interests of comparative chemistry, and for special reasons which will appear later on; but it was evident that a new point of attack must be found.

A preliminary experimental survey proved the possibility of forming numerous compounds of silicon containing nitrogen, and enabled me to select those which seemed most likely to afford definite information. For much of this kind of work silicon chloride was rather too energetic, hence I had a considerable quantity of the more manageable silicon tetrabromide prepared by Serullas's method, viz., by passing the vapour of crude bromine (containing a little chlorine) over a strongly-heated mixture of silica and charcoal. In purifying this

product I obtained incidentally the chloro-bromide of silicon, SiClBr<sub>3</sub>, which was required in order to complete the series of possible chlorobromides of silicon.\*

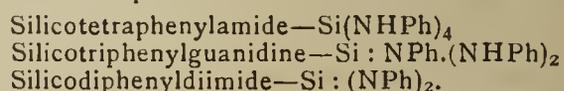
Silicon bromide was found to produce addition compounds very readily with many feebly-basic substances containing nitrogen. But one group of bromides of this class has yet been investigated in detail, namely, the products afforded by thioureas. The typical member of this group is the perfectly definite but uncrystalline substance—



Substituted thioureas afford similar bodies, the most interesting of which is the allyl compound. This is a singularly viscid liquid, which requires several days at ordinary temperatures to regain its level, when a tube containing it is inverted. But these are essentially addition compounds, and are therefore comparatively unimportant.

In most cases, however, the silicon haloids enter into very definite reaction with nitrogen compounds, especially when the latter are distinctly basic, such as aniline or any of its homologues. One of the principal products of this class of change is the beautiful typical substance on the table, which is the first well-defined crystalline compound obtained in which silicon is exclusively combined with nitrogen. Its composition is Si(NHC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>.† Analogous compounds have been formed with the toluidines, naphthylamines, &c., and have been examined in considerable detail, but it suffices to mention them and proceed to point out the nature of the changes we can effect by the action of heat on the comparatively simple anilide.

When silicon anilide is heated carefully *in vacuo* it loses one molecule of aniline very easily and leaves triphenyl guanidine, probably the *a* modification; if the action of heat be continued, but at ordinary pressure and in a current of dry hydrogen, another molecule of aniline can be expelled, and, just before the last trace of the latter is removed, the previously liquid substance solidifies and affords a silicon analogue of the insoluble modification of carbodiphenyldiimide, which may then be heated moderately without undergoing further material change. A comparison of the formulæ will make the relations of the products clear:—



Moreover, the diimide has been heated to full redness in a gas combustion furnace while dry hydrogen was still passed over it; even under these conditions little charring occurred, but some nitrogen and a phenyl radical were eliminated, and the purified residue was found to approximate in composition to SiNPh, which would represent the body as phenylsilicocyanide or a polymer of it. Even careful heating of the diimide in ammonia gas has not enabled me to remove all the phenyl from the compound, but rather to retain nitrogen, as the best residue obtained from such treatment consisted of Si<sub>2</sub>N<sub>3</sub>Ph, or the phenylic derivative of one of the substances produced by Schutzenberger and Colson from the ammonia reaction. It may be that both these substances are compounds of silicocyanogen with an imide group of the kind below indicated:—



Further investigation must decide whether this is a real relationship; if it be we should be able to remove the imidic group and obtain silicocyanogen in the free state. One other point only need be noticed, namely, that when the above silicon compounds are heated in oxygen they

\* Three years later Besson formed the same compound and described it as new.

† Harden has obtained an uncrystalline intermediate compound, SiCl<sub>2</sub>(NHC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>.

are slowly converted into  $\text{SiO}_2$ ; but the last traces of nitrogen are removed with great difficulty, unless water-vapour is present, when ammonia and silica are quickly formed.

Much remains to be done in this department of comparative chemistry, but we may fairly claim to have established the fact that silicon, like carbon, can be made to form perfectly well-defined compounds, in which it is exclusively united with the triad nitrogen of amidic and imidic groups.

Now, having proved the capacity of silicon for the formation of compounds of this order with a triad element, Nature very distinctively lets us understand that nitrogen is not the particular element which is best adapted to play the triad rôle towards silicon in its high-temperature changes, which are ultimately dominated by oxygen. We are not acquainted with any natural compounds which includes silicon and nitrogen; but large numbers of the most important minerals contain the pseudo-triad element aluminum combined with silicon, and few include any other triad. Phosphorus follows silicon in the periodic system of the elements as nitrogen does carbon, but silicates containing more than traces of phosphorus are rare; on the other hand, silicates are not uncommon containing boron, the lower homologue of aluminum; for example, axinite, datholite, and tourmaline.

Moreover, it is well known that silicon dissolves freely in molten aluminum, though much of the former separates on cooling. Winkler has analysed the gangue of aluminum saturated with silicon, and found that its composition is approximately represented by the formula  $\text{SiAl}$ , or, perhaps,  $\text{Si}_2\text{Al}_2$ , if we are to regard this as analogous to  $\text{C}_2\text{N}_2$  or cyanogen. Here aluminum at least resembles nitrogen in directly forming a compound with silicon at moderately high temperature. It would appear, then, that while silicon can combine with both the triads nitrogen and aluminum, the marked positive characters of the latter, and its extremely low volatility, suit it best for the production of permanent silicon compounds similar to those which nitrogen can afford.

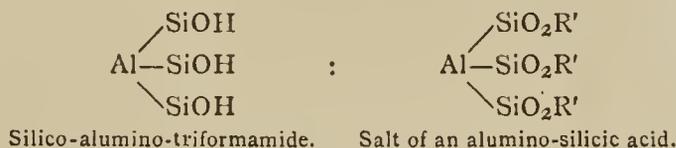
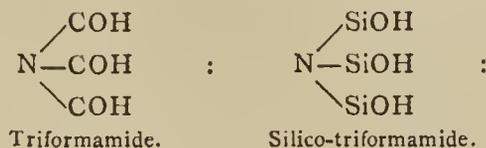
With these facts in mind we may carry our thoughts back to that period in the earth's history when our planet was at a higher temperature than the dissociation point of oxygen compounds. Under such conditions the least volatile elements were probably liquids, while silicides and carbides of various metals were formed in the fluid globe. We can imagine that the attraction of aluminum for the large excess of silicon would assert itself, and that, as the temperature fell below the point at which oxidation became possible, these silicides and carbides underwent some degree of oxidation, the carbides suffering most owing to the volatility of the oxides of carbon, while the fixity of the products of oxidation of silicides rendered the latter process a more gradual one. The oxidation of silicides of metals which had little attraction for silicon would lead to the formation of simple metallic silicates and to the separation of the large quantities of free silica we meet with in the solid crust of the earth, whereas oxidation of silicides of aluminum would not break up the union of the two elements, but rather cause the ultimate formation of the aluminosilicates which are so abundant in most of our rocks.

Viewed in the light of the facts already cited and the inferences we have drawn from them as to the nitrogen-like relationship of aluminum to silicon, I am disposed to regard the natural aluminosilicates as products of final oxidation of sometime active silico-aluminum analogues of carbo-nitrogen compounds, rather than ordinary double salts. It is generally taken for granted that they are double salts, but recent work on the chromoxalates by E. A. Werner has shown that this view is not necessarily true of all such substances.

Without going into undue detail we can even form some conception of the general course of change from simple

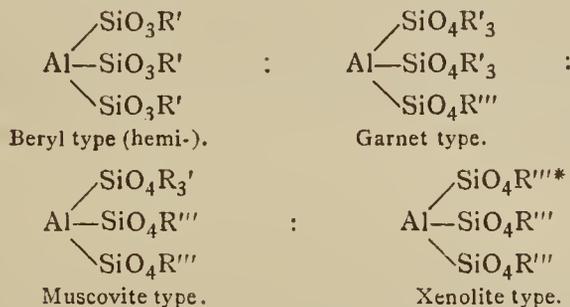
aluminum silicide to an aluminosilicate, if we allow the analogies already traced to lead us further.

We recognise the existence of silico-formyl in Friedel and Ladenburg's silico-formic anhydride; hence silico-triformamide is a compound whose probable formation we can admit, and, on the basis of our aluminum-nitrogen analogy, an aluminum representative also. Thus—



Now, oxidation of triformamide would lead to complete re-solution into nitrogen gas, carbon dioxide gas and water rendering it an extremely unstable body; under similar conditions silico-triformamide would probably afford nitrogen gas and silicic acid (or silicon dioxide and water); while the third compound, instead of breaking up, would (owing to the fixity of aluminum as compared with nitrogen) be likely at first to afford a salt of an aluminosilicic acid, in presence of much basic material.

The frequent recurrence of the ratios  $\text{Si}_3\text{Al}$ ,  $\text{Si}_3\text{Al}_2$ , &c., in the formulæ of natural aluminosilicates, suggests that some at least of these minerals are derived from oxidation products of the above triformic type. Without stopping to trace all the possible stages in the oxidation of the primary compound  $\text{Al}(\text{SiO}_2\text{R}')_3$ , or variations in basicity of the products, I may cite the four following examples out of many others which might be given of resulting representative mineral groups:—



Five years ago Professor F. W. Clarke, of the United States Geological Survey, published a most interesting paper on the structure of the natural silicates. In this he adapts the view that the mineral xenolite,  $\text{Si}_3\text{Al}_4\text{O}_{12}$ , is the primary from which all other aluminosilicates may be supposed to arise by various substitutions. Nature, however, seems to teach us that such minerals as xenolite, fibrolite, and the related group of "clays" are rather to be regarded as end-products of a series of hydrolytic changes of less aluminous silicates than primary substances themselves; hence the sketch which I have ventured to give above of the probable genesis of aluminosilicates seems to provide a less arbitrary basis for Clarke's interesting work, without materially disturbing the general drift of his subsequent reasoning.

We may now consider for a moment in what direction evidence can be sought for the existence in nature of derivatives of the hypothetical intermediate products of oxidation between a primary silicide and its fully oxidised silicate.

In the absence of a working hypothesis of the kind which I have already suggested, it is not probable that direct evidence would yet be obtainable—this must be work for the future—but when we consider that the exist-

\* In these cases where  $\text{R}'' = \text{Al}$  it is, of course, assumed that the latter is acting only as a basic radical.

ence of compounds of the order in question would manifest themselves in ordinary mineral analyses by the analytical products exceeding the original weight of material, we seem to find some evidence on the point in recorded cases of the kind. A deficiency of a single atom of oxygen in compounds having the high molecular weights of those in question, would be indicated by very small excesses (from 2 to 3 per cent) whose real meaning might be easily overlooked. Now, such results are not at all unusual in analyses of mineral aluminosilicates. For instance, *Amphiboles* containing a mere trace of iron have afforded 102.75 parts from 100, and almost all analyses of *Microsommites* are high, giving as much as 103 parts. In less degree *Vesuvianite* and members of the *Andalusite* group may be noted. All these cases may be capable of some other explanations, but I cite them to show that such excesses are commonly met with in published analyses. On the other hand, it is scarcely to be doubted that a good analyst, who obtained a really significant excess, would throw such a result aside as erroneous and never publish it. I therefore plead for much greater care in analyses of the kind in question, and closer scrutiny of results in the light of the suggestions I have ventured to offer. It is probable that silicates containing only partially oxidised aluminum are rare; nevertheless the search for them would introduce a new element of interest into mineralogical inquiries.

If the general considerations I have now endeavoured to lay before you are allowed their full weight, some of the aluminosilicates of our primary rocks reveal to us more than we hitherto supposed. Regarded from this newer standpoint, they are teleoxidised representatives of substances which foreshadowed in terms of silicon, aluminum, and oxygen the compounds of carbon, nitrogen, and hydrogen required at a later stage of the earth's history for living organisms. Thus, while the sedimentary strata contain remains which come down to us from the very dawn of life on this globe, the rocks from whose partial disintegration the preserving strata resulted contain mineral records which carry us still further back, even to Nature's earliest efforts in building up compounds similar to those suited for the purposes of organic development.

## LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1893.

By WILLIAM CROOKES, F.R.S.,

and  
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,  
Professor of Chemistry at the University of Oxford.

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

London, August 10th, 1893.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the 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 July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

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

In Table III. we have recorded the oxygen required to

oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples only one was recorded as "clear, but dull." All the others were clear, bright, and well filtered.

In our report for last month we drew attention to the long drought, which towards the end of June showed signs of breaking. The rainfall at the time of reporting was too slight to produce any difference in the quality of the waters. This month, however, the rain has been somewhat excessive, the total amount being 3.70 inches at Oxford, whereas the average fall for twenty-five years is 2.58 inches. The effect of this excess of rain is well seen in the following Table:—

	Common salt per gallon.	Nitric acid per gallon.	Hardness. Degrees.	Oxygen required for oxidation per gallon.	Organic carbon per gallon.	Colour.	
						Brown.	Blue.
May	2.196	0.611	14.66	0.029	0.062	11.3	: 20
June	2.155	0.601	14.74	0.033	0.065	—	: 20
July	2.114	0.674	13.96	0.036	0.070	15.9	: 20

The common salt and the hardness have diminished, consequent on the more flooded state of the river. The organic carbon and oxygen required to oxidise it have increased, but only in the third decimal place—a negligible amount; and the brown colour is also slightly higher, all pointing to more organic matter in the July than in the June waters. At the same time the nitric acid has risen, showing that whatever the source of the organic matter might have been, the self-purifying power of the stream was well able to deal with the nitrogen present. The colour of the water points to a peaty origin for the organic matter, and this is borne out by the reduction in the amount of common salt, showing that the organic matter must have been chiefly of vegetable origin. Considering that July has experienced a sudden and excessive rainfall, following on one of the longest droughts on record, the excellent quality of the Metropolitan waters during the month points to a very high average standard of purity.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

## ON ERBIA.\*

By GERHARD KRÜSS

MOSANDER'S investigations had shown in 1843 that the substance then known as yttria can be resolved into a yellow oxide and two colourless earths; he named the coloured earths erbia. The existence of such an earth was confirmed by Berlin in 1860, but it was again brought into question by Popp. By the researches of Delafontaine, and especially of Bahr and Bunsen, we finally reached the view that an erbia, a coloured yttrium earth, was really existent, and though by the further investigations of Marignac, Soret, Nilson, Cleve, Brauner, and others, further oxides, such as scandia, ytterbia, thulia, holmia (Soret's X), and terbia were separated from the erbia of the "sixties," the name erbia has up to the present day been retained for that earth which in its properties comes nearest to the former erbia. Among the group of the rare gadolinite earths precipitable by oxalic acid, erbia is that oxide which behaves more strongly basic than scandia and ytterbia, and also than Cleve's thulia, but is more feebly basic than Cleve's holmia, than terbia, and, above all, than yttria. Erbia ranges in colour from a tender rose to an amythest-red, and yields salts the solutions of which display in the absorption-spectrum the two

\* *Zeitschrift für Anorganische Chemie.*

bands characteristic of erbium, Er  $\alpha$  at  $\lambda = 654.7$  and Er  $\beta$  at  $\lambda = 523.1$ .

It must be mentioned that I have never been able to obtain an erbium preparation the solution of which on the examination of thick strata displayed merely the Er  $\alpha$  and Er  $\beta$  lines; there always occurred simultaneously some other lines, which are ascribed to holmium or to samarium. Many erbium preparations from the most different sources have been examined, including some in whose production more than 400 decompositions of nitrates have been executed.

The composition of erbium oxide was formerly taken as ErO, but it is now considered to be Er<sub>2</sub>O<sub>3</sub>. If we assume erbium as trivalent, we may calculate (according to the equivalent of erbia determined by P. T. Cleve and O. M. Höglund) for erbium the atomic weight of 170.4; subsequently it was determined by Humpidge and W. Burney = 171.3.

After characterising thulium <sup>III</sup>Tm = 171, and holmium <sup>III</sup>HO about 161, Cleve finally found, in 1880, by the analysis of the sulphate, <sup>III</sup>Er = 166. Subsequently no full investigation of erbia has been undertaken.

Some years ago I endeavoured to begin an examination of erbia ("Geschichte des Erbium and Didymium," *Liebig's Annalen*, cclxv., 1), as the spectroscopic examinations of L. F. Nilson and G. Krüss rendered it probable that erbia is not a unitary body. I endeavoured to furnish this proof, not in a physical but in a chemical manner. In the first place there resulted certain points of view with reference to the methods of examination and separation for the gadolinite earths, which have been communicated in *Liebig's Annalen* and in the *Zeitsch. für Anorg. Chem.*, iii., 44, 60, 89, 92, 108.

In particular the behaviour of aniline and aniline hydrochlorate with the solutions of the earthy salts proved very valuable. The application of the "aniline method" in conjunction with the well-known method of decomposing the nitrates, decomposing the earthy nitrates by partial fractionation with heat, has rendered possible the results given below on the nature of erbia.

Such researches can at present be carried out only with a relatively large quantity of the costly material of the rare earths. I am therefore bound to declare my thanks to the Trustees of the "Elizabeth Thomson Science Fund" for the support which they have afforded me for carrying out my investigation on the nature of erbium.

At the same time I am greatly indebted to H. L. F. Nilson, of Stockholm, since he sent me the valuable material which he had acquired during the discovery of scandia and during the examination of ytterbia from the gadolinite earths. It was 404.5 grms. yttria earths

<sup>III</sup>(R=89-92), 205.8 grms. of various holmia earths, 144.5 grms. erbium material, and 246.8 grms. ytterbia and thulia materials. If we consider what troublesome work is requisite to obtain such quantities of these earths in a relatively pure condition, we must highly appreciate the disinterested manner in which H. Nilson placed these specimens at my disposal.

The following experiments on erbia, holmia, and terbia were first made with rather smaller quantities of earths which I had prepared myself. Having thus felt my way, I took in hand the earths obtained from H. Nilson. The composition of the earths was ascertained, not merely spectroscopically, but by determining the equivalents of the earths. The methods were used described in *Zeitsch. f. Anorg. Chem.*, iii., 45-55. Before each determination of an equivalent, the earth to be analysed was carefully purified according to the instructions given in *Zeitsch. f. Anorg. Chem.*, iii., 48-49. In many cases it is sufficient to take for analysis only single fractions for the sake of a preliminary survey of the distribution of the several yttria-earth within a series of decompositions.

(To be continued.)

## OBITUARY.

C. W. HEATON, F.I.C., F.C.S.

THE death is announced of Mr. C. W. Heaton, Professor of Chemistry in Charing Cross Hospital. Mr. Heaton commenced his studies first in the laboratory of Dugald Campbell and afterwards under Dr. Stenhouse in the laboratory of St. Bartholomew's Hospital, where he was Fellow Assistant with Professor Kekulé, Dr. Attfield, and the late Prof. Tuson, of the Royal Veterinary College, Camden Town; with the last-named two he enjoyed a life-long friendship. He subsequently acted as Assistant and Demonstrator in the Royal Veterinary College and at Charing Cross Hospital, and he finally succeeded to the post of Lecturer in the latter institution in 1862, a post which he held up to the time of his death. He undertook with conspicuous success the teaching of chemistry at Repton School, Tunbridge School, and Epsom College. Mr. Heaton was Examiner in Chemistry to the Royal College of Physicians and to the Royal College of Veterinary Surgeons, was Treasurer to the Society of Public Analysts, and filled the office of Public Analyst to the parish of St. Martin-in-the-Fields. He was also Lecturer to the London School of Medicine for Women. His literary works included contributions chiefly to the *Lancet*, to the *Saturday Review*, and to other Science Journals, as well as to various Art Journals. He re-edited and almost re-wrote "Stöckhardt's Chemistry," a text-book still in favour with students of medicine and others. He was connected with many important investigations of a technico-chemical character, and was interested to the last in the improved purification of coal-gas and of the recovery of sulphur therefrom. Mr. Heaton's personal character was such as to secure for him the high and universal esteem and respect of his brother chemists, whilst his pupils will ever remember him as a generous, kind, and painstaking teacher.

## MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) of the Nottingham Meeting of the British Association:—

*President*—Prof. J. Emerson Reynolds, M.D., D.Sc., F.R.S., V.P.C.S.

*Vice-Presidents*—Prof. F. Clowes, D.Sc., F.C.S.; Prof. H. B. Dixon, M.A., F.R.S., F.C.S.; J. H. Gladstone, Ph.D., F.R.S.; Prof. H. McLeod, F.R.S., F.C.S.; W. H. Perkin, LL.D., Ph.D., F.R.S., V.P.C.S.; Prof. W. A. Tilden, D.Sc., F.R.S.

*Secretaries*—J. B. Coleman, F.C.S., A.R.C.Sc.; M. J. R. Dunstan, M.A., F.R.S.E.; D. H. Nagel, M.A., F.C.S.; W. W. J. Nicol, D.Sc., M.A., F.R.S.E., F.C.S. (Recorder).

*Committee*—A. H. Allen; C. H. Bothamley; H. T. Brown, F.R.S.; Prof. A. E. Dixon; T. Fairley; A. E. Fletcher; L. Fletcher; Prof. P. F. Frankland; G. Gladstone; A. Vernon Harcourt, F.R.S.; Prof. J. J. Hummel, H. Ingle; Dr. C. A. Kohn; Prof. V. B. Lewes; Dr. M. Meslans; S. U. Pickering, F.R.S.; Dr. S. Rideal; Dr. A. Richardson; Sir H. E. Roscoe, F.R.S.; Prof. A. Smithells; J. Spiller; Prof. J. E. Thorpe; T. Turner; W. Thomson; Dr. E. B. Truman; V. H. Veley; R. L. Whiteley.

The Papers brought before the Section were as follows:—

*President's Address.*

*Dr. J. H. Gladstone*—On Tools and Ornaments of Copper and other Metals from Egypt and Palestine.

Report of the Committee on International Standards for the Analysis of Iron and Steel.

*H. Harris and T. Turner*—On Native Iron Manufacture in Bengal.

*G. F. Fowler*—On Nitride of Iron.

Report of the Committee on the Silent Discharge of Electricity in Oxygen and other Gases.

Report of the Committee on the Action of Light on Dyed Colours.

*Dr. M. Meslans*—Demonstration of the Preparation and Properties of Fluorine by Moissan's Method.

Report of the Committee on the Formation of Haloids.

Report of the Committee on the Action of Light on the Hydracids of the Halogens in the presence of Oxygen.

*Dr. S. Rideal*—The Iodine-value of Sunlight in the High Alps.

*Dr. A. Richardson and F. Quick*—A Modified Form of Bunsen and Roscoe's Pendulum Actinometer.

*Dr. A. Richardson*—The Expansion of Chlorine and Bromine under the Influence of Light.

*Dr. C. A. Kohn*—The Cause of the Red Colouration of Phenol.

*Dr. Phookan*—The Rate of Evaporation of Bodies in Different Atmospheres.

*T. W. Hogg*—On the Occurrence of Cyano-nitride of Titanium in Ferro-Manganese.

Report of the Committee on the History of Chemistry.

Report of the Committee on the Wave Length Tables of the Spectra of the Elements.

Report of the Committee on the Bibliography of Spectroscopy.

Report of the Committee on the Bibliography of Solution.

Report of the Committee on Solution.

A Discussion on the Present Position of Bacteriology, more especially in its relation to Chemical Science, was opened by Prof. Percy F. Frankland.

*R. Warrington, F.R.S.*—Remarks on the Chemistry of Bacteria.

*F. T. Wood*—Fermentation in connection with the Leather Industry.

*Dr. G. Tate*—On some Ferments derived from Diseased Pears.

*G. E. Brown and Dr. W. W. F. Nicol*—The Action of Permanganate of Potassium on Sodium Thiosulphate and Sulphite.

*Dr. S. Rideal*—The Application of Sodium Peroxide to Water Analysis.

Report of the Committee on Isomeric Naphthalene Derivatives.

*Dr. C. A. Kohn*—The Application of Electrolysis to Qualitative Analysis.

Report of the Committee on the Proximate Constituents of Coal.

*Dr. E. B. Truman*—Apparatus for the Extraction of Gases Dissolved in Water and other Liquids.

A Discussion on Explosions in Mines, with special reference to the Dust Theory, was introduced by Prof. H. B. Dixon.

*Prof. F. Clowes*—Hydrogen Flame Cap Measurements and the Adaptation of the Hydrogen Flame to the Miner's Safety Lamp.

*Prof. P. P. Bedson*—On the Gases Enclosed in Coal Dust.

*Prof. A. Smithells*—A Note on the Temperature and Luminosity of Gases.

*Bevan Lean*—Ethylbutane Tetracarboxylate and its Derivatives.

*W. F. Sell and T. H. Easterfield*—On the Salts of a New Sulphurea Base.

*W. F. Sell and T. H. Easterfield*—On Citrazinic Acid.

*Prof. F. Clowes*—On a Nottingham Sandstone containing Barium Sulphate as a Cemetery Material.

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# THE CHEMICAL NEWS.

VOL. LXVII., No. 1766.

## AN INTERNATIONAL STANDARD FOR THE ANALYSIS OF IRON AND STEEL.\*

IN the previous report of this Committee it was mentioned that so far as the original four steel standards were concerned the work of the British analysts was completed. It was also stated that the American Committee had nearly finished its labours on these standards, and hoped to publish the results in a few months. Owing to the long distances over which the members of the American Committee are scattered, and the fact that some of the members of the Committee have still been labouring at the question of methods of carbon determination, it was not found possible to hold a meeting as originally intended, but the results of the analyses were to be communicated to, and the questions raised discussed at, the World's Congress of Chemists at Chicago. Professor Langley has, however, forwarded an advance report of the analyses, which is appended, together with the values obtained by the British analysts, which are added for comparison; the American results are subject to slight revision at Chicago, and should any alterations be made these will be inserted before this report is finally published.

### I.—Mean Results of the Analyses by the American Committee.

Standard.	No. 1.	No. 2.	No. 3.	No. 4.
Carbon .. ..	1·44	0·80	0·454	0·18
Silicon .. ..	0·270	0·202	0·152	0·015
Sulphur .. ..	0·004	0·004	0·004	0·038
Phosphorus ..	0·016	0·010	0·015	0·088
Manganese ..	0·254	0·124	0·140	0·098

### II.—Mean Results of the Analyses by the British Committee.

Standard.	No. 1.	No. 2.	No. 3.	No. 4.
Carbon .. ..	1·414	0·816	0·476	0·151
Silicon .. ..	0·263	0·191	0·141	0·008
Sulphur, not more than..	0·006	0·007	0·008	0·039
Phosphorus ..	0·018	0·014	0·021	0·078
Manganese ..	0·259	0·141	0·145	0·130

A report has also been forwarded by Professor Akerman on behalf of the Swedish Committee, but as the results included in this report have not yet been revised, they are intended for the guidance of the other Committees, and not for publication. It may, however, be stated that the agreement between the Swedish and British reports is quite as good as that between the two above given.

Standard 5, the preparation of which was mentioned in the previous report of this Committee, has been hermetically sealed in glass tubes, like Standards 1, 2, 3, and 4. It was thought well not to proceed with the analysis of this standard until an opportunity had been afforded of comparing the results obtained by the various Committees on the analyses of the standards already under examination. Otherwise, after the work of the British analysts was completed, questions as to methods of analysis or other points of detail might have arisen, without a convenient opportunity being afforded for their investigation.

\* Fifth Report of the Committee, consisting of Professor W. C. Roberts-Austen (Chairman), Sir F. Abel, Mr. E. Riley, Mr. J. Spiller, Professor J. W. Langley, Mr. G. J. Snelus, Professor Tilden, and Mr. Thomas Turner (Secretary). (Drawn up by the Secretary). Read before the British Association (Section B), Nottingham Meeting, 1893.

Now that reports from three out of the five International Committees are at hand for comparison, they will be considered by this Committee, and the analysis of the remaining standard completed.

## THE INFLUENCE OF THE SILENT DISCHARGE ON OXYGEN AND OTHER GASES.\*†

THIS Committee was first appointed in 1885; grants of money were made in that and in the succeeding year. The expenditure of these grants has already been duly reported. It therefore now only remains to give an account of the work that has been done. This has already been fully described in the *Journal of the Chemical Society* and elsewhere, and consequently it will be sufficient now to give an outline of the results obtained, with references to the fuller descriptions.

### I.—The Preparation and Storage of Oxygen.‡

In this note a method of preparing oxygen from a mixture of the chlorates of sodium and potassium was described. The process recommended has been found to be very convenient, and has since been adopted by other investigators. Its advantage lies in the ready fusibility of the mixture, and the consequent reduced risk of breaking glass apparatus in which the chlorate must be submitted to repeated fusion and solidification in the course of generating oxygen from it.

### II.—Ozone from Pure Oxygen. Its Action on Mercury, with a Note on the Silent Discharge of Electricity.§

By W. A. SHENSTONE and J. TUDOR CUNDALL.

The experiments described in this paper showed that a good yield of ozone (7·5 per cent) is readily obtained from carefully dried oxygen.

It has lately been suggested by Professor Armstrong that, in spite of the care taken, it is possible impurity may have been introduced into the gas by the action of the discharge, which might conceivably detach adherent moisture from the glass surfaces of the apparatus. Moreover, when these experiments were made the only liquid that was available for use in the manometers was oil of vitriol, and though this was screened from the dried oxygen by phosphoric anhydride, its use introduced a fresh element of uncertainty.

On the other hand, the proportion of ozone obtained was, considering the form of apparatus employed, sufficiently high to suggest that the conditions of the experiment were very favourable to the production of a high yield of ozone, and the mixture of ozone and oxygen obtained by the discharge was apparently without *chemical* action on mercury, which is inconsistent with the idea that moisture was present in it, whilst it is stated by Brodie in his "Classical Research" that in order to obtain a high yield of ozone *dry* oxygen must be employed.

The later experiments described in Section III. will make it possible now to investigate this point more severely than in 1885, and therefore this important question will very shortly be re-examined.

### III.—Studies on the Formation of Ozone from Oxygen.||

By W. A. SHENSTONE and MARTIN PRIEST.

The introduction of improved methods of working with ozone have enabled the authors of this paper to study the

\* Report of a Committee, consisting of Professor H. McLeod (Chairman), Mr. W. A. Shenstone (Secretary), Professor W. Ramsay, and Mr. J. Tudor Cundall. (Drawn up by the Secretary).

† Read before the British Association (Section B), Nottingham Meeting, 1893.

‡ "British Assoc. Rep.", 1886.

§ *Journ. Chem. Soc.*, 1887.

|| *Journ. Chem. Soc.*, 1893.

influence of various conditions on the converting of oxygen into ozone with increased exactness and facility.

The results obtained show that:—

1. Under constant conditions it is possible to obtain concordant results in converting oxygen into ozone by the silent discharge.

2. That the maximum yield of ozone is nearly independent of the difference of the potential employed to produce the discharge (the range of potential difference employed was from 33 to 69 C.G.S. units), provided that the path of the discharge be not too short.

3. That if the path of the discharge be very short, then the maximum yield of ozone has an inverse relation to the difference of potential employed.\*

4. The rapidity with which the discharge converts oxygen into ozone is greater when great potential differences are employed than for smaller differences.

5. That the maximum yield of ozone is less when the number of discharges is *very* great in unit time than when it is smaller.† But the yield is not affected by moderate variations of rapidity of the discharge.

6. The greatest yield of ozone was obtained by using an ozone generator made of the thinnest possible glass, and with closely-fitting tubes. In one case 17·15 per cent of ozone was obtained at 0°.

7. Under equal conditions less ozone was produced by the discharge obtained by means of a Wimshurst's machine than when a large induction coil was employed.

It has been suggested that this last phenomenon may be due to a difference in the quantity of electricity acting in the two cases, but the authors point out that under the conditions of their experiments‡ the "quantity" of the discharge inside the ozone generator depends on the difference of potential of the inducing charge, and that as the ozonising effect of the discharge is, under suitable conditions (see 2 and 3 above), independent of the potential difference of the inducing charge, it would seem that this suggestion does not afford a clue to the cause of the phenomenon. Moreover, it was found in the experiments made with the plate machine that when the quantity of the inducing charge was raised or reduced, by means of condensers, the yield of ozone remained unaffected.

Although a good deal of progress has now been made, much of the work undertaken remains to be done. As, however, no further grants are likely to be asked for, and as it is probable that in the future the work will be mainly in the hands of one member of the Committee, the Committee now recommends that it be not re-appointed.

#### ON NITRIDE OF IRON.§

By G. J. FOWLER, M.Sc.

THIS research was undertaken with the object of repeating and extending the work of Stahlschmidt (*Pogg. Ann.*, v., cxxv., 1865, p. 37) on the same subject, his results differing in many points from those of his predecessors.

The best way of preparing nitride of iron was found to be the following:—Iron is reduced from the hydrate by hydrogen, in a tube of such dimensions that it can be weighed, together with its contents, and thus the end of the reaction determined without exposing the iron to the air. When complete reduction has been effected, the iron is heated in a fairly rapid current of ammonia gas, until no further increase in weight is observed. The temperature should be kept a little above the melting-point of lead.

\* This is attributed to the difficulty of maintaining a sufficiently regular temperature of the gas under these circumstances.

† This is also probably due to imperfect refrigerating.

‡ Ozonisers of Brodie's type were employed.

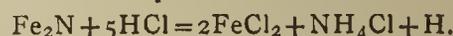
§ A Paper read before the British Association (Section B), Nottingham Meeting, 1893.

The product obtained when the reaction was complete was analysed. The nitrogen was determined by dissolving the substance in hydrochloric acid, evaporating with platinum chloride, and weighing the ammonium-platinum chloride obtained.

The hydrogen given off on solution of the substance in sulphuric acid was measured.

The iron was determined by ignition and weighing as oxide, and by solution in sulphuric acid and titration with permanganate.

As will be seen from the results obtained, the nitride prepared as above has a composition corresponding to the formula  $\text{Fe}_2\text{N}$ . On solution in hydrochloric acid the following reaction takes place:—



	Found.	Calculated for $\text{Fe}_2\text{N}$ .
N .. ..	11·07 .. .. .	11·11
Fe .. ..	88·46 (mean of two titrations)	88·89
	88·43 (by ignition)	
H .. ..	23·1 c.c. from 0·275 subst. ..	24·4 c.c.

In another sample 10·94 N was found. In a third case, in which the iron, after solution of the nitride in acid, was precipitated by ammonia and weighed as oxide, 89·44 per cent of iron was obtained and 10·5 per cent of nitrogen, showing again that the substance dissolves in acid according to the above equation, all the nitrogen being converted into ammonia.

No percentage of nitrogen above 11·1 could be obtained, while any percentage below that could be got according to the time during which the iron had been exposed to the current of ammonia.

These results are fully in agreement with those obtained by Stahlschmidt, and confirm his conclusion that only one nitride of iron exists, and that it has the above composition.

Nitride of iron is formed when iron amalgam is heated in ammonia, and also when ferrous chloride or bromide is heated in this gas. These methods, however, do not so readily give a product containing the full percentage of nitrogen, and free from the presence of a third element.

Nitride of iron is a grey powder, rather less blue in tone than iron reduced from the hydrate. On rubbing it is more gritty than iron prepared as above. It is feebly magnetic.

Heated in hydrogen, ammonia is produced at about the same temperature as that at which the nitride is formed.

It readily burns in chlorine, ferric chloride and nitrogen being formed.

Heated in carbon monoxide, no evidence of the formation of cyanogen compounds could be obtained.

Steam at 100° slowly oxidises the nitride, with evolution of ammonia.

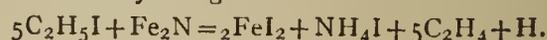
Hydrogen sulphide begins to react with it at 200°, forming ammonium sulphide and sulphide of iron.

Heated in nitrogen to the boiling-point of sulphur, no change occurs. The temperature at which nitrogen is evolved by the action of heat alone must therefore be above this point.

An ethereal solution of iodine is without action upon the nitride.

From a slightly acidified solution of copper sulphate, nitride of iron deposits copper.

Heated with ethyl iodide to 200° in a sealed tube, olefines are formed, and iodides of iron and ammonium, the reaction evidently being—



Heated similarly to 200° with phenol, no reaction occurred.

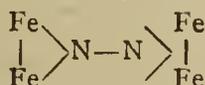
Treated with a mixture of hydrogen peroxide and sulphuric acid, analyses showed that very little, if any, of the nitrogen is oxidised, the whole dissolving as usual to form ammonium sulphate.

In conjunction with Mr. P. J. Hartog, the author has

determined the heat of formation of the nitride by dissolving it in sulphuric acid contained in a platinum calorimeter, and observing the rise of temperature. Three well-agreeing experiments showed that the substance is formed with evolution of about three calories.

In general the nitride of ammonia behaves as an ammonia derivative, the nitrogen being either evolved in the free state, or converted into ammonium compounds, according to circumstances.

Its possible constitution may be—



### LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1893.

By WILLIAM CROOKES, F.R.S.,

and

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,  
Professor of Chemistry at the University of Oxford.

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

London, September 7th, 1893.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the 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 August 1st to August 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 six were recorded as "clear, but dull," the remainder being clear, bright, and well filtered.

The long-continued dry-weather, which had lasted from March to the middle of June, showed signs of breaking during the latter month, and when writing our last month's report we were able to say that the rainfall for July had been 3.70 inches at Oxford, whereas the mean fall for twenty-five years was 2.58 inches, showing an excess of 1.12 inches. The effect of this was shown in a table, by which it was seen that the sudden and excessive rainfall, following one of the longest droughts ever recorded, was extremely slight in respect to the variation in quality of the metropolitan water, and imperceptible in respect to any injurious tendency.

The excessive rainfall was not kept up during August. The mean fall for this month, over an average of twenty-five years, is 2.24 inches at Oxford, while the actual fall has only been 1.01 inch, showing a deficiency of 1.23 inch. During the whole of the month there were only two really wet days, namely, the 4th, on which 0.35 inch, and the 22nd, on which 0.26 inch of rain fell; the rest of the month's rain, amounting to four-tenths of an inch, being distributed over eight days. The excess of rain in July being 1.12 inch, and the deficiency in August being 1.23 inch, it is seen that for the two months the rain has been 0.11 inch below the twenty-five years' mean, whilst, including June, the three months' deficiency amounts to 1.55 inch.

The dry August following the wet July has had the effect of minimising the divergences from the mean, which were shown in tabular form in our last month's report. The following Table shows the most noteworthy points on which comment may be desirable:—

	Common salt per gallon.	Nitric acid per gallon.	Oxygen required per gallon.	Organic carbon per gallon.	Organic carbon per gallon.	Colour.	
						Means.	Maxima.
June	2.155	0.601	0.033	0.065	0.083	—	—
July	2.114	0.674	0.036	0.070	0.098	15.9	: 20
Aug.	2.161	0.705	0.034	0.067	0.084	15.3	: 20

The common salt has slightly risen, as would be expected, from diminished dilution. The organic matter is a little less, as shown alike by the combustion test, the less amount of oxygen required for its oxidation, and the slightly diminished colour.

The colour, being of a vegetable, peaty origin, is higher than it is in colder weather, but the brown colour is a little less than it was in July. The nitric acid has risen, but only in the second decimal place, showing that, whatever the organic matter may have been at its entrance into the river, it has undergone efficient destruction before it leaves the Companies' reservoirs.

From the 21st to the 28th of August the colour of the water supplied by the Chelsea Company was somewhat below its usual high level. This was caused by a serious burst which occurred in one of their large 30-inch pumping mains. For a few days during repair the velocity of the water in the mains had to be retarded, occasioning a temporary deposit of harmless iron oxide. When the ordinary rate of flow was resumed some of this deposit was carried through the mains and caused a temporary discolouration, but in no case was the colour high enough to occasion a deficiency in brightness.

We are, Sir,  
Your obedient Servants,

WILLIAM CROOKES,  
WILLIAM ODLING.

### ON THE ACTION OF IODINE ON SOME PHENOLS AND ALLIED COMPOUNDS IN PRESENCE OF FREE ALKALI, AND A NEW CLASS OF DERIVATIVES RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 132).

#### THYMOL (C<sub>10</sub>H<sub>14</sub>O).

##### Products Obtained with Excessive Dilution at 15° C.

AN alkaline solution of thymol was prepared containing 1 gm. thymol and about 1.5 grms. caustic soda in about 5 litres of water, and to this was added a large excess of decinormal solution of iodine, when there was soon obtained a bulky precipitate of yellowish brown colour, which was collected, washed, and dried. This was dissolved in ether, filtered, recovered, and dried. It was then treated with successive quantities of boiling alcohol as long as anything was dissolved out, the alcoholic solutions being filtered off. The portion soluble in alcohol was then recovered and dried. It was of an orange-yellow colour, of sticky character, and melted about 56° C.

Total iodine of the alcohol-soluble portion:—

Quantity taken = 0.0924 gm.  
Silver iodide found = 0.0818 „ = 47.83 p.c. iodine.

The remainder of the alcohol-soluble portion was heated with water and copper in sealed tube for an hour at 60° C. The contents were then rinsed out and dried on water-bath, and the product dissolved out with ether, filtered, and recovered. Product of a whitish colour, melting with decomposition about 72° C.

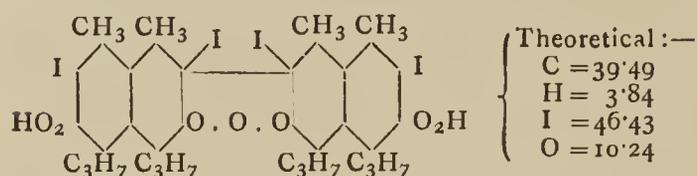
Total iodine of this product:—

Quantity taken = 0.1121 gm.  
Silver iodide found = 0.0948 ,, = 45.69 p.c. iodine.

Combustion of same:—

Quantity taken = 0.0930 gm.  
Water found = 0.0342 ,, = 4.08 p.c. hydrogen.  
Carbon dioxide found = 0.1352 ,, = 39.64 p.c. carbon.  
By difference .. .. = 10.59 ,, oxygen.  
Slight ash.

Those results may be well represented by the formula  $C_{36}H_{42}I_4O_7$ , or constitutionally thus:—



The remainder of the precipitate insoluble in boiling alcohol was treated with ether, in which it readily dissolved. The ether was allowed to evaporate and the residue dried. It was of a slightly yellowish white colour, of pulverulent character, quite amorphous, and melted with decomposition.

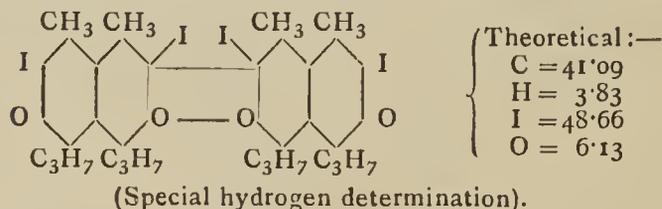
Total iodine of the alcohol insoluble portion:—

Quantity taken = 0.1070 gm.  
Silver iodide found = 0.0966 ,, = 48.78 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1142 gm.  
Water found = 0.0396 ,, = 3.85 p.c. hydrogen.  
Carbon dioxide found = 0.1710 ,, = 40.83 p.c. carbon.  
By difference .. .. = 6.54 ,, oxygen.  
Slight ash.

Those results may be well represented by the formula  $C_{36}H_{40}I_4O_4$ , or constitutionally thus:—



Products Obtained with Moderate Dilution and at a Temperature of 60° C.

There was taken 1 gm. thymol and 1.5 gm. caustic soda in 1 litre of water, the whole heated to 60°, and the iodine added as before. The precipitate obtained was of a brick-red colour, non-adhesive, and pulverulent. It was dissolved in ether, the solution filtered, the ether evaporated off, and the residue dried. It was then heated in an air chamber at about 100° C. until it had lost its red colour. This loss of colour was due to the driving off of what I may term the "enclused" iodine, which I have already dealt with under the character of "loosely-combined iodine" when treating of the simple phenol series. This "enclused" iodine is much more easily got rid of in the present series.

Total iodine of the whole precipitate:—

Quantity taken = 0.1270 gm.  
Silver iodide found = 0.1086 ,, = 46.20 p.c. iodine.

The precipitate was treated with boiling alcohol and the soluble portion recovered. When dried it was of a light yellow colour, of sticky character, and amorphous, melting with decomposition about 88° C.

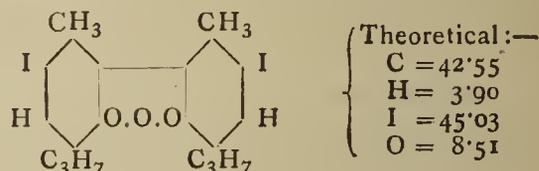
Total iodine of the alcohol-soluble portion:—

Quantity taken = 0.2405 gm.  
Silver iodide found = 0.1997 ,, = 44.88 p.c. iodine.

Combustion of same:—

Quantity taken = 0.0924 gm.  
Water found = 0.0347 ,, = 4.17 p.c. hydrogen.  
Carbon dioxide found = 0.1423 ,, = 42.00 p.c. carbon.  
By difference .. .. = 8.42 ,, oxygen.  
Slight ash.

Those results may be fairly well represented by the formula  $C_{20}H_{22}I_2O_3$ , or constitutionally thus:—



The residue from the alcohol-soluble portion of the precipitate was dissolved in ether and recovered. It was of whitish colour, pulverulent, and melted with decomposition about 172° C.

Total iodine of the alcohol-insoluble portion:—

Quantity taken = 0.2203 gm.  
Silver iodide found = 0.1839 ,, = 45.10 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1246 gm.  
Water found = 0.0470 ,, = 4.19 p.c. hydrogen.  
Carbon dioxide found = 0.1963 ,, = 42.96 p.c. carbon.  
By difference .. .. = 7.75 ,, oxygen.

It is pretty evident that the two portions of the precipitate were practically of the same composition. The great difference observed in the melting-points was undoubtedly due to the presence of practically free iodine in the alcohol-soluble portion, to which it owed its yellow colour, although it was no doubt also influenced by the quantity of hydrogen contained in the molecule, a difference of two atoms of hydrogen belonging to the benzene nuclei causing a large difference in the melting-point.

The red colour of the thymol product is not a peculiarity of the physical conditions predominating in such case as that just treated, as is evidenced by the following:— A new batch was set up under conditions similar to those used in the preparation of the yellow product (ordinary temperature and excessive dilution), with the only difference that a fresh sample of caustic soda was used containing a larger percentage of real hydrate. The precipitate obtained in this case was of a brick-red colour, of pulverulent character, similar in appearance to that obtained at 60° C., with a dilution of one litre, but was rather more readily fusible.

This precipitate was treated with boiling alcohol, the soluble portion filtered off, and the insoluble portion only examined.

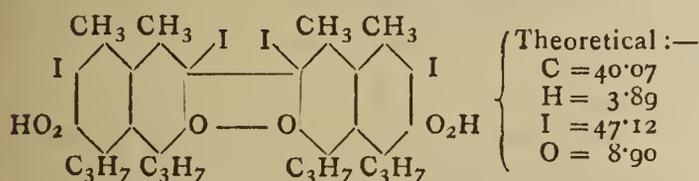
Total iodine of the alcohol-insoluble portion:—

Quantity taken = 0.1240 gm.  
Silver iodide found = 0.1077 ,, = 46.92 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1294 gm.  
Water found = 0.0484 ,, = 4.15 p.c. hydrogen.  
Carbon dioxide found = 0.1910 ,, = 40.25 p.c. carbon.  
By difference .. .. = 8.68 ,, oxygen.

Those results may be well represented by the formula  $C_{36}H_{42}I_4O_6$ , or constitutionally thus:—



Theoretical:—  
 C = 40.07  
 H = 3.89  
 I = 47.12  
 O = 8.90

### THE ACTION OF LIGHT UPON DYED COLOURS.\*

THE object of the Committee appointed to study this matter has been to determine by experiment the relative fastness to light of the colours dyed on textile fabrics with the various natural and artificial colouring-matters.

For this purpose patterns of silk, wool, and cotton have been dyed with equal percentages (2 per cent) of the various commercial artificial colouring matters. With the natural colouring-matters the patterns were dyed to approximately the same depth of colour.

The patterns were exposed to light at Adel, a country district about five miles to the north of Leeds, in order to avoid the influence of town smoke, sulphurous acid, &c., the prevailing winds being westerly. The patterns were pinned on deal boards covered with white calico, fixed in a vertical position in glazed wooden cases, so arranged as to permit free circulation of the air and moisture after filtration through cotton-wool to exclude dust, &c.

The exposing cases were set up in the grounds of Jas. A. Hirst, Esq., to whom the best thanks of the Committee are due for his kind permission to do so.

Each dyed pattern was divided into six pieces, one of which was protected from the action of light, while the others were exposed for different periods of time. The shortest period of exposure, or "fading period," was about three weeks (May 24 to June 14, 1892), and a record of the fading power of this period was kept by exposing along with the patterns a special series of "standards" dyed with the selected colouring-matters. These standards were removed from the action of the light along with the first set of dyed patterns at the end of the first "fading period" (May 24 to June 14, 1892). The faded standards were then at once replaced by a fresh unexposed series, and these were allowed to fade to the same extent as the first, when, a second period of exposure equal in fading power to the first having thus been marked off, a second set of the dyed patterns were removed from the action of light along with the second series of faded standards. The latter were again renewed as before to mark off the next "fading period." The fourth and fifth sets of dyed patterns were submitted to an exposure equivalent to two or three "fading periods," in order that the fifth set might have an exposure of one year.

The above method was adopted in order to be able to expose dyed patterns to an equal amount of fading in different years, irrespective of the time of the year or the conditions of light, moisture, temperature, &c. It was rendered necessary indeed in consequence of the practical impossibility of exposing simultaneously a complete set of dyed colours.

During the year 1892—93 the red dyes on wool and silk have been exposed. For want of sufficient exposing space, however, the Congo colours and some others, as well as the reds dyed on cotton, had to be omitted.

\* Report of Committee, consisting of Professor T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section E), Nottingham Meeting, 1893.

During 1893—94 the orange and yellow dyes are being exposed, and the remaining colours will be exposed in subsequent years until all have been examined. There is no doubt that the behaviour of dyed colours towards light and other agencies depends upon several factors, *e.g.*, the chemical constitution of the colouring-matter itself, the kind of fibre to which it is applied, the method of application, &c. With so many variables a full and complete examination of the question of the fastness of dyes proves to be one of extreme complexity and difficulty. Even to determine effectually the nature of the relationship existing between the molecular constitution of colouring-matters and their behaviour towards light seems to necessitate the employment of chemically pure dye-stuffs, and that the dyeing should be so arranged as to have an equal number of molecules of colouring-matter on a given weight of textile material. Having regard, therefore, to the difficulties connected with the purification of such a large number of colouring-matters as are now in use, their varying colouring-power, the different degree to which they exhaust the dye-bath, &c., it seemed better, for the present at least, to confine our attention to a comparison of the relative fastness to light of the various distinct commercial colours, the results of which might form a basis for a further examination in the direction alluded to.

The dyed and faded patterns have been entered in pattern-card books in such a manner that they can be readily compared with each other.

The following tables give the general result of the exposure experiments made during the year 1892—93, the colours being divided, according to their behaviour towards light, into the following five classes:—Very fugitive, fugitive, moderately fast, fast, very fast.

The initial numbers refer to the order of the patterns in the pattern-books. The S. and J. numbers refer to Schultz and Julius's "Tabellarische Uebersicht der künstlichen organischen Farbstoffen."

#### CLASS I.—Very Fugitive Colours. (Wool).

The colours of this class have faded so rapidly that at the end of the first "fading period" (May 24 to June 14, 1892) only a very faint colour remains, and at the end of the fifth period (one year) all traces of the original colour have disappeared, the woollen cloth being quite white or of a yellowish tint.

#### Triphenylmethan Colours. Phthaleïns.

Wool Book II.

#### Eosins.—

1. Eosin A. Alkali salt of tetra-brom-fluoresceïn. S. and J. 319.
2. Erythrosin G. Alkali salt of di-iodo-fluoresceïn. S. and J. 324.
3. Methyl-eosin. Potassium salt of tetra-brom-fluoresceïn-methyl-ether. S. and J. 320.
4. Erythrosin JN pure.
5. Eosin S. Potassium salt of tetra-brom-fluoresceïn-ethyl-ether. S. and J. 321.
6. Eosin F.
7. Phloxin P. Potassium salt of tetra-brom-di-chlor-fluoresceïn. S. and J. 325.
8. Eosin BN. Potassium salt of di-brom-di-nitro-fluoresceïn. S. and J. 322.
9. Erythrosin B. Sodium salt of tetra-brom-tetra-chlor-fluoresceïn. S. and J. 328.
10. Cyanosin (spirit soluble). Potassium salt of tetra-brom-di-chlor-fluoresceïn-methyl-ether. S. and J. 326.
11. Cyanosin B. Sodium salt of tetra-brom-tetra-chlor-fluoresceïn-ethyl-ether. S. and J. 329.
12. Phloxin tetra (pure).
13. Rose Bengale NTO.
14. Phloxin.
15. Rose Bengale NT pure.
16. Bengaline PH.

17. Bengal red B. Potassium salt of tetra-iodo-tetra-chlor-fluorescein. S. and J. 330.  
18. Cyclamine. Eosin from the thio-dichlor-fluorescein. S. and J. 334.

*Azine Colours. Safranines, &c.**Basic Reds.—*

6. Safranine B extra. From 1 mol. *p*-phenylene-diamine and 2 mols. aniline. S. and J. 356.  
7. Safranine T extra. From 1 mol. *p*-toluylene-diamine, 1 mol. aniline, 1 mol. *o*-toluidine. S. and J. 358.  
8. Diamido-phenazin-nitrate.  
9. Neutral red. From dimethyl-diamido-toluphenazine hydrochloride. S. and J. 253.  
11. Fuchsia. From 1. mol. dimethyl-*p*-phenylene-diamine and 2 mols. aniline. S. and J. 357.

*Induline Colours. Rosindulines.*

## Wool Book I.

*Acid Reds.—*

9. Rosinduline 2 G.  
30. Rosinduline G.

*Azo Colours.**Acid Reds.—*

43. Roxamine. From azo-deriv. of naphthionic acid and dioxynaphthalene (2'7).

NOTES.—Among the eosins, eosin BN is distinctly faster than the rest. Cyanosin B fades as rapidly as the rest during the first "fading period," but the pale tint then left is remarkable for its fastness, since it remains almost unchanged even after a year's exposure.

The eosins, rosindulines, and roxamine do not alter in tint when fading, but the safranines leave, at the end of the first "fading period," a dull brownish pink tint.

CLASS II.—*Fugitive Colours. (Wool).*

The colours of this class show very marked fading at the end of the second "fading period" (June 14 to July 21, 1892), and after a year's exposure they have entirely faded, or only a tint remains.

*Triphenylmethan Colours. Roanilines.*

## Wool Book II.

*Basic Reds.—*

12. Fuchsin MN.  
13. Para-rosaniline. Para-rosaniline (base).  
14. Rosaniline. Rosaniline (base).  
15. Acetic acid Rubin. Rosaniline acetate.  
16. Magenta. Rosaniline hydrochloride.  
17. New magenta. Trimethyl-*p*-rosaniline hydrochloride.

## Wool Book I.

*Acid Reds.—*

99. Acid Magenta. Alkaline salt of rosaniline-tri-sulphonic acid. S. and J. 279.

*Phthaleïns.*

## Wool Book II.

*Basic Reds.—*

1. Rhodamine. Phthalein of diethyl-*m*-amido-phenol (basic hydrochloride). S. and J. 331.  
2. Rhodamine B extra. As No. 1.  
3. Rhodamine S. Succineïn of diethyl-*m*-amido-phenol-hydrochloride. S. and J. 333.  
4. Rhodamine S extra. Succineïn of di-methyl-*m*-amido-phenol-hydrochloride. S. and J. 332.

*Diphenylmethan Colours.*

10. Pyronin G. Tetra-methyl-diamido-oxy-diphenyl-carbinol hydrochloride. S. and J. 261.

*Acridine Colours.*

5. Acridine red 3 B.

*Azine Colours. Safranines.*

18. Magdala red. Diamido-naphthyl-naphthazonium chloride. S. and J.

*Azo Colours.*

## Wool Book I.

*Acid Reds.—*

12. Acid ponceau. From  $\beta$ -naphthylamine-mono-sulphonic acid and  $\beta$ -naphthol. S. and J. 92.  
16. Double brilliant scarlet G. From  $\beta$ -naphthylamine-mono-sulphonic acid (Br.) and  $\beta$ -naphthol. S. and J. 94.  
\*50. Phenanthrene red.  
54. Cresol red. From amido-ortho-cresol-ethyl ether and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 57.  
58. Milling red G.  
59. Clayton Cloth red. From dehydro thio-*p*-toluidine-sulphonic acid and  $\beta$  naphthol. S. and J. 99.  
60. Cloth red 3 G extra. From amido-azo-toluene and  $\beta$ -naphthylamine-mono-sulphonic acid Br. S. and J. 116.  
61. Caroubier.  
62. Fast red A. From naphthionic acid and  $\beta$ -naphthol. S. and J. 84.  
\*68. Fast red BT cmc. From  $\alpha$ -naphthylamine and  $\beta$ -naphthol-mono-sulphonic acid S. S. and J. 62.  
73. Cloth red 3 B extra. From amido-azo-toluene and  $\beta$ -naphthylamine-mono-sulphonic acid S. S. and J. 115.  
\*76. Ponceau 2 S extra. From amido-azo-benzene and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 110.  
83. Naphthorubin. From  $\alpha$  naphthylamine and  $\alpha$ -naphthol-di-sulphonic acid. S. and J. 63.  
84. Thiorubin. From dehydro-thio-*p*-toluidine and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 68.  
88. Orchil substitute N. From *p*-nitraniline and  $\alpha$ -naphthylamine-disulphonic acid. S. and J. 39.  
89. Bordeaux BX. From amido-azo-xylene and  $\beta$ -naphthol- $\beta$ -mono-sulphonic acid. S. and J. 117.  
90. Orchil substitute V. From *p*-nitraniline and naphthionic acid. S. and J. 36.  
92. Milling red R.  
94. Orchil substitute 3 VN. From *p*-nitraniline and  $\alpha$ -naphthylamine-mono-sulphonic acid L. S. and J. 38.  
96. Fast red B. From  $\alpha$ -naphthylamine and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 65.

*Natural Colouring Matters.*

## Wool Book II.

*Acid Reds.—*

7. Lima-wood red (alumina mordant).  
8. Lima-wood red (tin mordant).  
9. Cam-wood red (alumina mordant).

NOTES.—The magentas are peculiar by becoming at first much bluer, so that at the end of the first "fading period" they appear somewhat darker; the purplish colour produced soon fades, however, and at the end of a year a pale grey remains. Acid magenta becomes duller but not bluer.

The rhodamines, Pyronin G, and Acridine Red become yellower.

Among the azo-colours those marked thus (\*) are more fugitive than the rest. Cloth red 3 G extra and 3 B extra become distinctly yellower; ponceau 2 S extra becomes much bluer.

Cam-wood red is remarkable for becoming quite brown and appearing, therefore, darker at the end of the first fading period. This colour soon fades, however, and leaves at the end of a year a pale drab tint.

CLASS III.—*Moderately Fast Colours. (Wool).*

The colours of this class show distinct fading at the end of the second period (June 14 to July 21, 1892), which

becomes more pronounced at the end of the third period (July 21 to August 14, 1892). A pale tint only remains at the end of the fourth period (August 14 to February 16, 1893), and at the end of a year's exposure the colour has entirely faded, or, at most, mere traces of colour remain.

*Azo Colours.*

Wool Book I.

*Acid Reds.—*

3. Scarlet G. From xylidine and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 49.
4. Scarlet B.
5. Brilliant scarlet GG. From *m*-xylidine and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 50.
7. Lake scarlet GG. Same as 5.
10. Brilliant scarlet G. Same as 3.
11. Scarlet GR. From xylidine and  $\beta$ -naphthol-mono-sulphonic acid S. S. and J. 47.
14. Lake scarlet R. Same as 3.
15. Ponceau R.
17. Scarlet R. From *p*- and *m*-xylidine and  $\beta$ -naphthol-di-sulphonic acid R.
21. Scarlet 2 R. Same as 5.
22. Double brilliant scarlet 2 R.
23. Pyrotin red 3 RO.
25. Persian red.
27. Croceïn scarlet OXF. From naphthionic acid and  $\beta$ -naphthol-mono-sulphonic acid B. S. and J. 86.
28. Ponceau 2 R. From amido-azo-benzene and  $\beta$ -naphthol-mono-sulphonic acid B and S. S. and J. 108.
29. Cochineal scarlet 2 R. From toluidine and  $\alpha$ -naphthol-mono-sulphonic acid C. S. and J. 40.
31. Cochineal scarlet 4 R. From xylidine and  $\alpha$ -naphthol-mono-sulphonic acid C. S. and J. 45.
32. Ponceau 3 R. From amido-ethyl-dimethyl-benzene and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 51.
33. Coccin BB.
34. Naphthol scarlet.
37. Cochineal scarlet R.
38. Anisol red. From ortho-anisidine and  $\beta$ -naphthol-mono-sulphonic acid S. S. and J. 54.
39. Ponceau 4 R. From cumidine and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 51.
40. Azo-eosin. From ortho-anisidine and  $\alpha$ -naphthol-mono-sulphonic acid NW. S. and J. 55.
41. Coccinin. From ortho-amido-phenetol and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 41.
42. Crystal ponceau. From  $\alpha$ -naphthylamine and  $\beta$ -naphthol-di-sulphonic acid G. S. and J. 64.
49. Fast red E. From naphthionic acid and  $\beta$ -naphthol-mono-sulphonic acid S. S. and J. 87.
52. Cloth scarlet G.
64. Fast red C. From naphthionic acid and  $\alpha$ -naphthol-mono-sulphonic acid NW. S. and J. 85.
66. Croceïn B. From amido-azo-benzene and  $\alpha$ -naphthol-di-sulphonic acid Sch. S. and J. 107.
67. Cloth red G extra. From amido-azo-toluene and  $\beta$ -naphthol-mono-sulphonic acid S. S. and J. 113.
69. Bordeaux G. From amido-azo-toluene-mono-sulphonic acid and  $\beta$ -naphthol-mono-sulphonic acid S. S. and J. 126.
70. Orchil substitute G. From para-nitraniline and  $\beta$ -naphthylamine-mono-sulphonic acid Br. S. and J. 37.
71. Granat liquid.
72. Cloth red No. OG. Same as 67.
74. Cloth scarlet R.
75. Buffalo rubin. From  $\alpha$ -naphthylamine and  $\alpha$ -naphthol-di-sulphonic acid Sch. S. and J. 61.
77. Œnanthin. From naphthionic acid and naphthol-di-sulphonic acid.
79. Azo-red A. From amido-azo-naphthalene and  $\alpha$ -naphthol-di-sulphonic acid.

80. Wool red.
81. Fast red D. From naphthionic acid and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 89.
86. Palatine red. From  $\alpha$ -naphthylamine and naphthol-di-sulphonic acid. S. and J. 66.

*Induline Colours. Rosindulines.*

78. Rosinduline B.
82. Rosinduline BB.

*Natural Colouring Matters.*

Wool Book II.

*Acid Reds.—*

3. Cochineal crimson (alumina mordant).
4. Kermes crimson (alumina mordant).

CLASS IV.—FAST COLOURS. (WOOL).

The colours of this class show comparatively little fading during the first, second, and third periods. At the end of the fourth period a pale shade remains, which at the end of the year's exposure still leaves a pale tint.

*Azo Colours.*

Wool Book I.

*Acid Reds.—*

1. Ponceau 4 GB. From aniline and  $\beta$ -naphthol-mono-sulphonic acid S. S. and J. 27.
2. Ponceau 2 G. From aniline and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 29.
6. Ponceau RT. From toluidine and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 42.
8. Milling Red FGG. Constitution not published.
13. Wool Scarlet R. From xylidine and  $\alpha$ -naphthol-di-sulphonic acid Sch. S. and J. 46.
18. Azo-coccin 2 R. From xylidine and  $\alpha$ -naphthol-mono-sulphonic acid NW. S. and J. 44.
19. Brilliant Croceïn MOO. From amido-azo-benzene and  $\beta$ -naphthol-di-sulphonic acid  $\gamma$ . S. and J. 109.
20. Palatine Scarlet. From *m*-xylidine and naphthol-di-sulphonic acid. S. and J. 48.
24. Cotton Scarlet NT.
26. Croceïn Scarlet 3 B. From amido-azo-benzene-mono-sulphonic acid and  $\beta$ -naphthol-mono-sulphonic acid B. S. and J. 120.
35. Double Brilliant Scarlet 3 R. From  $\beta$ -naphthylamine-sulphonic acid Br. and  $\alpha$ -naphthol-mono-sulphonic acid NW. S. and J. 95.
36. Cochineal Red A. From naphthionic acid and  $\beta$ -naphthol-di-sulphonic acid G. S. and J. 88.
44. Fast Ponceau B. From amido-azo-benzene-di-sulphonic acid and  $\beta$ -naphthol. S. and J. 121.
45. Milling Red FR. Constitution not published.
46. Erythrin X. From amido-azo-benzene and  $\beta$ -naphthol-tri-sulphonic acid. S. and J. 111.
47. Croceïn Scarlet 7 B. From amido-azo-toluene-mono-sulphonic acid and  $\beta$ -naphthol-mono-sulphonic acid B. S. and J. 125.
48. Ponceau S extra. From amido-azo-benzene-di-sulphonic acid and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 122.
51. Phoenix Red A. Constitution not published.
53. Cloth Red G. From amido-azo-benzene and  $\alpha$ -naphthol-mono-sulphonic acid NW. S. and J. 106.
55. Ponceau 6 R. From naphthionic acid and  $\beta$ -naphthol-tri-sulphonic acid. S. and J. 90.
56. Coccinin B. From amido-*p*-cresol-methyl-ether and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 56.
57. Brilliant Croceïn 9 B. Constitution not published.
63. Croceïn AZ. From amido-azo-benzene and  $\alpha$ -naphthol-di-sulphonic acid.
65. Erythrin P.
85. Croceïn 3 B. From amido-azo-toluene and  $\alpha$ -naphthol-di-sulphonic acid Sch. S. and J. 112.

(To be continued.)

## ON ERBIA.\*

By GERHARD KRÜSS.

(Continued from p. 149).

*Experimental Part.*

For the experiments there were used fractions rich in erbia which had been obtained from 5 kilos. of gadolinite earths by systematic precipitation of the total material with ammonia. The production of this material is given in *Liebig's Annalen*, cclxv., 10—12. The nitrate solution of the nitrate of these earths showed the erbium bands very intensely, but in a layer of 15 c.m. in thickness (a solution of 300 grms. nitrate in 150 grms. water) there was no trace of the didymium bands  $\lambda=579\cdot2$  and  $575\cdot4$ , which are generally very intense. This erbium material contained, as it is shown below, in addition to erbia other yttria earths. It was therefore first worked up by driving off the nitrates, and the nitrates were not, as it was sometimes formerly done, decomposed by heat so far as to give off red vapours of  $\text{NO}_2$ .

In the first place a smaller portion of this material was fused as nitrate, kept for some time in clear flux, and heated, with constant stirring, until the melt becomes turbid.

The cold melt was entirely soluble in water at the temperature of the room. The solution, however, when heated to  $90^\circ$  gave a crystalline deposit. This was filtered off, briefly washed with cold water, and yielded the first fraction; the filtrate of this separation was evaporated down, and the residue was treated in the same manner as the entire material had been. Thus there were obtained:—

Weaker bases  $\leftarrow$  — — — — —  $\rightarrow$  Stronger bases.

Fractions† 1 2 3. 4 5 6 7 (residue).

Series 1. R = 161 — — — — — 147 131

Fractions 1 to 4 were united, and from this material there was obtained the first relatively large separation‡ of basic nitrate called *ytterbia* material (showing the  $\text{Tm } \alpha$  line at  $\lambda=684$  equally strong with  $\text{Er } \alpha=654$ ). The filtrate of this ytterbia material was added to fractions 5+6, and from this mixture the two first heavy precipitations (basic nitrate) were marked as "*Erbia material* No. 1," and the filtrate from these precipitations put back to fraction 7 (residue) as "*Yttria material*" after the above described manner of the partial decomposition of the earthy nitrates has been found practical, according to the spectrum of the several fractions. The main bulk of the erbiferous material was first worked up in a similar manner.

Weaker bases  $\leftarrow$  — — — — —  $\rightarrow$  Stronger bases.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15 (res.)	
Ser. 2.	165	62	—	—	162	—	—	—	—	149	1	—	—	109	7

*Spectroscopic Examination.*—Absent in the residue  $\text{Tm } \alpha$ , which in Fraction 1 was equal to  $\text{Er } \alpha$ .  $\text{X } \alpha$  (holmium) increases in comparison to  $\text{Er } \alpha$  towards Fraction 15 (residue).

There were first mixed together as—

- Fraction 1, with 6 of second series, and ytterbia material from Series 1.
- Fractions 7, with 14 of Series 2, and erbia material of Series 1.
- Fractions 15 of Series 2 and yttria material of Series 1.

\* *Zeitschrift für Anorganische Chemie.*

† For the sake of brevity the results of the determinations of equivalents carried out as a preliminary on the earths of the several fractions are given in the sequel solely in the form of tables, the triple equivalent being placed beneath the number of the fractions.

‡ The quantity of the R found is a measure for the Sc, Yb, Tm, Er, Ho, Tr, and Y.

§ The quantity of the separation may be increased if, after heating the dissolved melt the solution is evaporated down and heated again.

The present B material was characterised as erbia material No. 2.

There were then separated out as basic salts by heating the nitrates:—

- Three precipitates—residue (strongest bases) to—
- Of this the first heat-product (weaker bases) were added to A, six following nitrate fractions were kept separate as B, and the residue was added to—
- Of the present C material, the first separation of basic nitrates was added to B, and of the entire B material now present, the first separation product was again added to A.

A was again resolved into fractions by heating the nitrates\* :—

Weaker bases  $\leftarrow$  — — — — —  $\rightarrow$  Stronger bases.

	1	2	3		4	5	6
Series 3.	171'94				172'6		

and the residue was added to A.

- Eight fractions were separated:—

Weaker bases  $\leftarrow$  — — — — —  $\rightarrow$  Stronger bases.

	1	2	3	4		5	6	7	8
Series 4.	165	9†				163	5		

and the earths which remained in solution after the last separation of basic nitrate.

- This was the yttria material obtained from the yttria earths rich in erbia, as—
- The fractions 1 to 8 of Series 4 were united, and were now marked as erbia material No. 3.

The few determinations of equivalents were merely executed for accessory orientation.

A. Fraction 1 to 6 of Series 3 now formed the ytterbia material.

These three materials were further decomposed by precipitation with aniline in alcoholic solution, as described elsewhere by the author.

(To be continued.)

ON THE PHOTOGRAPHY OF THE  
LUMINOUS RAYS OF THE SHORTEST  
WAVE-LENGTHS.‡

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 133).

THE case is not distinguished in form and arrangement from the ordinary wooden cases. It has a slide and a cover like these, and it can also be displaced for the reception of spectra placed below each other in the direction of the spectral lines according to a scale applied laterally, so that a plate with a sufficiently short slit-aperture may serve for a great number of proofs. The internal surfaces of the camera and of the cases, as the glass of which they are made is transparent, have a thin lining of a dead black colour. The outside is coated with black paper and shellac varnish. The size of the plates is 30 by 65 m.m. I have used glass for the camera in preference to wood, because, notwithstanding the requisite—and perhaps little trustworthy—paper coating, it is not greatly suscep-

\* It was again heated until the melt became turbid. The product was soluble in cold water, and their solution when heated gave a precipitate which was at first soluble and then became crystalline.

† The nitrate melt of B was soluble in hot water, but the solution on cooling deposited a strongly red crystalline precipitate = Fraction 1, Series 4.

‡ From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

tible to the changes of atmospheric heat and moisture, and because wooden cases for such small plates can scarcely be made more accurately than those of glass. During use extending for months the glass camera has never given occasion for dissatisfaction.

#### *Setting up the Spectral Apparatus and the Auxiliary Plant.*

The source of light must be adjusted with the aid of a telescope. In order to keep the telescope and the collimator as much as possible co-axial during the duration of the entire experiment, a foundation was required as little sensitive as possible to atmospheric influences. For this purpose also I selected glass. A quadrilateral disc of mirror-glass with sides of 1 metre in length and 10 m.m. in thickness was fixed upon a very stable wooden foundation in such a manner that it was supported only in some few points. The position of the supports was selected so that the changes to which the wooden foundation was liable could be conveyed to the direction of the apparatus only in a very reduced proportion.

The apparatus directly concerned in obtaining the proofs was set up on the glass plate as follows, and, where practicable, it was especially secured against lateral displacement:—

Opposite to the spectroscop, and co-axially with the collimator, stood the reading telescope; between both, the spark-support; and close before the slit, a second stand with a slit-shaped screen of adjustable length. Between the spark-stand and the screen there was placed, for a portion of the proofs, a condenser, of which more below. The screen came into use if the aperture of the slit was to be opened to the rays only for a part of its length. It could also be displaced along the slit by means of rack-work in the support, so that the slit could be opened at any point to the length desired, and, if necessary, also in an uninterrupted succession at the transitions. The screen, as well as the sparks, required the reading-telescope for accurate adjustment. This will be more intelligible if I add that the aperture of the slit-length moved within very narrow limits, and often did not exceed the modest measure of 0.2 m.m., and that, on the other hand, the sparks and the screen were generally at the distance of some centimetres.

#### *The Source of Light.*

The primary current was supplied by a chromic acid battery of four large immersion elements. Besides the inductorium (formerly used) of 25 c.m. spark-length and the Leyden jars, there were also used this time a smaller inductorium for sparks of only 8 c.m. in length. In some cases the inductorium was exchanged for an induction machine (four pairs of discs of 62 and 70 c.m. diameter) connected with a Riess's jar-battery (nine Leyden jars with an external coating of  $1\frac{1}{2}$  metres).

As electrodes there were again used temporarily cadmium and zinc; afterwards, permanently, aluminium, and finally, Ag, As, Au, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mo, Na, Ni, Pb, Pd, Pt, Sb, Si, Sn, Tl, W, all in the state of wire or short rods (Ca, K, Na, W), or crystals (Si), which were held in clamps of copper or platinum.

#### *The Photographic Process.*

This time also, when the utmost sharpness of design was needful, plates of my own preparation were used. But in general the photos were obtained upon plates by Herrn E. Zettnow. In all cases I preferred them to my own plates, on account of their great sensitiveness and intensity, except where the utmost sharpness of the spectral lines was essential. Some spectra were taken upon Schleussner plates. The Schleussner plate works also clear and is very sensitive, but its negatives betrayed the above-mentioned defect of all commercial plates—they were wanting in the intensity required for taking

spectra. The developer and the fixing agent consisted, as formerly, of pyro-soda and sodium thiosulphate.

The number of the negatives thus obtained is relatively large. The author's diary gives a conscientious account of the conditions under which each proof was taken. Every plate, even if a failure, is given in the order of time, and with a progressive number and the negative bases have the same number.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

THE following is the text of the Address presented to Sir John Lawes, Bart, &c., and Dr. Gilbert, on July 29th, on the occasion of the Rothamsted Jubilee:—

We, the President and Officers of the Chemical Society of London, on behalf of the Council and Fellows generally, desire on this occasion to express our sense of the extraordinary value of your labours in the field of agricultural science, our admiration of your researches, and our gratitude for the immense number of exact data which you have placed at the disposal of chemists.

Few men have been able to conduct experimental researches during so long a period, and there is no parallel in the history of science to your achievement in carrying on a single research without interruption during a period of over fifty years. The plan laid down at its commencement has throughout been most rigidly adhered to, which is evidence of the skill originally displayed in its inception, and gives to your work its peculiar value.

While affording guidance to the agriculturist, your researches have elicited information which will ever serve as the foundation of a truly scientific knowledge of the correlation of plant growth and manurial constituents of the soil, and will be of the utmost value in all discussions of the chemistry of plant life. Your researches on the feeding of animals, in like manner, are not only of practical importance, but also shed much light on the processes of animal life.

Great, however, as is the actual value to agriculture and agricultural science of your work, the example your single-minded devotion to the cause of scientific truth and research has afforded to the world is unquestionably to be regarded as of far greater value. Yours is the model of all agricultural experimental stations, and the methods that you have introduced are everywhere regarded as classical.

The rare and enlightened munificence which has led the one of you to institute and maintain such a series of enquiries having been supplemented by a provision for the future conduct of the experiments in order especially to make it possible to deal with the great question of the ultimate exhaustion of the soil, the debt of gratitude which science owes to the founder of the Rothamsted experimental station is extended into the distant future.

It is, consequently, with a full sense of the inadequacy of our expressions that we to-day offer to you our heartfelt thanks and our warmest congratulations on your having been able to achieve results of such magnitude and importance.

The Birkbeck Institution.—The Committee of the Birkbeck Institution, adopting the principles laid down in the Report of the London County Council on Technical Education, purpose appointing a Professor of Chemistry who shall devote his whole time to the work, including practice in original research. Mr. Chaloner, who has had charge of the Inorganic Classes for the last twenty-five years, will accordingly shortly retire.

## CORRESPONDENCE.

## THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—Now that we members of the Institute of Chemistry are last in the proud position of having a house of our own in London, may I ask through your columns whether the Council propose making any use of it, or whether they intend keeping it simply for ornament?

It seems that there are a number of rooms (five or six), I understand, which will not be required for office and other accommodation, and an idea has got abroad that they might be used as the head-quarters of a chemical club. Can we not persuade the authorities to take up this idea, and furnish the rooms so that they might be available for this purpose, and also as a place where Fellows—especially the country ones—could meet their clients for consultations, or even pass the night during their visits to London? If this suggestion were taken up, there is little doubt that the town members would gladly pay a small local subscription for the convenience; and to the country men the Institute would become something more than a name—high-sounding, it is true—but still perilously near being an empty one.—I am, &c.,

AN EAST-END LONDONER.

September 20, 1893.

## 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. cxvii., No. 10, September 4, 1893.

This issue contains no chemical matter.

No. 11.

Presence of a Ferment Analogous to Emulsine in Fungi, and Especially in Fungi Parasitic on Trees and Living on Wood.—Em. Bourquelot.—The author finds that many fungi contain a ferment capable of splitting up various glucosides, such as amygdaline, salicine, and coniferine. It acts in the same manner as the emulsine of almonds. The author enumerates the species in which he has proved the presence of a ferment.

A Method of Determining the Density of Gases Applicable in Industry.—Maurice Meslans.—This paper does not admit of useful abstraction.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. viii., No. 90.

This number contains no chemical matter.

*Bulletin de la Société Chimique de Paris.*  
Series 3, Vols. ix. and x., Nos. 15 and 16.

Precipitation of Manganese by Oxygenated Water and Ammonia, for its Determination, Gravimetric or Volumetric.—Adolphe Carnot.—This paper will be inserted in full.

Carbohydrates of the Jerusalem Artichoke.—Ch. Tanret.—The carbohydrates present in the juice of the *Helianthus tuberosus* are—Inuline, pseudo-inuline, inulinone, helianthenine, synanthrine, saccharose, levulose, and glucose. Of these substances synanthrine is the most

abundant. For separating these substances the author first treats the juice of the tubers in heat with basic lead acetate, removes excess of lead with dilute sulphuric acid, and adds a large excess of concentrated baryta water. He then precipitates all the carbohydrates with alcohol at 90°. He decomposes the precipitate with CO<sub>2</sub>, boils, filters, and evaporates to dryness. The residue treated with boiling alcohol at 84° gives up the helianthenine, of which only 1-300th part remains in the liquid. The insoluble residue is then treated with boiling alcohol at 70°, which takes up the inulenine. The residue contains merely pseudo-inuline and inuline, which are separated by treatment with 10 parts of boiling alcohol at 60°. The pseudo-inuline dissolves and the inuline remains undissolved.

On Calcium Oxyiodide.—M. Tassilly.—The compound obtained has the composition CaI<sub>2</sub>.3CaO.16H<sub>2</sub>O, corresponding to the oxychloride studied by André.

The Reaction of Ethyl Bromo-propionate and Sodium Nitrite.—G. Lepercq.—The crystalline compound obtained, C<sub>5</sub>H<sub>9</sub>NO<sub>3</sub>, is probably the ethyl nitroso-propionate obtained by V. Meyer and Züblin by the action of nitrous acid upon methyl-acetylacetic ether (*Berichte*, 1878, p. 693).

## MISCELLANEOUS.

Chicago Exhibition, 1893.—The following description of the platinum, precious metals, and manufactures exhibited by Johnson, Matthey, and Co., will be read with interest:—

*Platinum Apparatus of the Most Improved Form, "Double Delplace," for Concentration of Sulphuric Acid.*—This apparatus is capable of concentrating 22,000 lbs. O. V. 94 per cent per twenty-four hours under ordinary working conditions, and about one-half this quantity of 97½ per cent H<sub>2</sub>SO<sub>4</sub>. It is the most universally adopted and approved form of apparatus, and some hundreds have been supplied throughout the world by Johnson, Matthey, and Co., since its introduction by them in the year 1875. It is a form which assures the greatest productive power, economy, and regularity in working, and can be adjusted to produce any strength of acid required up to the maximum 97/98 per cent H<sub>2</sub>SO<sub>4</sub>.

*Gold-Lined Platinum Apparatus for the Concentration of Sulphuric Acid, Manufactured by Johnson, Matthey, and Co.'s Process of 1854.*—(Platinum 75 per cent, gold 25 per cent).—The gold surface is alloyed with 5 per cent platinum to give the necessary hardness and durability. This alloy has been proved by the most careful tests as to wear and tear under working conditions at highest pressure to be subject to only one-half the loss of that of pure gold. A large boiler so manufactured was exhibited by Johnson, Matthey, and Co. in the Paris Exhibition, 1855, as shown by the annexed extract from Mr. Alfred Tylor's "Report on the Paris Exhibition, 1855, on Metal Work," p. 275, Part 2. Published by Eyre and Spottiswoode for Her Majesty's Commissioners, 1856. "Johnson and Matthey exhibit a retort of a different form to any previously used, and which they say has been highly approved by a sulphuric acid maker, who is now working a similar one. They state that after fifteen or twenty years, platinum by use loses one-fifth of its weight, probably from the action of impurities in the acids boiled in it, and requires frequent repairs with gold solder. They observed that these patches of gold were perfectly untouched, and have therefore welded an ingot of gold upon the platinum, so that, when manufactured, the interior of the pan should have a surface of gold."

*International Standard Metre and Kilo.*—Platinum 90 per cent, Iridium 10 per cent, Density 21.552.—This

alloy, finally adopted after long experiment by the Paris International Commission, was recommended by Johnson, Matthey, and Co., and shown by them at the Vienna Exhibition, 1873, and all the standard metres and kilos. for international use have been subsequently prepared and supplied by them of this alloy and form to the International Committee of Weights and Measures, the experts appointed by whom to determine the quality of the platinum employed (the most distinguished *savants* in this branch of metallurgy—M. H. St. Claire Deville and M. Debray, of Paris, and M. Stas, of Brussels) reported its purity = 999.98773 per 1000, a degree of purity heretofore (1873) considered commercially impossible, and, except by their special process, even now only attainable in laboratory experiments of a very costly nature and dealing with small quantities. The weight of platinum employed in the manufacture of these standards was 250 kilos. (about 8000 ounces troy). The preparation of so large a quantity of platinum to the above high degree of purity is considered by scientists to be unsurpassed in metallurgical annals.

Metre Tubes in Iridio Platinum—for measuring the coefficient of expansion of the international geodesic rule and thermometric metre, prepared specially for experimental work carried out at the École Normale, Paris.

Platinum Basins and Crucibles Gold-Lined, 10 per cent to 25 per cent—Gold.

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*Pure Metals of the Platinum Group.*—Ingot of Pure Palladium, 1000 ozs., value £7000, extracted from gold and platinum of the value of about £2,250,000. Pure Melted Iridium, weight 240 ozs., value £1500. Pure Melted Ruthenium. Pure Melted Rhodium. Pure Melted Osmium. Pure Metallic Osmium, crystalline.

A Series of Oxides, Salts, and Compounds of Ruthenium.

Specimen of Silk Dyed with Ruthenium.

Pure Crystalline Boron and Silicon.

Aluminium Coins—hardened with 2 to 10 per cent of nickel. The alloy prepared and recommended for coinage purposes by Johnson, Matthey, and Co. in 1878.

**An Irreverent Practical Joke.**—According to an eminent medical contemporary, at the celebration of the birthday of the Emperor Francis Joseph some irreverent joker introduced a quantity of silver nitrate into the holy-water recipients at Trieste Cathedral. The effect upon the fingers and faces of the faithful may easily be imagined.

**The Composition of the Moon.**—Among a number of books advertised by an eminent Hamburg publishing firm we find a pamphlet from the pen of "Dr. Mises" (apparently a pseudonym for G. Th. Fechner) proving that the moon is composed of iodine. Perhaps in time the renowned green cheese theory may yet be demonstrated. In another pamphlet the same author contends that shadows are alive, and that the world has been produced, not by a primal creative, but by a destroying principle.

**Mr. C. Watson Smith.**—A copy of the Address given in University College, London, during last winter, on the "Diseases Incident to Workpeople in Chemical and other Industries," by Mr. Watson Smith, has been recently forwarded by him, along with a letter, to the Emperor of Germany, who, as is well known, takes a lively interest in the welfare of the workpeople of his realm. The following graceful acknowledgment has just been received by Mr. Watson Smith:—"The German Ambassador presents his compliments to Mr. Watson Smith, and has the honour to inform him that the copy of his treatise on diseases of occupation in connection with chemical industries, which he offered for the acceptance of His Majesty the Emperor, has been accepted by His Majesty. By command of the Emperor, the Ambassador begs to convey to Mr. W. Smith his thanks for the kind attention shown to him.—German Embassy, London, Sept. 16, 1893."

**Proposals for Standardising in Acidimetry and Alkalimetry.**—E. Brentel (*Oest. Chem. Gesellschaft* and *Zeit. Anorganische Chemie*) recommends potassium bichromate as the starting-point for acidimetry. It is heated to fusion, weighed when cold, and the titration is effected with baryta water, using phenolphthalein as indicator. E. Rimbach (*Berichte*), in the course of his studies on the atomic weight of boron, has satisfied himself that the soda in borax can be very sharply titrated with hydrochloric acid, using methyl orange as indicator. As borax can be obtained sufficiently pure for ordinary purposes by re-crystallisation and exposure to the air, he proposes to use it instead of sodium carbonate for determining acids. 1 gm. of crystalline borax weighed in air with brass weights corresponds to 5.2391 c.c. normal acid. Hence 1 litre normal acid equals 190.872 grms. borax. Th. Salzer (*Berichte*) states that he made the same proposal some time ago, and it is consequently found in the second edition of "Mohr's Text-book of the Volumetric Method. In a second paper (*Pharm. Centralhalle*) Salzer discusses the question what indicator should be selected when using borax, and shows that the methyl orange preferred by Joly and Rimbach is preferable to litmus only in concentrated solutions, but that it is less sensitive in dilute liquids. The author recommends the use of a decinormal solution, with litmus as indicator, titrating from an onion-red to a bluish red. M. Weinig (*Zeit. Angew. Chemie*) recommends, whilst considering the gravimetric standardising of sulphuric acid, besides precipitation with barium chloride and standardising with sodium carbonate, the two following methods:—1. Of two equal portions of sulphuric acid, the one is titrated with baryta water and into the other is distilled ammonia evolved from a solution of ammonium chloride of known strength, the residue of the sulphuric acid being again titrated with baryta water. The standard of the sulphuric acid may be calculated from the result. 2. The method recommended by Schaffgotsch for the determination of nitric acid, *i.e.*, evaporation with an excess of ammonia, is also applicable for sulphuric acid. A known quantity of sulphuric acid is put in a platinum capsule along with a slight excess of ammonia (about 0.5 c.c. more than requisite for neutralisation), evaporated to dryness, dried for half an hour at from 115° to 120°, and weighed. This proposal has been tested by H. Eckenroth (*Pharm. Zeitung*), and found very convenient, as also for hydrochloric and oxalic acids.

## 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.

**Etching Glass.**—Will any reader kindly tell me where to get information relative to the practical working of etching glass by fluorine compounds?—C. M. SILVERBURN.

## TO CORRESPONDENTS.

*Edouard.*—We should recommend a year at the Royal School of Mines. Obtain the books there in use.

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## THE CHEMICAL NEWS.

VOL. LXVII., No. 1767.

ON THE  
OCCURRENCE OF CYANO-NITRIDE  
OF TITANIUM IN FERRO-MANGANESE.\*

By T. W. HOGG.

IN this paper is given a short account of the fact that there are probably about half a million isolated crystals of cyano-nitride of titanium in each cubic inch of the high percentage ferro-manganese now used for steel-making purposes, titanium carbide and nitride being also occasionally present. The size of these crystals generally lies between 1-10,000th and 1-1000th of an inch, comparatively few of them being greater than this.

The number of crystals has been counted, and the lowest estimate gave 336,000 to the cubic inch of alloy; as a matter of interest the weight of this number of cubes of cyano-nitride of titanium of 1-10,000th of an inch has been calculated, and found to be only 0.00003 of a gramme; similarly the weight of the same number of cubes of 1-1000th of an inch weigh 0.03 grm. The crystals are possessed of a high metallic lustre, with brilliant mirror-like facets, and occur in the form of cubes, octahedra, and forms resembling the icositetrahedron; there are also present beautiful combinations of prisms and pyramids, and many of the cubes have interesting symmetrical face modifications. As these different forms are all found together, they are microscopic objects of great beauty and interest to the student of crystallography.

These crystals are obtained by careful elutriation of the carbonaceous residue left after treating considerable quantities of the ferro-manganese with hydrochloric acid, cupric chloride, or dilute nitric acid. This latter is recommended as being the most convenient; in using it the mixture is kept as cold as possible, and allowed to stand for about twenty-four hours; the large crystals separate at once, the smaller forms being retained in the residue, which must be dried and gently pounded before submitting it to elutriation: this is best performed in a large porcelain basin, using plenty of water and gently rocking and rotating the mixture, and allowing it to rest at intervals; the lighter portions are then sucked up by means of a pipette, this being continued until nothing but the copper-coloured crystals are left.

The largest quantity which has been separated in this way is equal to 0.032 per cent.

Ferro-manganese containing different percentages of manganese and of different makes has been examined, and, with the exception of spiegeleisen containing 11 per cent Mn, they have all been found to contain this remarkable compound.

As the quantities available for examination are only small, with the exception of specific gravity and the titanium, only qualitative tests have been applied. In different specimens the sp. gr. has been found to vary between 4.1 and 5.1, and the titanium from 60.5 to 79.8 per cent. These latter determinations include a small proportion of iron, which has always been found to be present: this is also the case with crystals separated from an old blast furnace "bear"; after several days heating with hydrochloric acid there is still 1.5 per cent of iron retained, and probably this is the cause of the crystals being slightly but distinctly magnetic.

Attention is especially directed to the fact that much

valuable information with regard to the condition of the foreign elements may be obtained by decomposing large quantities of the alloys with suitable reagents, and separating the substances of different specific gravity from the residue: in doing this it is pointed out that there is great danger of decomposing the compounds originally present, and forming new ones as a result of the reaction which takes place between the reagent and the various substances present. Such a method as is indicated in this paper is recommended to be used in conjunction with the examination of etched specimens, which of themselves do little beyond revealing changes of structure induced by different modes of manipulation and varying temperatures; the insufficiency of etched specimens to give us information with regard to the condition of impurities is evident from the fact "that, being opaque, so nearly alike in colour, and in such minute and uniformly distributed particles, they escape observation."

THE CAUSE OF THE RED COLOURATION  
OF PHENOL.\*By CHARLES A. KOHN, Ph.D., B.Sc.,  
Lecturer on Organic Chemistry, University College, Liverpool.

THE cause of the turning red of phenol has from time to time been the subject of investigation, but the published results are both vague and conflicting. Whilst the balance of opinion has favoured the view that the colouration is to be traced to some impurity—generally metallic—present in the phenol, others have traced the colouration to the presence of cresol, which in combination with phenol is supposed to give rise to the formation of rosolic acid. More recently, Fabini has stated that the colour formed is produced by the combined action of hydrogen peroxide, metallic salts, and ammonia, and that all three reagents must be simultaneously present for the colouration to ensue.

Since alkalis (especially ammonia), metallic salts, and oxidising agents play an important part in the turning red of phenol, their separate and combined actions on specially purified phenol has been investigated. The purest commercial phenol, known as "absolute phenol," was used in a portion of the experiments; in the remainder, a specially purified sample, kindly prepared by C. Lowe, Esq., of Manchester.

This phenol was first purified by repeated distillation from glass vessels, the first and last portions of each distillate being rejected. The distilled product was then tested with hydrogen peroxide, ammonia, caustic potash, iron and copper salts, after one, six, nine, and fifteen distillations respectively.

The tests were carried out by placing 2—3 c.c. or the melted phenol in a test-tube and adding one of two drops of the reagent or mixtures of the reagents. The reagents were employed in various strengths.

Under all conditions a colouration was found to result, even with the fifteen-times distilled product, whilst comparative tests showed that no further purification had been effected after the second distillation. Ammonia in concentrated solution produces a deep blue colouration, identical with Phipson's "phenol blue," and probably the same product as phenol-quinone-imide. The formation of this colour has long been known, and seems to have been quite overlooked by Fabini in his statement that, in addition to ammonia, metallic salts and hydrogen peroxide are also necessary for a colouration to be formed. Very dilute ammonia, in common with hydrogen peroxide, caustic potash, hydrogen peroxide in presence of ammonia, or of caustic alkali, metals, or metallic salts, with or without hydrogen peroxide, produces a reddish

\* Read before the British Association (Section B), Nottingham Meeting, 1893.

\* Abstract of a Paper read before the British Association (Section B), Nottingham Meeting, 1893.

colouration. The intensity and tint of the colours produced by these different reagents vary considerably, but in most instances it inclines to red—the colour usually formed in commercial phenol. Whilst it is not likely that these colours are identical, it is probable that they are closely allied products, and the conditions of their formation point to their being oxidation products of phenol. Gentle heating in all cases aids the formation of these colourations.

The phenol, both after nine and after fifteen distillations, was carefully tested for metallic impurities and was found to be quite free from the same. Further, in order to test whether iron and copper salts were readily carried over by phenol when distilled, the product was distilled after the addition of these metals and of their salts, with the result that after two careful distillations from glass vessels the distillate was found quite free from metallic contamination.

That pure phenol behaves as described with the above reagents was confirmed by applying the same tests to phenol purified by sublimation, and also to that obtained by the saponification and subsequent decomposition of gaultheria oil.

The incorrectness of Fabini's view of the cause of the colouration was thus fully confirmed. The complete concordance in the behaviour of the phenol prepared from such different sources, and purified by different methods, shows that the re-distilled "absolute" phenol is in reality a pure product, and that the colour reactions observed with it are not to be traced to the presence of hidden impurities.

Of greater importance than the action of these various reagents upon purified phenol, is the fact that the pure product obtained by each of the above processes does of itself become coloured when exposed to ordinary moist air. The colouration, which gradually deepens from pale pink or brown to red, is always accompanied by the absorption of moisture, and the reddening is especially conspicuous in the partially liquefied parts of the sample. This colouration does not take place in the dark, nor under red glass; it is the work of the more refrangible rays of light only.

As has often been observed, sublimed phenol does not redden as rapidly as the distilled product; in fact, according to Bidet, it does not colour at all on exposure when thus purified. This, however, is not the case, the sublimed product becomes coloured quite as quickly as distilled phenol when in solution, and that it is slower in turning pink when in the solid state is due to the fact that the crystals obtained by sublimation are less hygroscopic than the distilled product. In absence of moisture, under all conditions, no colouration ensues; hence the appearance of the colour in those portions of the sample which have become partially liquefied. Phenol placed *in vacuo* can be exposed to light for months without becoming red, nor does it colour either in presence of moisture when air is absent, or in presence of air when perfectly dry. Both air and moisture are necessary for the colouration to take place.

The similarity between the coloured product formed by the action of moist air and phenol and that produced by hydrogen peroxide naturally led one to look to the latter as the real factor in the oxidation. That such is the case has been conclusively shown by Dr. A. Richardson, who has succeeded in detecting the presence of hydrogen peroxide in reddened phenol, both by the chromic acid and by the titanous acid test.

Dr. Richardson very kindly communicated his results to me, as I had myself not succeeded in detecting the presence of this body with certainty; a fact due, as I subsequently ascertained, to the exposures having been made under conditions in which the hydrogen peroxide formed was used up for the oxidation of the phenol as rapidly as it was produced. Dr. Richardson further ascertained that the blue rays of light and not the red are the active agents in the production of hydrogen peroxide when

phenol is exposed; a fact which further emphasises the relation of its formation to the colouration.

This same colour is produced, together with a complexity of other substances, when phenol is electrolysed in acid solution. The nature of the coloured product formed is still under investigation, and not until the colouring-matter itself is more completely studied can any conclusion be drawn as to the course of the oxidation. Meanwhile the fact that phenol, when perfectly pure, does possess the intrinsic power of turning red when exposed to ordinary moist air is of some technical importance, and points to the futility of the numerous processes proposed for preventing such colouration, as well as to the conditions under which the product can be best prepared and kept so as to impede the formation of the colour.

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 159).

### The Photographic Proof.

THE commencement of my proofs fulfilled my expectations only to a very modest extent. My apparatus, indeed, as it was to be expected from the size of its aperture, was found very light-proof: but the two most refrangible rays of cadmium, Nos. 25 and 26, contrary to my anticipation, had gained little in intensity. It was not much better with the most refrangible lines of zinc, Nos. 27, 28, and 29. They certainly appeared earlier than previously, but their intensity still decreased decidedly with their wave-length. Hence it seemed as if the suspected action of the atmosphere might chiefly be reduced to a specific property of the lines concerned. But even this, as it appeared in the course of my subsequent researches, was in part correct; the main difficulty in my earlier proofs of the most refrangible rays lay in the imperviousness of the air to light. This resulted clearly from the proof of the aluminium spectrum which next followed. All the main lines appeared in a few minutes, and in greater intensity than heretofore. The most refrangible—the double line, No. 32—acted now always first, in contradistinction to former results, and its components were of equal strength, a circumstance which I emphasize merely because it acquired especial importance for certain subsequent proofs. Next to it there appeared the least refracted line, No. 30, and only some time after the intermediate line, No. 31, the least refracted component always first. On brief exposure the more strongly refracted component did not appear at all, and even on prolonged exposure it remained far behind all the other lines.

This behaviour of the aluminium spectrum with the new apparatus ensued whether the proof was taken with or without a condenser, and with plates of high or low sensitiveness. In contrast to earlier observations the lines, after an exposure of three minutes, displayed an intensity and distinctness quite sufficient for the purpose of measurement.

On more prolonged exposure the more effective lines acquired the greatest intensity which the gelatin plate admits of. But very remarkably the action of light in this reagent is confined to these rays, whilst the less deflected portion of the ultra-violet is distinguished by an exactly opposite phenomenon,—the access of new lines and their growth to a continuous band of the deepest blackness. Owing to this circumstance the proofs have a

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. ciii., Part II., April, 1893).

peculiar appearance: they produce the impression as if the activity of their most refrangible half were still checked by some hindrance. We are compelled to this conclusion by the great intensity of lines No. 32, with which the effective band of the aluminium spark in the ultra-violet suddenly ends, and whereby, at the same time, the assumption of its prolongation towards the more refrangible side, where hitherto no action of light has been observed, receives a certain justification. It was this consideration which led my work from the path of reproductivity, on which it had hitherto mainly moved, towards new facts.

My endeavours were henceforth directed to bring into photographic activity the region between the lines Nos. 30 and 32, which hitherto, with the exception of line No. 31, had evinced no reaction to light whether in my hands or in those of other experimenters. I sought to effect this, in the first place, without reference to graphic completeness, proceeding on the assumption that the previous want of success was due not to the absence of all radiation, but to the imperfection of the method of observation.

I first strengthened the illumination with energetic short sparks, springing over close in front of the widely-open slit, and, with the lenses fully open, I obtained on a Zettnow plate, after exposure for half an hour between the components of the line No. 32, first two marked lines, then—on prolonged exposure on both sides of the same line—a band of action composed of dense groups, which continually extended further with the increase of the illumination.

On an exposure of an hour and a half the entire aluminium spectrum consisted of an almost continuous band, which ended only beyond the previous boundary of the ultra-violet, about at the wave-length  $183 \mu\mu$ . That we have here to do with the spectrum itself, and not with an action of diffused light, was shown by the fluctuating intensities and the marked lines by which the newly-acquired region is distinguished. In how far this is to be ascribed to the aluminium or to its impurities, or to the atmosphere, I must leave an open question. But for me a more important consideration was the fact now ascertained, that the region between the main lines of aluminium and a slight distance beyond, though hitherto regarded as void of light, displayed a quite unexpected wealth of rays.

Such being the case it was to be expected that not aluminium alone, but other substances, would admit rays of such strong refrangibility. This conjecture was actually confirmed when I submitted a series of elements to examination.

I adduce below these spectra in chronological order. In place of a photographic reproduction, which I reserve for a future occasion, I give the main data of the experimental arrangement and the photographic result, in order to furnish some basis as to the energy and the number of the new lines, in as far as they lie beyond the wave-length  $188.8 \mu\mu$ .

(To be continued.)

## ON ERBIA.\*

By GERHARD KRÜSS.  
(Continued from p. 158).

### The Ytterbia Material.

	Weaker bases ←				→ Stronger bases.				
Series 5.	1	2	3	4	5	6	7	8	9 (residue).
	173.6	175.5	—	172.5	—	—	173.4	174.6	172.5

Colour of Oxides.—White from 1 to 7; from fraction 8 onwards, distinctly reddish.

Spectrum of the Earth Solutions.—1 to 7 without bands. Fractions 8 and 9 showed faint Tm and Er lines. For a general view to ascertain whether the feebly basic scandia was present in the ytterbia material, the fractions 1 and 2 were mixed and about one-fourth was precipitated with aniline, R of this precipitation =  $173.2$ , whence scandia is probably absent.

### Erbia Material No. 3.

Series 7.					
Weaker bases ←					
I	2	3	4	5	6
148.0	—	139.8	140.5	—	142.3
→ Stronger bases.					
7	8	9	10	11	12 (residue).
135.8	125.7	—	—	115.4	93.9

Colour of the Oxides.—Deep yellow up to the residue, which is nearly white.

Spectrum.—Chiefly X lines, which become very faint towards the end of the series.

According to P. Cleve, on fractionating ytterbia-erbia earths, nearly colourless earths are obtained as fractions of mean basicity; the spectrum of which contains chiefly an absorption band at  $\lambda = 684$ . Cleve found the R resulting from the equivalent of these earths situate between

the values of ytterbium and erbium,  $\overset{\text{III}}{\text{Yb}} = 173$   $\overset{\text{III}}{\text{Er}} = 166$ , and inferred hence the existence of a substance which he

named thulium,  $\overset{\text{III}}{\text{Tm}} = 171$ . The above experiments fully confirm those phenomena first observed by Cleve; which, however, do not contain any binding proof that we have

here an unitary earth corresponding to  $\overset{\text{III}}{\text{R}} = 171$ . To this point we shall return in a subsequent memoir. In the meantime, the earths corresponding to Cleve's thulia were united as—

### Thulia Material.

Series 5, Fraction 9, ytterbia material; and  
Series 6, Fractions 1, 2 and 3, erbia material.

The first precipitate from this with aniline in an alcoholic solution was returned to the total ytterbia earth, Series 5, and the rest was further decomposed in the same manner.

### Thulia Material.

	Weaker bases ←			→ Stronger bases.	
Series 8.	1	2	3	4	5 (residue).
	171.6	—	—	157.5	156

After the erbiferous yttria earths originally taken in hand, as shown in the Series 5—8, had been decomposed, those fractions were selected for preparing the true erbia earth which, (1) according to their position in the above series, contained earths rather more basic than those present in the thulia material. (2) Those which in the determination of their equivalents gave values of

about 166 for R; and (3) those which on analysis certainly yielded values rather lower than  $\overset{\text{III}}{\text{Er}} = 166$ , but which, according to their position in the series, contained along with holmia, terbia and yttria; and, according to the spectroscopic examination, contained erbia in quantity.

Hence there were united as the present *Erbia Material* No. 4—

Series 6, Fractions 4 to 9 inclusive, erbia material; and  
Series 7, Fraction 1, yttria material.

These earths in an alcoholic solution of their chlorides were partially precipitated with aniline, and yielded—

\* Zeitschrift für Anorganische Chemie.

	Feebler bases ←			→ Stronger bases.			
Series 9.	1	2	3	4	5	6	7
	172.4	168.8	167.7	165.9	158.5	115.5*	140.2

(To be continued).

ON THE  
ACTION OF IODINE ON SOME  
PHENOLS AND ALLIED COMPOUNDS IN  
PRESENCE OF FREE ALKALI, AND  
A NEW CLASS OF DERIVATIVES  
RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 155).

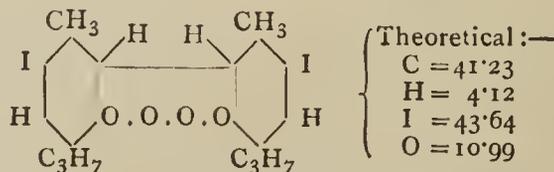
ANOTHER batch was prepared under the same conditions as those which yielded the red precipitate at 60° C., excepting that the fresh sample of caustic soda was used, as in the last case. The precipitate obtained was of a yellow-brown colour, similar in appearance to the large dilution one at the ordinary temperature, but of less sticky character. This was dried at a low temperature (40° C.), and when dry was of a yellowish white colour. It was then treated with boiling alcohol, and the alcoholic solutions filtered off. The united alcoholic solutions were then partially evaporated, when a considerable portion fell out of solution. The remaining solution was then filtered off, and the deposited portion collected, washed with alcohol, and dried. (Call this portion  $\alpha$ ). The alcoholic solution which was filtered off was treated with a little water, when a flocculent yellowish white precipitate was obtained, which was filtered off, washed with water, and dried. (Call this portion  $\beta$ ). The remainder of the original precipitate insoluble in alcohol was dissolved in ether, filtered, and recovered. (Call this portion  $\gamma$ ).

Analyses of  $\alpha$ .

Total iodine:—  
Quantity taken = 0.1308 grm.  
Silver iodide found = 0.1062 „ = 43.86 p.c. iodine.

Combustion of same:—  
Quantity taken = 0.0957 grm.  
Water found = 0.0372 „ = 4.31 p.c. hydrogen.  
Carbon dioxide found = 0.1460 „ = 41.60 „ carbon.  
By difference .. .. = 10.23 „ oxygen.

Those results may be fairly well represented by the formula  $C_{20}H_{24}I_2O_4$ , or constitutionally thus:—



Analyses of  $\beta$ .

Total iodine:—  
Quantity taken = 0.1151 grm.  
Silver iodide found = 0.0902 „ = 42.34 p.c. iodine.

Combustion of same:—  
Quantity taken = 0.0830 grm.  
Water found = 0.0332 „ = 4.44 p.c. hydrogen.  
Carbon dioxide found = 0.1259 „ = 41.36 „ carbon.  
By difference .. .. = 11.86 „ oxygen.

\* This sudden fall of the atomic weight as observed in this fraction, which corresponded to an oxide lying between erbia and holmia, has been explained by further experiments, and will be discussed in a separate memoir in the *Zeit. für Anorg. Chemie*.

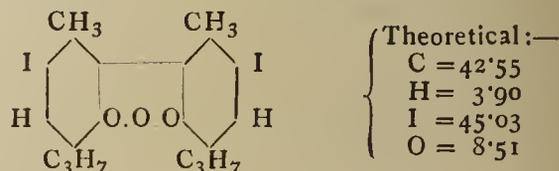
No likely single formula can be adduced from those results. They point to admixture of a compound of similar composition to the last one treated, together with one of similar constitution but containing less iodine, very probably one only of the benzene nuclei being substituted.

Analyses of  $\gamma$ .

Total iodine:—  
Quantity taken = 0.1824 grm.  
Silver iodide found = 0.1518 „ = 44.96 p.c. iodine.

Combustion of same:—  
Quantity taken = 0.0983 grm.  
Water found = 0.0376 „ = 4.24 p.c. hydrogen.  
Carbon dioxide found = 0.1516 „ = 42.05 p.c. carbon.  
By difference .. .. = 8.75 „ oxygen.

Those results agree well with the formula  $C_{20}H_{22}I_2O_3$ , and may be constitutionally represented thus:—



A new batch of the excessive dilution product was prepared with the following proportions:—1.3 grms. thymol and 2 grms. caustic soda in about 5 litres of water (ordinary temperature). The precipitate, which was of a yellowish brown colour and would not settle as in the previous case, was filtered off, washed, and dried. The precipitate was then treated with successive portions of boiling alcohol, and the soluble portion of precipitate recovered. This was then treated with warm alcohol, in which a small portion was insoluble. The insoluble portion was filtered out and neglected. (It should be pointed out here that nearly all the compounds dealt with in this paper exhibit inter-solubility, that is, a solution of one will render to a slight extent soluble one which is otherwise insoluble in the solvent simple. The presence of iodine, free or "enclused," also seems to greatly influence the solubility. Probably the most important external factor capable of influencing the solubility is the presence of minute quantities of metal oxides of sufficiently intimate combination as to enable them to pass with the compounds into the lightest solvents. As was remarked at the outset, this fact has been taken advantage of throughout, and in some cases the fact may be further applied in order to effect separations by heating the mixture with a metal oxide and water, magnesia being a good one for the purpose).

The soluble portion was recovered from the alcohol, dissolved in ether, the ethereal solution floated on water in a stoppered vessel, and treated with sodium amalgam for three days. The product was then recovered, dried, and taken for analysis.

Total iodine of the partially reduced compound:—  
Quantity taken = 0.1094 grm.  
Silver iodide found = 0.0953 „ = 47.06 p.c. iodine.

Combustion of same:—  
Quantity taken = 0.0802 grm.  
Water found = 0.0292 „ = 4.04 p.c. hydrogen.  
Carbon dioxide found = 0.1168 „ = 39.71 „ carbon.  
By difference .. .. = 9.19 „ oxygen.  
(The hydrogen was specially determined).

Those results may be represented by the formula  $C_{36}H_{42}I_4O_6$ .

The remainder of the partially reduced product was again dissolved in ether, transferred to a flask placed under an upright condenser, and treatment with hydrogen from zinc and sulphuric acid carried on for a week at a

slightly elevated temperature. At the end of this time a portion was taken for analysis.

Total iodine of the further reduced product:—

Quantity taken = 0.0996 grm.  
Silver iodide found = 0.0834 „ = 45.24 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1114 grm.  
Water found = 0.0494 „ = 4.94 p.c. hydrogen.  
Carbon dioxide found = 0.1854 „ = 45.38 „ carbon.  
By difference .. .. = 4.44 „ oxygen.

Those results show that the iodine and oxygen had now both been attacked, but, it will be observed, not proportionately. This will be important when the position of the iodine atoms come to be discussed.

The remainder of the further reduced product was transferred and treated in like manner with zinc-dust and solution of caustic potash for fourteen days more, the temperature being sufficiently raised to maintain the ethereal solution in a brisk state of ebullition. At the end of this time the product was recovered, when it was found to have parted with all its iodine. When dried it appeared colourless and transparent in thin layers, but amber-yellow in mass; it possessed a strong odour, somewhat pine-like, and was of soft and sticky consistence.

Combustion of the reduced product:—

Quantity taken = 0.0836 grm.  
Water found = 0.0788 „ = 10.47 p.c. hydrogen.  
Carbon dioxide found = 0.2744 „ = 89.51 „ carbon.  
(Only one analysis could be made).

It would thus appear to have been reduced to a hydrocarbon.

*Analyses of the Original Non-reduced Compound.*

Total iodine:—

Quantity taken = 0.1021 grm.  
Silver iodide found = 0.0870 „ = 46.03 p.c. iodine.

Combustion of same:—

Quantity taken = 0.0796 grm.  
Water found = 0.0292 „ = 4.07 p.c. hydrogen.  
Carbon dioxide found = 0.1151 „ = 39.43 „ carbon.  
By difference .. .. = 10.47 „ oxygen.

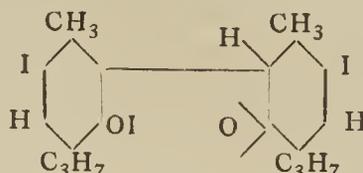
Formula,  $C_{36}H_{42}I_4O_7$ .

It is apparent that the effect of the first partial reduction was simply the removal of an atom of oxygen, which greatly strengthens the assumption as to the distribution of the oxygen atoms in the molecule, as pictured in the constitutional representation already given.

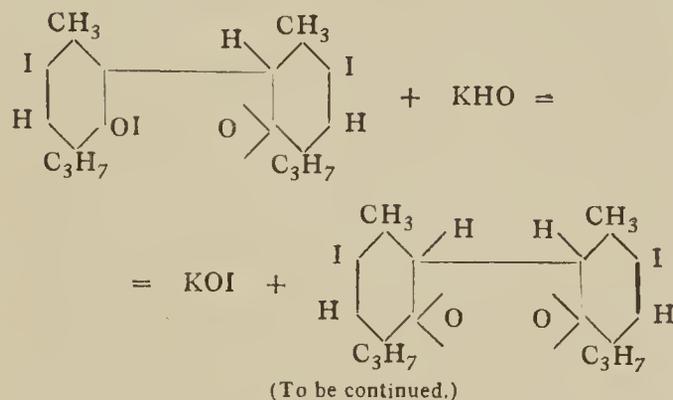
Messinger and Vortman in their paper treat of the action of iodine on thymol at considerable length. They were of opinion that the product of the reaction was a di-thymol iodide, but I consider that I have shown quite conclusively that no such compound is formed under any circumstances. As in the case of the phenols, they failed to recognise that they were dealing with a mixture of substances, and also the fact that the compounds contained iodine other than that of substitution. By boiling with a solution of potash and other means, they obtained a yellow body which they considered to be a decomposition product, which assumption was erroneous. The total iodine of this body they estimated as 47.24 per cent. On reduction they obtained a body which corresponded generally with Dianin's di-thymol, and they considered it to be, or to contain, a di-thymol molecule. The ultimate analysis, however, gave only 75.6 per cent carbon, whereas di-thymol requires 87.26 per cent. The results, they point out, agree better for an oxy-di-thymol, which requires 76.41 per cent of carbon.

The iodine percentage given above 47.24 agrees well with that given by me for a class of compounds which can be best represented by assuming the existence in the molecule of a ring of carbon atoms of the naphthalene type, and which could not possibly yield a di-thymol by reduction. Further, the percentage of carbon found by them for the reduced product could be much more easily reconciled by this assumption.

The red body they represent thus:—



and the formation from this of the yellow body, thus:—



NOTE ON EXPERIMENTS  
ON THE SPECIFIC GRAVITY OF GOLD  
CONTAINED IN GOLD-SILVER ALLOYS.\*

By HENRY LOUIS, Singapore, Straits Settlements.

Four alloys of gold and silver were prepared, containing the metals in the following proportions by weight:—

1. Gold : Silver :: 1 : 2.62.
2. Gold : Silver :: 1 : 3.15.
3. Gold : Silver :: 1 : 4.11.
4. Gold : Silver :: 1 : 5.17.

These alloys were rolled, with repeated annealing, into thin strips, rather thinner than is usual for assay-cornets. The strips were thoroughly annealed, cut into pieces, and dropped into hot parting-acid. They were boiled with No. 1 parting-acid for one hour and ten minutes altogether, and then with No. 2 parting-acid for thirty minutes, washed thoroughly with boiling distilled water, and left under water under the exhausted receiver of an air-pump for thirty hours.

Their specific gravities were then taken with the following results, the temperature being 15° C.:—

No. of Experiment.	Weight of Gold in Air.	Weight of Gold in Water.	Weight of equal bulk of Water.	Specific Gravity.
	Grains.	Grains.	Grains.	
1.	9.408	8.946	0.462	20.36
2.	13.897	13.219	0.688	20.20
3.	13.627	12.956	0.671	20.31
4.	13.170	12.566	0.604	21.8

The quantities operated on were very small, and the balance and weights by no means first-rate, so that the results are not likely to be very accurate. The first three results are sufficiently close together, but the very high figure obtained in the fourth experiment must, in all likelihood, be due to some error. Hence, it will be safest

\* International Engineering Congress, August, 1893.

to average the results of the first three experiments, and, pending a more complete and accurate investigation, which I hope to make of this subject, to take the specific gravity of the gold residue left on dissolving the silver-gold alloys at about 20.3 at 15° C. Apparently the varying proportions of the two metals in the alloys do not affect the result.

Gold thus left, on dissolving out the silver, is highly spongy, and, on annealing, it undergoes a very evident shrinkage. The result now obtained proves that, on annealing, the molecule of gold does not contract, but, on the contrary, expands, the shortage of bulk being due to a diminution of the physical interspaces between the particles of gold, while the interatomic distances must increase, the diminution being, of course, greatly in excess of the increase.

With regard to the figures here given it may be noted that Rose obtained, for the sp. gr. of precipitated gold, results varying between 19.49 and 20.72. His figures, taken together with mine, seem to point clearly to the existence of a heavy allotropic modification of gold. It is, of course, possible that the brown amorphous gold obtained, either by precipitation or by the removal of the silver from a silver-gold alloy, may be a mixture of ordinary and allotropic heavy gold, in varying proportions: there can, however, be little doubt of the allotropism, and of the further fact that gold exists in the alloy in this allotropic form.

A further partial and indirect justification for this latter statement may be found in the experiments of Matthiessen on the specific gravity of alloys (*Phil. Trans.*, 1860, p. 177), in which he shows that the observed specific gravities of gold-silver alloys exceed the calculated ones (calculated upon the sp. gr. of ordinary gold) in the ratio, approximately, of 1 : 0.997. This would appear to suggest that the gold in these alloys is in a heavier state than ordinary normal gold; but any conclusions based on these observations are liable to modification, seeing that it is not yet known in what condition the silver in these same alloys exists.

It is possible that these results may afford a clue to the explanation of the widely different specific gravities found by different observers of native gold specimens (containing silver), of approximately the same composition, but from different localities.

In order to complete our knowledge of this subject it will be necessary to study the character of the gold by dissolving out the alloying metal from a series of alloys of gold with different metals, and I hope to be able to undertake this investigation before long.

The above experiments were conducted, by the kind permission of Prof. W. Chandler Roberts-Austen, in the research-laboratory of the metallurgical department of the Science Schools, South Kensington.

#### NOTES UPON THE COMPOSITION AND SOME PECULIARITIES OF MULES' MILK.

By A. B. AUBERT, M.S., and D. W. COLBY, B.S.

THE animal from which the milk was obtained is the property of Mr. McLaughlin, railroad contractor, and is now worked, singly or with mate, on the construction of the Bangor and Aroostook railroad; is about eleven years old; weighs 1100 lbs.; usual feed, hay and oats of good quality.

The mule showed no signs of heat previous to or at the time of milking; was milked several times a day, giving about two quarts of milk in all. Two samples of milk were received at an interval of about three weeks, the flow of milk having begun about six weeks previous to the sending of the first sample.

When received, the milk was of a pure white colour

without yellowishness, of alkaline reaction, which upon being kept in a cool room it only lost on the eighth day, becoming slightly acid. In spite of this change in reaction no curdling as exhibited by cows' milk took place, but simply the separation of a very fine-flocculent floating coagulum. The fat globules generally proved rather small, approximately ten per cent averaging 0.001 m.m. in diameter, forty per cent from 0.0018 to 0.0037 m.m.; forty per cent varied from 0.0037 to 0.0092 m.m., the remainder running from 0.0092 to 0.0222 m.m. and over.

A column of milk allowed to stand in a cool place for three days gave a separation of cream equal to one-seventeenth of the total height of the column. In the first sample of milk it was practically impossible to precipitate the casein with dilute acetic acid and carbonic anhydride.

By treating the milk with 70 per cent alcohol a white, fine, flocculent precipitate was obtained, which upon being filtered and washed with 70 per cent alcohol, strong alcohol, and lastly ether, dried and weighed, gave 2.52 per cent and 2.17 per cent of albumenoids, while by Kjeldahl's process 2.94 per cent of albumenoids were obtained, the factor used being 6.25.

The albumenoids of the second sample exhibited rather different properties from those of the first sample, precipitating more readily by the addition of dilute acid.

This milk was diluted with fifteen times its own volume of water, very dilute acetic acid added, carbonic anhydride was passed through for twenty-five minutes, and it was then set away in a cool place for forty-eight hours. A precipitate of casein was obtained, which proved most difficult to filter and wash. The results obtained were 2.33 per cent and 1.92 per cent, while the results by a method similar to Wanklyn's were 2.21 per cent and 2.42 per cent for total albumenoids. This would indicate that the quantity of albumen could not be greater than 0.5 per cent, if as much.

#### RESULTS OF ANALYSIS.

##### Sample No. 1 (Specific Gravity at 15°, 1.032).

Total solids .. .. .	10.65 per cent.
Fats .. .. .	1.86 "
Albumenoids .. .. .	2.94 "

##### Complete Analysis of Sample No. 2 (Specific Gravity at 15°, 1.033).

Analysis No.	I.		II.		III.		IV.	
	Per cent.							
Total solids ..	10.92	10.86	10.81	10.83				
Albumenoids ..	2.21	2.42	—	—				
Fats .. .. .	1.99	1.97	2.30	2.25				
Sugar .. .. .	6.07	5.96	—	—				
Ash .. .. .	0.52	0.53	—	—				

I. and II. by A. B. Aubert; III. and IV. by D. W. Colby.

The fat in III. and IV. was extracted by petroleum benzene, which usually gives higher results than by ether extraction.

The only other American analysis of mules' milk which has come to our notice is that by E. F. Ladd (*Agricultural Science*, i., 108).

Below is given the composition of mules' milk, as well as that of the mare and ass. The similarity is very apparent.

	Mules' milk.		Average composition given in "Die Milch," by Hermann Scholl.	
	Average of analyses I. and II.	Mules' milk. Results of E. F. Ladd.	Asses' milk.	Mares' milk.
	Per cent.	Per cent.	Per cent.	Per cent.
Water .. .. .	89.14	91.59	89.64	91.00
Albumenoids	2.31	1.64	2.22	1.99
Fat .. .. .	1.98	1.59	1.64	1.18
Sugar .. .. .	6.04	4.80	5.99	5.31
Ash .. .. .	0.53	0.38	0.51	0.43

Mares' milk, like that of the mule, is quite alkaline, remaining so for some time. It coagulates with difficulty, giving a very fine flocculent coagulum. The fat globules of asses' milk resemble those of mules' milk, being on the average very small.—*Journal of Analytical and Applied Chemistry*, vii., No. 6.

## ON CARBORUNDUM.

By WM. P. BLAKE.

A NEW abrasive material has been produced, and is in the market, for the various uses to which emery, or corundum, is applied. It is on exhibition in the metallurgical collection in the gallery of the Mines and Mining Building at Chicago by the Carborundum Company, of Chicago.

It is an artificial compound. The name which has been coined for it is misleading as to its composition, for it is not a compound of carbon and corundum, but is a definite compound, atom for atom, of carbon and silicon; a true silicide of carbon, or a carbide of silicon. The name carbo-silicon would have been more scientific and appropriate, but not as useful for trade purposes.

The appearance and properties of this substance are more nearly those of the diamond than of corundum, the lustre being highly vitreous and adamantine, and the hardness being extreme, sufficient, in the form of a rapidly rotating wheel, to cut the hardest steel and corundum crystals, and the material is said to have been used with success in polishing diamonds.

We owe the formation of this carbide of silicon to the prodigious chemical power of the electric current and the high temperature at which the carbon and silicon are brought together. The process and the apparatus are extremely simple. Carbon and silica are intimately mixed and are exposed to the force of the current in a simple trough or box made of firebrick or clay. The current flowing through the mixture reduces the silicic acid to metallic silicon, which unites with the carbon at one pole, while the oxygen passes to the other pole.

The crusts of the carbide so obtained are, on cooling, washed and cleansed in acid to remove soluble impurities, and are then crushed and sifted into different sizes to be used for making cutting-wheels, whetstones, or polishing-cloth. The cleansed crusts of carborundum are aggregates of very small but highly brilliant crystals, with highly polished faces, reflecting light like mirrors. The angles are sharp, and the general arrangement or grouping of the crystals is columnar, giving the masses a rude prismatic structure made up of tabular crystals.

The industrial and scientific world is indebted for the introduction and utilisation of this very important and interesting compound to Mr. Edward G. Acheson, of Chicago, who obtained a United States patent, and in June, 1891, organised a joint-stock company under the title of the Carborundum Company for its manufacture. In June, 1892, improvements in the process of manufacture had been made; the production was increased to 25 lbs. per day, and the price lowered to 2 dols. and 4 dols. per pound. In September, 1892, the manufacture of cutting and grinding wheels was commenced, and has since continued with increasing success. The present capacity of the works at Monongahela, Pa., for the production of the carborundum is said to be 100 to 150 lbs. a day. Its use at present is confined to the smaller-sized discs and wheels, which have found especial use and favour with the dental profession for cutting porcelain teeth and for other uses, for which they have hitherto relied on emery. It is claimed for the new wheels that they cut faster, are more enduring, and that they do not heat up the object being cut so much as wheels made of emery. An explanation of this may be found in the fact that the carborundum is an excellent and rapid conductor of heat, a decided advantage in many ways.

The physical properties of this substance, so far as I have been able to determine them, may be summarised as follows:—

*Crystallisation.*—Hexagonal. Generally in rhombic tabular plates, with angles of  $120^\circ$ , and the terminal edges of the prism bevelled, giving the following forms as seen, among others, in the field of a microscope, magnified about 20 diameters. The general habit is tabular, with long and irregular pedicles apparently shading off in a series of thin plates to the point of support or growth. Or, if viewed from the point of support or growth of the mass outward, the thickness and regularity of crystallisation increase by additional plates toward the end where the elongated irregular crystallisation ends in well-formed angles and brilliant planes, often showing in very fine parallel lines upon the edges, but without any foliation. The fracture is conchoidal and there is no evidence of cleavage. The edges are replaced by minute perfectly formed planes, and the intersection of these planes may give the appearance of striations when viewed by transmitted light in the microscope.

*Colour.*—As seen in mass by the reflected light, the dominant colour is bluish green, but varies from a pale yellowish green to dark blue green and emerald-green. Under the microscope, by transmitted light, the thin transparent plates have a pale green tint, but the depth of colour in the crystals varies, some being apparently nearly colourless or pale greenish yellow, while others are very dark olive-green, or emerald-green, much like the green colour shown by green tourmalines and by olivine. In some masses the colour and lustre are adamantine grey, a pale tint like that seen in rough uncut diamonds. A bronze-like lustre may also be seen on some samples with iridescence, reminding one of the tints of newly-formed crystals of bismuth. Fragments of a sapphire-blue colour have also been noted. When crystals are seen on edge, in a strong light, the colouring becomes more dense and pronounced. All the crystals appear to be perfectly transparent. When reduced to powder the colouring is lost, and the fine powder is ash grey. As seen in the manufactured wheels the pervading colour is a light epidote green. I have not obtained any satisfactory evidence of dichroism, though this character is strongly suggested by the appearance of the compound. It has a high index of refraction.

*Specific Gravity.*—Nearly 3. One determination upon a small mass, freed from air by boiling, gave me 2.946.

*Hardness.*—The great hardness of carborundum has already been described, but carefully conducted tests are yet required to show its exact hardness compared with corundum and the diamond, and its exact comparative practical value as an abrasive substance compared with emery, corundum, and diamond powder. It will scratch sapphire, but not diamond, and its hardness is therefore between 9 and 10, or about  $9\frac{1}{2}$  on the hardness scale.

*Future Possibilities.*—This discovery and its application are of great industrial importance. While at present the quantity of the material produced daily is comparatively small, it would seem that practically there is no limitation of the amount of this substance which may be produced. The requisite conditions are cheap power, an abundance of clean sand and of carbon, and these are not difficult to find. We may expect at no distant day to see large grindstones made of it for ordinary purposes; its superior "grit" and cutting power making it much more desirable than the sandstone of which our grindstones are made. Or we may find it moulded into tyre-like rims to slip upon large core wheels for economy of material and speed of mounting, with maintenance of diameter.

If by any modification of the process, by possibly slower action, and an equable high temperature, long maintained, large crystals of this compound could be formed, we should have a brilliant gem added to our list of precious ornamental stones. Its fine colour, splendid adamantine lustre, and its hardness, all fit it to occupy a high place in the series of gems.—*Engineering and Mining Journal*.

APPARATUS FOR EXTRACTION FOR  
ANALYSIS OF GASES DISSOLVED IN WATER.\*

By EDGAR B. TRUMAN, M.D., F.C.S.,  
Borough Analyst, Nottingham.

A GLASS flask, A, of 500 c.c. capacity, is joined by means of its tubular termination to a second lower flask, B, of 200 c.c. capacity, by means of a water-joint. In the lower flask is suspended from the upper one a thermometer, reading up to 150° C. From the neck of the upper

m.m. from 0 to 400 in two directions, downwards in the open limb, and upwards in the long limb, starting in each case from the level of the horizontal tube. This tube is filled with mercury up to the zero points, and indicates the rate of exhaustion of the apparatus, and is also a test of leakage.

The second tube, a little further on, E, points downwards for attachment to a Geissler's water-pump. Still further on a stopcock is let into the main horizontal tube, which then bends downwards for communication with a Sprengel pump.

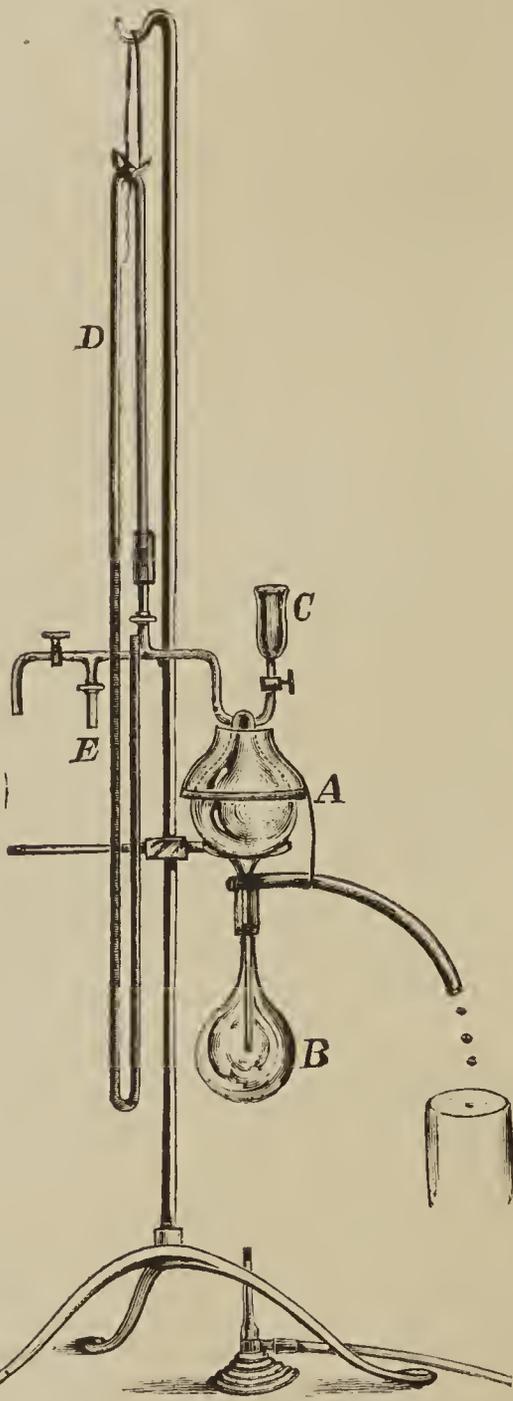
The apparatus is put into connection with both mercurial and water pumps, and the stopcock at the base of cup c is closed. By means of the water pump the apparatus is exhausted in a great measure of air; five minutes' pumping with a high pressure water produces a vacuum of 730 m.m., when the barometer stands at 753. The water-pump stopcock is then closed, and exhaustion is completed by the Sprengel in about thirty minutes more.

The liquid to be examined for gases is then, after measurement, introduced by the cup, c, into the upper flask, whence it flows into the lower one.

The liquid is allowed to stand for an hour, so that gases disengaged at ordinary temperatures may come off. These are collected by the Sprengel and analysed in the usual way.

The vacuum having been restored, heat is cautiously applied to the lower flask by means of a Bunsen burner. If carefully done there is no bumping. The effect of heat is, by disengaging gas, to increase tension, and to enable the water to become hotter. The mercury in the mercurial tube and that in the thermometer rises. When the mercury in both places remains constant the Bunsen burner is removed.

The gas given off by boiling is then collected and analysed.



flask proceed two millimetre tubes. The right-hand one, after receiving a stopcock, expands into a cup, c, having a capacity of 30 c.c. The tube on the left rises to the level of the bottom of the cup. This tube has two tubes supplied with stopcocks joined on to it at right angles—one above and one below. To the one above is attached, by a water or glycerin joint, a mercury tube, d, doubled on itself above and below, as shown, and having a length when so doubled of 880 m.m. This tube is graduated in

THE ACTION OF LIGHT UPON DYED  
COLOURS.\*

(Concluded from p. 157.)

CLASS IV.—FAST COLOURS. (WOOL). (Continued).  
Azo Colours.

Wool Book I.

Acid Reds.—

87. Cloth red B. From amido-azo-toluene and  $\alpha$ -naphthol-mono-sulphonic acid NW. S. and J. 115.
91. Orseillin BB. From amido-azo-toluene-mono sulphonic acid and  $\alpha$ -naphthol-mono-sulphonic acid NW. S. and J. 124.
93. Cloth Red No. OB. From amido-azo-toluene and  $\beta$ -naphthol-di-sulphonic acid R. S. and J. 114.
97. Azo Fuchsin G. From sulphanilic acid and di-oxy-naphthalene (1·8)- $\alpha$ -mono-sulphonic acid. S. and J. 229.
98. Azo Fuchsin B. From toluidine and di-oxy-naphthalene (1·8)- $\alpha$ -mono-sulphonic acid. S. and J. 228.

Wool Book II.

Chromotropes.—

3. Chromotrope 6 B cryst.
4. Chromotrope 8 B cryst.
5. Chromotrope 10 B cryst.

Induline Colours. Rosindulines.

Wool Book I.

Acid Reds.—

95. Azo Carmine. Sodium salt of phenyl-rosinduline-di sulphonic acid. S. and J. 369.

\* Report of Committee, consisting of Professor T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Nottingham Meeting, 1893.

\* Read before the British Association (Section B), Nottingham Meeting, 1893.

CLASS V. VERY FAST COLOURS.

The colours of this class show a very gradual fading during the different periods, and even after a year's exposure a moderately good colour remains.

*Azo Colours.*

Wool Book II.

*Chromotropes.*—

1. Chromotrope 2 R cryst.
2. Chromotrope 2 B cryst.

*Oxyquinone Colours.*

5. Alizarin Red (alumina mordant).
10. Alizarin Turkey Red (cotton).

*Natural Colouring Matters.*

6. Madder Red (alumina mordant).
1. Cochineal Scarlet (tin mordant).
2. Kermes Scarlet (tin mordant).

SILK PATTEKNS.

The foregoing colours were dyed on silk, employing 2 per cent colouring matter, and the patterns were exposed to light, along with those on wool, with the result that the relative fastness of the various colours was practically the same as on wool.

GENERAL RESULT.

The experiments extend at present over too limited a number of colouring matters to enable one to draw fixed general conclusions, but it may be well already at this point to record the following observations.

The most fugitive reds on wool and silk are the eosins and allied colours. Curiously enough, the introduction of the methoxy group, as in methyl-eosin, &c., increases the fastness, not of the colour as a whole, but of the pale faded tint which results after the first few weeks' exposure. As already stated, this tint remains practically unchanged even after a whole year's exposure.

With respect to the rosindulines, it is interesting to note that the G shades are very fugitive, while the B shades are moderately fast.

All basic reds belong to the more or less fugitive class, including, namely, the magentas, safranines, and rhodamines. The nature of the acid with which the colour base is combined seems to have no influence upon the fastness of the dyed colour.

Comparatively few (about twenty) of the azo reds examined are fugitive, and these belong chiefly to the simple monazo colours.

The great bulk of the fast and moderately fast reds belong to the azo colours, the so-called secondary diazo colours being generally faster than the rest. It is evident, however, that the fastness of these azo colours depends, not only on the base which is azotised, but also upon the character of the naphthol sulphonic acid employed. This is especially noticeable in the chromotropes, in which a particular dioxynaphthalene disulphonic acid is employed, and all of which are remarkable for their fastness. The particular azo compound and phenol united together is also of importance.

With respect to the milling and cloth reds, it does not appear that the use of mordants with them increases their fastness to light.

The number of very fast reds is extremely limited, but it includes both natural and artificial dyes—namely, madder, cochineal, kermes, alizarin, and the chromotropes 2 R and 2 B. When it becomes possible to expose the Congo reds, one or two others will no doubt have to be added to the list of very fast artificial red dyes. In this connection it may be pointed out that certain reds obtained from the natural dye-stuffs are fugitive, namely, those obtained from Lima-wood, Cam-wood, and the allied woods.

It is well to add that there are no sharp lines of division with respect to fastness to light among the various reds,

and each of the five classes into which they have been here arbitrarily divided includes colours which differ from each other more or less in this respect.

DETERMINATION OF THE TRUE ATOMIC WEIGHT OF COPPER.\*

By Dr. GUSTAVUS HINRICHS, St. Louis, Mo.

CHEMISTRY of precision is at present in a very peculiar condition, especially that branch thereof which has for its object the determination of the atomic weights of the chemical elements. On the surface it seems that this department is in a most flourishing condition; the number of determinations never was greater than at present, the space devoted to this topic in the chemical periodicals never was more extended, and the accuracy of the results is stated with an astonishing degree of precision, quite often expressed by means of refined methods of calculation, such as we formerly used to meet in astronomy only.

Under such conditions it is exceedingly unpleasant to be in duty bound to present an abundance of facts which demonstrate that all this glory is but a hollow mockery and a sham, and it even becomes difficult to obtain a hearing for the purpose of submitting these facts for examination. Since the very renown of Stas depends upon the failure of chemists to practise mathematical and chemical criticism, it can scarcely be expected that these faculties will now respond promptly to our call after having been dormant for a quarter of a century. Our modern chemist seems to be as unwilling to find errors in the work of Stas as philosophers were to look through the first telescope for spots on the sun.

Nevertheless the recorded facts show that the eminent analyst of Brussels has entangled the entire subject of the atomic weights in a web of systematic errors both chemical and mathematical, and has besides committed some of the most astonishing errors in the detail of his work.

However unwilling chemists may be to look doubtingly at the work of their recognised master, it seems worth trying to make them join us in the critical examination of the work of a disciple of the school of Stas. To bring it more nearly home to the chemical public of this day and of this country, let us select for such examination the work of recognised merit recently completed by an American chemist according to the general methods of Stas, with the single exception of the use of enormous quantities, which much-extolled peculiarity of Stas was one of the worst features of his system.

In looking over the entire field, I can find no example more fair for this critical examination than the work of Professor Theodore W. Richards on the atomic weight of copper. This work has been republished in full in Germany, in the new *Zeitschrift für Anorganische Chemie*, Bd. I., 1892. The results thereof have been accepted as practically final by Ostwald (*Zeitschrift*, ix., p. 383, 1892), who is generally recognised as an authority on the subject of atomic weights. I will further add that I have the highest regard for the analytical skill of Prof. Richards, who has spent on this work four years of his time in the best appointed laboratory of research in America.

If therefore I am constrained to declare that the final results of Prof. Richards are without permanent value to chemistry, being nearly one-fifth of 1 per cent in error; that, moreover, this entire research was superfluous, because a more accurate determination was known before this work was published; and that finally the only two reliable results which he obtained in his laborious research were not recognised by him as such, but were with great labour and much chemical acuteness blotted out from his

\* See accompanying letter

work by himself; if I shall be compelled to declare all of this, I shall equally insist that the fault thereof is not in the excellent chemist personally, but is due to the school, the system of Stas which he represents.

To keep this paper within reasonable bounds, it will be necessary to proceed directly to the determination of the atomic weight of copper; thereafter the critical part can be very briefly given.

The electrolytic ratio  $2\text{Ag} : \text{Cu}$  is 3.402, if we adopt temporarily 63.5 as the atomic weight of copper, and take Ag at 108 as standard. For 63 and 64 the ratio would be 3.375 and 3.438.

Now the determinations of Shaw (1886) gave 3.400; Lord Rayleigh found 3.404 to 3.408, and Gray 3.401. These values are almost identical with the one corresponding to 63.5 as the atomic weight of copper. This therefore is approximately the value sought. It only remains to find the minute deviation of this number from the true atomic weight, or to establish that this deviation is zero.

The mean value given by Richards himself is Cu 63.61, resulting from the means of all his eleven series, oxygen being taken as 16.000. Of course this mean involves the use of several of the erroneous values of Stas; but as in the different series the elements employed are different, it is impossible to make allowance for these errors in the general mean. Part of the variation of the individual means is due to this fact; they run from 63.593 to 63.641. The actual range of these means is 0.048, or say 0.05.

Professor Richards next throws out six of his eleven series, and thereby reduces the range to 0.008, or say 0.01 in the means of the series retained, and gets 63.604 as a sort of selected final mean. This is a tacit admission that more than half of his series were made according to methods not fit to yield results of precision. This final selection of the best agreeing results is quite generally practised in the school of Stas to-day. Thus Van der Plaats freely omits entire series of Stas, according to his own sweet will and pleasure (*Annales de Chimie*, vii., p. 512, 1886). The most glaring example of the kind—a genuine parody on sound science—may be found in Van Laar's "Thermodynamics" just published (p. 8). Having tabulated the results obtained by the different chemists—and he seems to consider the determinations of Leduc and Lord Rayleigh as legitimate determinations of atomic weights—he says drily, and with absolute unconcern, "If we except the value under *a* as being certainly too low, and those under *d* and *e*, which are certainly too high, we get, as mean of the values under *b* and *c*, 15.881—exactly the value of Morley. For  $O=16$ , then follows  $H=1.0075$ ." This work is highly commended in a Preface by van 't Hoff, and has been equally highly recommended by Oswald. The selection made by Richards, therefore, is in keeping with the practice of the school, for which it would be unjust to blame the individual.

Next the question arises, Is the value 63.61, or say 63.60, of Richards, the true atomic weight of copper? In that case the deviation of 63.5 would be 0.10. But the determinations of Richards showed a range of 0.05, which is exactly half of the quantity in question. No scientist will pretend that a quantity is established with precision when it is affected with an uncertainty of half its own value. In other words, the work of Richards has not established the atomic weight of copper at 63.6.

A careful examination of the methods used by Richards in his eleven series compels the condemnation of ten thereof as unfit for the purposes of precision. Only the use of *blue vitriol* as material, and the electrolysis and dissociation thereof, remain as legitimate processes for the determination of atomic weights. Of such determinations Richards has made three excellent series. The results obtained, expressed in parts by weight in hundred thousand, are as follows, the reference page being to the German edition:—

Series	..	..	..	I.	II.	III.
Page	..	..	..	162	168	171
Copper	..	..	..	25455	25450	25448
Water	..	..	..	35958	36067	36067
At degrees C.	..	..	..	250	360	370

Professor Richards also determines the amount of sulphuric acid left after electrolysis; it is the ghost of Stas demanding the famous *complete analyses* at the expense of precision. Richards uses a *volumetric* process for this purpose, involving two indicators, also pure sodium carbonate, hence demanding the exact value of the atomic weights of sodium and of carbon. Such complex processes will give concordant results in so skilful hands as those of Richards; but the unknown residual errors make the final result useless in chemistry of precision.

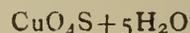
Now right here Prof. Richards loses himself in the labyrinth of Stas. Summing up the three ingredients determined, Richards finds a deficiency of *five in ten thousand* outstanding. In other words, 1 m.grm. of blue vitriol in every 2 grms. has been lost—a quantity entirely too large to be overlooked in chemistry of precision.

Not knowing that volumetric processes can claim no place in the determination of the precise value of atomic weights, Prof. Richards thinks his sulphuric acid determination right; he is properly certain of his copper determination; hence he concludes that the error can only have occurred in his determination of the water of crystallisation. He now pushes the heating of the blue vitriol to the dissociation of the sulphate. He reaches a dark red heat. He thus has secured that elasticity which Stas utilised in the precipitation of the silver chloride, and which Richards alone has properly condemned in his work on the atomic weight of barium.

However, Professor Richards is too good a chemist to hide for himself the very unsatisfactory outcome of this search for the missing substance. He admits the absence of the necessary *evidence*, but says: "There is no doubt of its great probability." This is one of the classical phrases of the school of Stas. It has absolutely no place in the chemistry of precision.

Professor Richards adds:—"Upon such a matter it is difficult to see how more definite results could have been obtained." He does not know that he had the most definite and admirably exact results when he started out on this chase after the lost water, not dreaming that it was the acid that had been lost by him. He thus throws away the only valuable determinations of his four years of work. But, also, this stupendous error is due to the school he follows.

To show this in the shortest manner possible, let us adopt the atomic weights of  $H=1$  and  $S=32$ , established by my limit method, and also put  $\text{Cu}=63.5$ ; the analysis thereafter will show how much the "deviation" of this atomic weight amounts to. Thus the formula—



for the atomic weights specified requires per hundred thousand parts of blue vitriol—

Copper	..	..	..	..	25451
Water	..	..	..	..	36072

It is plain that these calculated values are practically identical with those found by Professor Richards given in the preceding pages. The correction to be applied to the observed values to obtain the calculated values are—per hundred thousand parts of blue vitriol—as follows:—

Series	..	..	..	I.	II.	III.
Copper	..	..	..	..	-4	+1
Water at 360°	..	..	..	..	+5	+5

The agreement is remarkable; the error of the determinations is only *one milligram in twenty-five grms.* if we take 4 as the mean of the above numbers. Thereby these determinations of Richards stand in the front rank of atomic weight determinations. That he failed to see this and started upon the long chase for more water is exclu-

sively due to the dense fog that for a quarter of a century has been darkening this entire field of chemistry, so that at present, not only the old, but also the young, chemists seem to have lost the faculty of sight in the broad light of day, and refuse to look at truth.

Thus it is established by these two determinations of Richards—the only two accurate ones in his entire research, but which he himself, as faithful Stasian chemist, had corrected away from truth—enable us to assert that the deviation of the true and exact atomic weight of copper from 63.5 is certainly not over 0.002.

A series of determinations carried on in accordance with the conditions of my limit method will no doubt show that the atomic weight of copper is exactly 63.5 in the mathematical sense.

In conclusion, I beg leave to express the hope that the young chemists—at any rate, those in this country—will no longer take part in the blind worship of an authority that has covered the immortal work of Dumas and Berzelius with the rubbish of a spurious accuracy and an imaginary analysis, and hereafter rather assist in the determination of the true and exact values of the atomic weights of the chemical elements.

To the Editor of the Chemical News.

Your journal has contained very brief and misleading notices of my recent papers on atomic weights. I do not wonder at this; the subject being quite intricate, thanks to the indirect combinations made use of by Stas and his admirers.

I have therefore thought it desirable to take up a single case, and have selected that of copper, which Stas did not meddle with. The determinations of Richards (whose papers you have reprinted) are generally accepted as the best. I have carefully examined them, and offer you the result for the CHEMICAL NEWS in the paper enclosed.—G. H.

**Announcement.**—We are requested to mention that Mr. W. Brown, of 11, Dale Street, Liverpool, is now assisted by Mr. George Stevens, who until lately practised in Liverpool on his own account as an analytical chemist. Mr. Stevens is considered one of the most expert sugar chemists in Great Britain.

**The Use of Calcium Plumbate in the Analysis of Ashes.**—K. Wedemeyer (*Archiv der Pharmacie*).—The formation of calcium plumbate from calcium carbonate and lead oxide is not as expeditious as Kassner alleges. The experiments took a favourable course in as far as the combustion of the organic matter was very rapid.

**Valuation of Hides for Glue.**—F. Gantter.—The author takes an average portion of the sample in question (100 grms.), adds to it 1 litre of water in an evaporating basin, adds a few drops of soda-lye, and boils until the hide is entirely dissolved. The liquid is made up exactly to 2 litres in a suitable graduated vessel, and allowed to subside for ten hours. Of the clarified solution 20 c.c. (=1000 grms. of substance) are evaporated to dryness, dried at 105°, the residue is weighed, and its ash is determined. He thus finds the crude glue-ash. A second portion, of 10 c.c., is placed in a graduated flask holding 100 c.c., diluted with 30 c.c., neutralised with acetic acid, and solution of tannin is added as long as a precipitate is formed. The flask is then shaken up and filled to the mark. This solution, which contains the non-precipitable constituents "not glue" along with the slight excess of tannin, is filtered through a dry folded filter, a sufficient quantity of hide powder to precipitate the tannin, and the mixture is allowed to stand for ten hours. If after this time the solution gives no further tannin reaction, it is filtered, and the dry matter (free from ash) in 50 c.c. of it (=0.500 grm. of substance) is determined. If this is multiplied by 2, and deducted from the ascertained weight of crude lime (free from ash), the remainder is the quantity of pure lime.—*Zeitschr. f. Anal. Chem.*, xxxii., Part 4.

## CORRESPONDENCE.

## ARRANGEMENT OF CHEMICAL LECTURES.

To the Editor of the Chemical News.

SIR,—A recent paper by Professor Lothar Meyer in the *Berichte der Deutsch. Chem. Gesell.*, xxvi., 1230, has now been abstracted in the September number of the *Transactions of the Chemical Society*, p. 408. It treats of Prof. Meyer's system of arranging his lectures in accordance with the periodic arrangement of the elements, instead of adopting the traditional plan of arbitrarily dividing elements into ill-defined groups of metals and non-metals, a plan sanctioned by antiquity, but hardly defensible on any other ground.

I take this opportunity of strongly urging on those of your readers who are engaged in teaching chemistry to give this plan a trial. I have used it with great success since 1884, and have published two text-books of which this system forms the basis. Prof. Meyer is perfectly correct in his statement that this method of treatment saves a great deal of time; but other inducements towards its adoption might be readily suggested. It ensures the consideration (if desired), in its correct place, of each and every discovered compound; it renders the facts of chemistry, which by their number and apparent arbitrariness tend so frequently to dishearten students, easily remembered; and it teaches the use of that all-important guide in all chemical work, analogy.

Prof. Meyer differs, however, from the method I adopt in certain details, I consider it on the whole advisable to consider methane along with hydrogen chloride, water, and ammonia; and I do not think it desirable to treat of all the compounds of hydrogen with other elements before taking up the more simple halides. But such minor changes may well be left to individual taste.

It is, however, in my opinion, very important that the student should realise that chemistry is not a cut-and-dry store of facts, but is in active progress; and it appears to me proper to draw attention, where possible, to gaps in our knowledge. Students worth their salt invariably conceive a desire to complete such series of compounds, and often offer suggestions which, whether practicable or not, always lead to some profitable talk.—I am, &c.,

WILLIAM RAMSAY.

University College, London, W.C.  
September 30, 1893.

**Rapid Dialysis of Liquids.**—C. E. Linebarger.—The author's device is especially distinguished by its automatic supply of water. It consists of a funnel suspended by means of wire to one end of the beam of a balance; into the funnel is introduced the filter of parchment paper, receiving the liquid to be dialysed and previously well soaked in water.—*Zeitschrift für Analyt. Chemie*, xxxii., Part 3.

**Arrangement for Determining the Quantity of a Volatile Ingredient present in any Substance.**—O. Petterson (*Chemiker Zeitung*).—The apparatus consists of two vessels of equal size in juxtaposition, each of which is connected with one limb of a differential manometer. By means of cocks the vessels can be shut off from the manometer or connected with the air. In the manometer there is a displaceable thread of liquid. If into one vessel there is introduced a liquid containing a known quantity of a known volatile substance, and into the other one containing an unknown quantity of the same to be ascertained, and both vessels after being placed in communication with the manometer and then with the air are then exposed to a given equal temperature, the position of the liquid thread in the manometer shows in which vessel is the substance with the smaller proportion of volatile constituents.

## 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. cxvii., No. 12, September 18, 1893.

**Periodic Maxima of Spectra.**—M. Aymonnet.—This paper is drawn up in such a manner that it does not admit of useful abstraction, whilst it is not of sufficient importance to claim insertion in full.

*Revue Universelle des Mines et de la Metallurgie.*  
Vol. xxiii., No. 2.

**Volumetric Determination of Copper, Iron, Antimony, and Zinc-powder.**—The methods proposed are those of F. Jean and Weil, and they have been already noticed under the *Bulletin de la Soc. Chimique de Paris* and the *Zeitschrift für Analyt. Chemie*.

*Zeitschrift für Analytische Chemie.*  
Vol. xxxii., Part 3.

**Analysis of Tobacco and its Preparations.**—Dr. Viktor Vedrödi.—This paper is too voluminous for insertion in the CHEMICAL NEWS.

**On Sjögvist's Method for the Determination of Free Hydrochloric Acid in the Gastric Juice.**—Stan. Bondzynski.—The author concludes that the Sjögvist process is the most trustworthy method of determining the physiologically effective hydrochloric acid.

**Cadmium Mirror Obtained from Zinc-powder on the Examination of Urine for Mercury.**—According to E. Ludwig's method, mercury is precipitated from urine by means of zinc-powder. It is necessary to remark that commercial zinc-powder contains cadmium. Zinc-powder, according to Ludwig's method, was somewhat strongly heated in a covered porcelain crucible. When cold it was placed in a tube stoppered with asbestos, superstratified with copper, and the open end of the tube drawn out to a point and closed by fusion. On moderate heating, not exceeding the temperature necessary for the expulsion of the mercury, a metallic mirror was obtained which in appearance could scarcely be distinguished from a mercurial mirror. On stronger ignition, shining globules were observed at the beginning of the capillary part of the tube closely resembling drops of mercury, but on the touch they proved to be hard granules of metallic cadmium. The proportion of cadmium in the zinc-powder used was 1.63 per cent. It was not completely removed by strong ignition, as cadmium is volatilised very slowly. The same zinc-powder, after ignition for an hour in a current of hydrogen, still retained 1 per cent of cadmium. An examination of the metallic mirror obtained by the iodine test must never be omitted. Or copper-powder or copper-turnings may be used instead of zinc-powder.

**A New Method for the Detection of Cotton-oil in Lard and Olive-oil, and on an Approximate Estimation of Cotton-oil in Lard.**—F. Gantter.—Cotton-oil now occurs in commerce which does not show Becchi's reaction—blackening in contact with silver nitrate. The author therefore proceeds as follows:—He places in a test-glass 1 c.c. melted fat or oil (which must be clear as water), dissolves it in 10 c.c. of petroleum ether, allows a drop of concentrated sulphuric acid to fall into the solution, and shakes it up briskly at once. The colour phenomena thus produced are very distinct, and show characteristic differences in the behaviour of various fats. Pure lard if thus treated takes a colour from a pale straw to a faint reddish yellow. The solution remains at first

clear, but there are by degrees separated heavy drops of a strong reddish yellow colour, whilst the supernatant liquid remains of a scarcely yellowish colour, in most cases clear as water. Cotton-oil, on the contrary, takes at once a deep brown or black colour, and retains this colour on very prolonged standing. Mixtures of lard and cotton-oil take a more or less deep brown according to the proportion of the latter. The dark colour appears if only 1 per cent of cotton-oil is present in lard. Olive-oil on similar treatment behaves quite similarly to lard. Earth-nut oil behaves like cotton-oil. A pure lard must give with the sulphuric acid test merely a straw-yellow or at most a reddish yellow. The iodine number must not exceed 27.

**The Use of the Fluoresceine Reaction for the Detection of Saccharin in Beer.**—F. Gantter.—Already inserted.

**Separation of Barium, Strontium, and Calcium.**—R. Fresenius.—Already inserted.

**The Ascent of Saline Solutions in Filter-paper.**—E. Fischer and E. Schmidmer (*Liebig's Annalen*).—Already inserted.

**The Change in the Specific Gravity of Nitric Acid in Consequence of the Presence of Hyponitric Acid.**—G. Lunge and L. Marchlewski (*Zeit. f. Angew. Chem.*).—The authors show that great errors may be committed by depending solely on the specific gravity of acids. They give a table showing alteration in the specific gravity by the presence of  $N_2O_4$  in quantities varying from 0.25 to 12.75 per cent.

**A Volumenometer.**—A. v. Kalecsinsky.—This apparatus is quite similar to that described by A. Paalzow.

**Instruments for Determining High Temperatures in Flues, &c.**—F. Fischer (*Zeit. für Angew. Chemie*).—This paper requires the four accompanying cuts.

**Examination of the Behaviour of Fuel in Watery Vapour, Air, and Carbonic Acid.**—F. Fischer.—This paper requires the accompanying figure.

**Air Pyrometer.**—This instrument was described in its original form in *Zeit. Anal. Chemie*, xxix., 62, and has been remodelled by J. Wiborgh (*Stahl and Eisen*, xi., 913).

**A Modified Cornu Photometer for High Temperatures.**—Le Chatelier (*Comptes Rendus*, cxiv., 214 and 340).

**A Critique of Le Chatelier.**—H. Becquerel (*Comptes Rendus*, cxiv., 255 and 390).

**Le Chatelier's Thermo-element for the Measurement of High Temperatures.**—Emilio Damour.—Already inserted.

**Convenient and Uniform Division of Samples of Ores.**—H. L. Bridgman.—From the *Journal of Analytical and Applied Chemistry*.

**Instrument for Sampling Liquids.**—O. Steinba.—It consists of a tube open below, with a sheath open laterally, and enclosing the lower end elastically, in which the tube can slide up and down.

**Arrangement for Washing Precipitates.**—Matthew Forbes.—From the CHEMICAL NEWS.

## 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.

**Water Freezing in Pipes.**—Can any of your correspondents kindly tell me how I can make the water in hot water pipes non-freezing? We warm our works with hot water, low pressure. Last winter, one Sunday night, it froze and burst the pipes. I suppose it will do so this winter, unless we go on Sunday and fire the boiler.—A. P. JEVON.

## THE CHEMICAL NEWS.

VOL. LXXVII., No. 1768.

REMARKS ON  
THE CHEMISTRY OF BACTERIA.\*

By R. WARINGTON.

THE immense variety of substances produced in the vegetable kingdom has always been a source of astonishment to the chemist. The plant is, indeed, the finest chemical laboratory with which we are acquainted. While some kinds of chemical work are common to all plants, there is hardly a species which does not possess some special capacities—which does not produce some products different from its neighbours. When we survey the whole vegetable kingdom, the extent to which this specialisation is carried, and the immense variety of the products obtained become simply overwhelming. Chemists are still unacquainted with the larger part of the substances produced by plants. When we turn from the products of plant work to the materials employed our wonder still increases, for these materials are of the simplest kind—water, carbonic acid gas, oxygen, nitric acid, and a few inorganic salts—yet out of these the whole of the immense variety of vegetable products is constructed.

This being the case, we need hardly say that the methods of plant chemistry are of supreme interest, both to the chemist and to the vegetable physiologist. By the aid of what forces, through what course of reactions, are the simple materials moulded to their final issue? The higher plants are in some respects unfavourable subjects for the study of plant chemistry. Their different parts have different functions, and the changes in progress are obscured to the student by the fact that changes of a very different type are in progress at the same time, and in places very near to each other. What would not the physiologist give if he could isolate a single cell, and grow it by itself in solutions of known composition; when by studying the nature of the cell's new growth, and the variations taking place in the nourishing solution, he might hope to be able to grasp the facts of cell nutrition, and the nature of its waste products? Such an opportunity is actually afforded when we study the chemical changes brought about by bacteria.

In bacteria we have the vegetable cell in its simplest form: we have a mass of protoplasm and a cell-wall, but the cell is single or united with a few others, and, as far as we know, the life changes in all the cells of every species living under the same conditions are the same. Moreover, these organisms grow freely in suitable solutions, and the chemical changes produced in the materials held in these solutions can be readily ascertained. We have thus in a study of the chemistry of bacteria a splendid opportunity for enlarging our knowledge of plant chemistry, and, indeed, of becoming acquainted with the fundamental reactions on which synthetical organic chemistry depends.

The study of the chemical work performed by bacteria has occupied as yet but a few years, but the results have been most remarkable. The immensely numerous species of bacteria have been found to exhibit an almost equally great diversity of action. Different members of the class have been found to flourish under entirely opposite conditions, to feed on wholly different materials, to perform an immense variety of chemical work upon the media in which they live, and yet the chief product of plant life—

the formation of protoplasm and cell-wall—is probably in each case practically the same. The study of the chemistry of bacteria has thus greatly enlarged our conceptions of the chemical power of the vegetable cell.

As a contribution to the discussion to-day, I propose to call attention to the chemical actions displayed by three species of bacteria existing in the soil, and all of first-class importance in their relations to agriculture.

It is well known that all ordinary soils contain organisms possessing a vigorous power of oxidising—of bringing about a combination between the oxygen of the air and various organic and inorganic bodies. Thus dead vegetable and animal tissues in soil are, under favourable conditions of heat and moisture, resolved into carbonic acid, water, and nitric acid.

Particular experiments show that the nitrogen of albumin, gelatin, asparagine, urea, ammonia, ethylamine, and thiocyanates is converted by soil into nitric acid. Nor is the action confined to organic matter; for nitrites are oxidised to nitrates, iodides to hypiodites and iodates, and bromides to hypobromites and bromates.

The organisms producing nitric acid have been made the subject of study by many chemists, and after much labour and many disappointments they have been satisfactorily isolated.

We now know that the production of nitrates in the soil—a process of the greatest importance for the nutrition of agricultural crops—is accomplished by the action of two organisms, each of which performs a distinct stage in the work. By one organism ammonium carbonate is oxidised and the nitrogen converted into a nitrite. By the second organism nitrites are converted into nitrates. We have here an excellent example of the way in which certain special functions, certain narrowly limited lines of work, are exercised by individual species of bacteria. The nitrous organism can oxidise ammonia to nitrite, but it cannot change a nitrite into a nitrate. The nitric organism, on the other hand, oxidises nitrites readily, but it cannot oxidise ammonia. Both organisms are present in all fertile soils, but the formation of nitrites is not usually perceived, as they are at once converted into nitrates.

The organisms we have mentioned grow and exercise their functions in dilute solutions of appropriate composition, and it is therefore possible to study exactly the mode of their nutrition.

Like every other living organism, they develop and perform their functions only when certain inorganic salts supplying phosphates, sulphates, potassium, calcium, and magnesium are present. The continued omission of one of these has been proved in several cases to bring about a cessation both of growth and function. The general fact is familiar to physiologists, but it is singular that we have as yet no rational idea of the mode in which these various inorganic bodies assist in plant nutrition, with the exception of the fact that sulphur, and possibly in some cases phosphorus, are constituents of albuminoid bodies.

As to nitrogenous food, these organisms are amply furnished by the ammonia, the nitrite, or nitrate which is intentionally added to the solution; the addition of no other nitrogenous substance is necessary. Here, too, we are on familiar ground. Ammonia and nitrates are both well known as the most appropriate nitrogenous food for plants.

When we inquire, however, what is the source of carbon to the nitrifying organisms, we are confronted by a startling novelty. It is found to be quite unnecessary to supply these organisms with any carbonaceous food save carbonates, bicarbonates being preferred. The fact of the conversion of carbonates into organic cell substance has been conclusively proved in the case of the nitrous organism; it is at present assumed to be also true of the nitric organism, as this also requires the addition of no organic carbon to its nutritive solution.

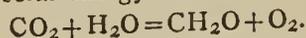
The fact that green plants exposed to sunlight are

\* A Paper read before the British Association (Conference of Sections B and D), Nottingham Meeting, 1893.

capable of forming organic substances from the carbonic acid and water of the atmosphere is well known to physiologists, but it is equally certain that this action does not occur in the dark. Yet here we have a colourless cell, destitute of chlorophyll, growing in the dark, which, nevertheless, is capable of decomposing carbonic acid, and producing from it carbonaceous cell-substance. From a purely chemical point of view this reaction may well appear at first sight incredible, as the decomposition of carbonic acid is an action requiring the consumption of much energy, which in the case of the green plant is supplied by the sun's rays, but in the case of the nitrifying organism is supplied in no such way.

This theoretical difficulty disappears, however, when we look at the whole reaction brought about by the nitrous organism. This organism attacks carbonic acid in its combination as ammonium carbonate, and the formation of an organic carbon compound proceeds at the same time as the oxidation of the ammonia; the result of the whole reaction being the liberation of heat, and not its consumption. A supply of external energy is thus not required.

Expressed in its simplest terms, the green plant manufactures carbohydrates from carbonic acid and water by a consumption of solar energy as follows:—



The nitrous bacterium oxidises ammonium carbonate, producing at the same time ammonium nitrite and a carbohydrate: this reaction we may express in its simplest form as follows:—



The equation, however, by no means fully expresses what actually occurs, as Winogradsky finds that 35 parts of nitrogen as ammonia are oxidised for one part of carbon assimilated; the whole reaction is thus strongly exothermic.

The nitric organism multiplies more slowly than the nitrous, and does not therefore afford so good a subject for quantitative experiments; its nutrition has not yet been fully studied.

The last organism I wish to speak of is the one of which Winogradsky has given a preliminary description during the present summer. It has been obtained from soil, and possesses the remarkable power of assimilating the free nitrogen of the atmosphere. To accomplish this assimilation it is simply necessary to grow it in a solution containing sugar (dextrose) and the necessary salts, no combined nitrogen being supplied. Under these circumstances a vigorous growth of the bacillus takes place, the sugar undergoes a butyric fermentation, and at the end of the operation it is found that the culture has acquired nitrogen, the amount being apparently about  $\frac{1}{300}$ th of the weight of the sugar fermented. By using as much as 7 grms. of sugar, an assimilation of 14 m.grms. of nitrogen has been obtained. Washed air, free from ammonia and nitrates, was used in these experiments.

That a vegetable organism should be able to acquire from the air the whole of the nitrogen which it needs is certainly very remarkable, and is an extraordinary fact both to the physiologist and chemist.

We have no clue as yet to the mode in which the nitrogen enters into combination; but it is evident that in this case, as in the nutrition of the nitrous organism, the difficult piece of chemical work forms but a small part of a much larger reaction that is at the same time in progress, and with which it is essentially connected.

It seems not improbable that these results of Winogradsky will explain some facts which have hitherto presented much difficulty. That a special organism, when in union with the roots of a leguminous plant, is capable of bringing about the assimilation of the free nitrogen of the air is now admitted by all; but it is denied by Schloesing and other accurate observers that the same organism when living in the soil has any such property.

May we not suppose that for the assimilation of nitrogen to occur the organism must be supplied with sugar or its equivalent, and that this supply of sugar to the organism only takes place when the organism gains access to the sap of one of the higher plants.

In conclusion, I think we shall all agree that, however imperfect is our knowledge of the chemistry of the three species of bacteria we have considered, the facts which have been established have at least enlarged our conception of the capabilities of a vegetable cell, and I trust that some light has also been thrown on the general method by which some of the extraordinary chemical results are attained.

### ON A NOTTINGHAM SANDSTONE CONTAINING BARIUM SULPHATE AS A CEMENTING MATERIAL.\*

By Professor FRANK CLOWES, D.Sc.

THE author draws attention to papers presented by him to former meetings of the British Association ("British Association Reports," 1885, p. 1038, and 1889, p. 594). These papers described sandstone extending over a large area at Bramcote and Stapleford, in the immediate neighbourhood of Nottingham, in which crystallised barium sulphate occurred in large quantity. Bramcote and Stapleford Hills and the Hemlock stone were wholly composed of such stone. The largest quantity found in the specimens analysed reached 50 per cent; complete analyses were given of specimens of sandstone from different parts of this district. The sulphate was in a beautifully micro-crystalline condition, and the crystals had been identified and separated both by Professor Lebour and by Mr. J. J. H. Teall. In some parts of the sandstone the barium sulphate uniformly permeated the mass. In other parts the sulphate occurred in streaks or network, the latter distribution leading to a curious mammillated weathering of the surface of the rock, owing to removal of the uncemented grains. Occasionally the cementing material occurred in nodular patches, as seen in sections of the sandstone; this led to the formation of the so-called "pebble sand-beds" at the top of one of these sandstone hills. The beds were the effect of weathering; the uncemented sand-grains became loose sand, and disseminated amongst the loose sand were the "pebbles," consisting of masses of sand-grains bound together by barium sulphate. The author has not been able to obtain from any source evidence of the occurrence of similar sandstone in any other part of this country; he is still without direct evidence whether the sulphate has been deposited as such, as in the colliery boxes of Durham, or is the result of chemical change occurring between calcium sulphate in solution coming into contact with barium carbonate already deposited in the sandstone.

### ON ERBIA.†

By GERHARD KRÜSS.

(Continued from p. 166).

ACCORDING to the points of view now established there were then united as—

*Erbia Material No. 5,*

*Series 9, fractions 2, 3, 4, and 5; and*

*Series 8, fractions 3, 4, and 5.*

These earths were again dissolved as chlorides, fractionated by precipitation with aniline, and yielded—

\* Read before the British Association (Section B), Nottingham Meeting, 1893.

† *Zeitschrift für Anorganische Chemie.*

Series 10.

Weaker bases ←— . —→ Stronger bases.  
 1 2 (very slight) 3 (heavy precip.) 4 (small residue)  
 172·4 172·9 162·7 —

The fractions 1 and 2 of this series were doubtless nearly pure ytterbia (Yb=172—173), and after the examination of the values found on determining the equivalents of fractions 2 and 3, the separation of erbia from ytterbia seemed to have been effected much more easily than in former series of decompositions, where the erbia-material was still of a complicated composition.

Fraction 4 of Series 10 was intentionally selected small in order, as far as possible, to keep back all erbia (which now especially contained all the earths of low equivalents, Ho=161, Tr=157, Yb=90) in the third fraction of Series 10. This fraction 3 with R=162·7 therefore forms—

Erbia Material No. 6.

From this point the erbia material was no longer fractionated by heating the nitrates or, as latterly, by simple precipitation with aniline, but it was alternately resolved into aniline precipitates and aniline solutions by the action of aniline hydrochlorate. In this manner the most feebly basic and the most strongly basic portions were separated, so that finally there was left a "mean" portion. This has proved to be the most effective method for working up earths supposed to be almost pure. As regards details, I refer to my earlier treatise on this subject (*Zeitschr. Anorg. Chemie*, iii., 108—115).

The erbia material No. 6 yielded on this fractionation—

Series 11.				
Feebler bases ←— . Precipitates.				
1	2	3	4	
167·9	167·9	169·6	167·8	
—→ Stronger bases. Solutions.				
Mean.	4	3	2	1
168·6	161·5	—	158·3	—

If we bear in mind that this erbia material was fraction 3 of Series 10, and if we compare the values which have been found for fractions 1 and 2 of Series 10 with those of the first and second precipitates of Series 11, we see that in Series 10 by a fortunate manœuvre the erbia has been at once abruptly separated from ytterbia. Further, the analysis of the four precipitates, as also of the middle Series 11 gave values approximately corresponding with the atomic weight of erbium. Here, therefore, exactly the same phenomenon was observed as that previously encountered by P. Cleve and others, *i.e.*, on isolating the reddish earth from a mixture of yttria earths, the atomic weight of R, calculated from the determinations of the equivalents of the earths, approached more and more to the number 166, or to a rather higher value, remaining almost constant on further fractionation. At the same time the solutions of these earths showed sharply the lines in the absorption spectrum marked Er $\alpha$ , Er $\beta$ . All these facts taken together might readily lead to the conjecture that in the reddish yttria earth (erbia) there is present an unitary oxide, and that this erbia earth contains a trivalent element of the atomic weight 166, 167, and 168. The following experiments caused this assumption to appear unwarranted.

In order to obtain the erbia earth containing probably R=166 to 168 from the "aniline solutions" of Series 11, there were united—

Solution 4+3+2 of Series 11.

From this mixture the more strongly basic portion was eliminated by two successive solutions; the residue of

the material was used as the "middle" of Series 11, and the neighbouring precipitates, 4 and 3 (Series 11), were added. Thus after the elimination of the stronger bases, this entire middle part of the erbium material of Series 11 was united in order to be subsequently submitted to purification by treatment with aniline hydrochlorate.

There were taken—

Weaker bases ←— .		—→ Stronger bases.	
"Aniline precipitate,"		"Aniline solution."	
I	Middle	I	
Series 12.	—	166·6	—

and this precipitate (No. 1, Series 12) to which, according to the entire course of the transaction, there corresponded a value of more than 166·6 (= middle of Series 12) is added to the precipitates 1 (167·9) and 2 (167·9), Series 11. These three fractions, with values between 167 and 168, formed—

Erbia Material No. 7.

This, when decomposed with aniline hydrochlorate, gave—

Weaker bases ←— .		—→ Stronger bases.	
Aniline precipitate.		Aniline solution.	
I	Middle	I	
Series 13.	167·4	167·0	—

The aniline solution 1 (Series 13) stands towards the side of stronger basicity, and must join to the middle of Series 12, for in obtaining the erbium material No. 7 only the aniline precipitate 1 of Series 12 was used.

There were therefore mixed:—Solution Series 13 and middle Series 12, and from this mixture the most feebly basic part was separated out by precipitation with aniline. For the R of this earth there was found the value 167·8; according to the entire system of the experiments, this was to be united with the precipitate and with the middle of Series 13. Thus was obtained—

Erbium Material No. 8.

This consisted, therefore, of the portions R=167·4, 167·0, 167·8. Since the feebler bases (ytterbia earth) had been well removed from the erbia material No. 5 by Series 10, and since in the erbia material No. 6 the stronger bases had been more and more separated by the solutions of Series 11, the true erbia earth had united in the erbia material No. 8 as a reddish oxide, with the Er spectrum lines and the values 167·4, 167·0, 167·8 for Er. In the operations carried out with erbium material No. 6 and 7, especial care had been taken to remove the more strongly basic parts from the erbia. After these portions finally consisted of oxides with R of 166·6, the erbia No. 8 now remaining must consist almost exclusively of an unitary earth if an Er<sub>2</sub>O<sub>3</sub> exists. Hence the attempt was made to furnish the proof of the homogeneity of material No. 8, in the first place by fractionation, in order then to undertake exact determinations of the atomic weight of erbium.

This erbia earth was now treated by partially dissolving the hydroxide in aniline hydrochlorate. Thus, by directly succeeding aniline solutions, there were obtained fractions 1 to 3, and the precipitate remaining from the third fraction was called fraction 4. The erbia was thus resolved into—

Stronger bases ←— .		—→ Weaker bases.	
I	2	3	5
Series 14.	164·0	165·8	168·7 170·3

The above experiments show that if erbia earth is still mixed with other erbia earths (ytterbia and yttria), in fractionating the earths we seem gradually to come nearer the isolation of an unitary earth, exactly as if there existed an erbium with an atomic weight between 165 and 168. When the weaker and stronger basic portions are

removed, the properties of the erbia earth are no longer affected by those of other earths, and it no longer appears so stable, and behaves with aniline hydrochlorate like a non-unitary oxide—like a mixture or a compound of oxides of different equivalents.

This subject will be more minutely explained below.

(To be continued.)

## A SIMPLE METHOD OF STERILISING WATER FOR DOMESTIC PURPOSES.

By FRANCIS WATT, S.F.I.C.,  
Analyst to the Government of the Leeward Islands.

SOME time ago it became necessary to devise a process for the removal of suspended finely-divided particles of clay from water, for a delicate technical process. Considerable difficulty was experienced in rendering the water quite bright; some of the finer particles of clay remaining suspended rendered the water opalescent, and such forms of filter as could be used failed to remove this opalescence. It occurred to me to experiment with various precipitates which could be produced in the water and carry down with them these troublesome particles. Finally, the formation of aluminium hydrate was decided upon, and this was accomplished by adding alum, or some other suitable aluminium salt, in small quantities to the water and precipitating with lime water. The precipitate was allowed to subside and the water drawn off. The most troublesome waters were found to be rendered quite bright by this treatment.

Subsequently, the problem of purifying considerable quantities of water for drinking purposes was presented to me, when it appeared reasonable to suppose that if the fine particles of clay were removed by the aluminium hydrate, other minute bodies, and amongst them any micro-organisms that happened to be present, would be largely removed also. But in this case the use of ferric hydrate suggested itself, on account of the readiness with which it parts with its oxygen to organic matter, it being thought that some additional purifying effect would be derived from this.

Experiments were undertaken to ascertain the effect upon the micro-organisms of precipitating ferric hydrate in the water in question. The water being a moderately hard one merely required the addition of a small quantity of a nearly saturated solution of ferric chloride for a precipitate to form; this was filtered through sterilised filter paper, and small quantities of the water introduced into nutrient solutions. In practically every case, no development of micro-organisms took place even when the solutions were kept for over a week. Similar tubes were treated with the water before the addition of the iron solution, and growth in every case followed in eighteen hours.

These experiments have been repeated at intervals over a period of two years, and always with the same results. Even when small quantities of water are drawn from the mass in which the ferric hydrate has subsided, without filtration, the supernatant water appears to be sterile.

It would appear, then, that we have here a simple process for rendering water for drinking and domestic purposes sterile with but little trouble or loss of time, and that this process will render water as completely sterile as boiling will. Boiling water for drinking purposes is always a troublesome operation; the quantity to be operated upon is usually greater than can be dealt with conveniently; a considerable time elapses before it is fit for use, and, when ready, the flat mawkish taste is objectionable; in fact the operation is rarely faithfully carried out, save in time of panic.

To carry out the process suggested in the case of a hard water, it suffices to add sufficient solution of ferric chloride (which should be as nearly neutral as possible) to produce a perceptible precipitate, the carbonates dis-

solved in the water being in many cases sufficient to effect this. In the case of a soft water—*i. e.*, one in which no precipitate is produced on the addition of ferric chloride, after the ferric chloride is added—a small quantity of lime-water, or of dilute solution of carbonate of soda, is thrown in, and this causes a precipitate to form. It is found that vigorous stirring promotes the granulation and subsidence of the precipitate.

The precipitate is allowed to subside, and the clear water is drawn off for use. It is often preferable to pass the water through some simple form of filter, such as a felt bag, or through clean sand placed in a shallow box, or in a flower-pot, in order to keep back any particles of the precipitate which may have been disturbed in the operation of drawing the water; but with large quantities of water this is seldom necessary.

It is found that 1 to 1½ fluid ounces of strong solution of perchloride of iron (British Pharmacopœia strength) are sufficient to purify 100 gallons of water. For domestic use it is advisable to dilute the solution considerably, say 10 times, and to use a teaspoonful of the diluted solution for each gallon of water.

If a sufficient quantity of water for one day's use be treated at night, a supply of pure water will then be ready for use every morning, with a very moderate expenditure of trouble or money.

With prevalence of diseases capable of being spread by the use of polluted drinking water, it would seem worth while to make a trial of a process which appears at once efficient, inexpensive, and equally applicable to large or small quantities of water.

A memorandum of this process was published in the *Official Gazette of the Leeward Islands*, xviii., No. 48, Nov. 27, 1890, since which time the process has been employed in public institutions and private houses in this Colony, with apparently good results. It would at least be interesting if others repeated these experiments with a view to their correction or confirmation.

## GELATINOUS SILVER CYANIDE.\*

By LEE K. FRANKEL.

IN the *Comptes Rendus* (lxiii, 998) Stas has described the occurrence of four different varieties of silver chloride, viz.—

- (a) The gelatinous.
- (b) The cheesy, flocculent.
- (c) The pulverulent.
- (d) The granular crystalline variety.

No methods are given for obtaining these varieties, nor could the author find any reference in the literature to any other salts of silver having the above properties. The following will therefore be of interest.

Recently the author instructed one of the students in the University laboratory to reduce silver chloride to metallic silver by fusion with potassium cyanide. As the work was purely experimental, no weighed quantities of the substances were taken, nor was any notice taken of the temperature at which the fusion took place. The cooled mass and porcelain crucible were placed in a beaker, covered with water, boiled for thirty minutes, and then put aside until the following day. On examining the contents of the beaker, instead of finding the liquid above the crucible clear, as had been expected, it was filled with a transparent gelatinous mass, somewhat resembling aluminum hydrate, but of greater consistency. A portion of this precipitate was removed from the solution, carefully washed with cold water until the filtrate reacted neither with silver nitrate nor with dilute hydrochloric acid, and then carefully dried.

\* Read before the Chemical Section of the Franklin Institute, June 20th, 1893.

A qualitative examination showed the following:—The substance is readily soluble in ammonium hydroxide, from which solution it is re-precipitated by nitric acid. It does not fuse on heating, but decomposes readily, leaving a residue of metallic silver. The presence of cyanogen was readily detected by the "prussian blue" reaction. No chlorine was found.

A quantitative estimation of the silver in the substance gave a result which was 5 per cent lower than the theoretical amount of silver in silver cyanide.

This is in all probability due to the impurities contained in the compound, which arise from the potassium cyanide used in its preparation.

The amount of substance used in the analysis was very small, since what appeared to be a rather large quantity of the original, moist, gelatinous compound, shrivelled to a very small bulk on drying.

Repeated attempts have since been made to procure more of the substance for analysis, but all efforts have so far been futile. The amounts of silver chloride and potassium cyanide used have been varied, and the fusion likewise has been made at different temperatures, but without success. It is the intention of the author to fuse silver cyanide with potassium cyanide, and thereby to obtain the desired result.

## ON CARBORUNDUM.

By E. G. ACHESON,  
President of the Carborundum Company.

THE author read a description of carborundum at the meeting of the Franklin Institute, June 21st, and recites his early experiments, as far back as the year 1890, for the production of crystallised carbon in the electric furnace, which led to the formation of the carbide of silicon, to which he gave the name carborundum, under the supposition that he had formed a combination of carbon and aluminium, the mixture in the furnace originally consisting of carbon and corundum, for which, later, a mixture of carbon, siliceous earth, and common salt was substituted. Salt was found to be beneficial in facilitating the fusion and in protecting the mass from oxidation. Experience has shown that a good proportion for the mixture is 20 parts of carbon, 25 parts of sand, and 10 parts of salt, by weight. A core of carbon is used to connect the poles, and is found unaltered after the operation, it being surrounded by the mixture, while it serves to conduct the current, and by its resistance to transform the electrical energy into heat energy. In later forms of the furnace four carbon electrodes are used at each end of a rectangular box, or trough, built of fire-brick, and 6 ft. long, 18 in. wide, and 12 in. deep. The core is tabular and extends nearly the length of the box. An alternating, and not a direct, current is used. To produce 150 lbs. per day of twenty-four hours requires an expenditure of 78 h.-p. for a like period, amounting to 12 h.-p. hours for each pound of carborundum produced. A furnace of the capacity and construction named requires from seven and a half to eight hours' time to complete the transformation of a portion of the charge into 50 lbs. of carborundum, and three charges are worked in twenty-four hours.

The carborundum as removed from the furnace is a mass of crystals incrusting the core in comparatively loose radial aggregates, which are crushed in water, and then digested with dilute sulphuric acid for seven days, to remove iron and other impurities. It is found that the crystals are not acted upon by any of the acids, not even hydrofluoric acid, which may be used to remove any excess of silica, nor are they affected by a current of hot oxygen by which any excess of carbon is removed, but they are slightly acted on by the caustic alkalis and the carbonates of the alkalis, and are decomposed by fusion with carbonate of soda. Analysis of a sample well

cleaned by the above indicated methods showed the composition to be:—Silicon, 69.10; carbon, 30.20; with small quantities of alumina, iron, and lime as impurities, the presence of which gives the colour, for if pure carbon and pure silicon are used the crystals are white.

The author gives the results of several analyses by Dr. Mulhaeuser, the company's chemist. He found the specific gravity of some of the green crystals to be 3.22. Prof. J. W. Richards found the specific gravity as 3.123 for the green crystals, and that the blue crystals have a lower specific gravity.

A crystallographic examination has been made by Prof. B. W. Frazier, of Lehigh University, who finds that the crystals are rhombohedral, their disc shape being due to the predominance of the basal pinacoid. He says:—"The observed forms consisted of numerous direct and inverse rhombohedra with the basal pinacoid, and in some crystals the prism of the first order. In some crystals the rhombohedral symmetry was evident, in others the direct and inverse rhombohedra of the same parameters were found on the same crystal, so as to impart to it an appearance of holohedral hexagonal symmetry. This holohedral habit was observed in bluish green and blue crystals, while in those yellowish green crystals which were examined in the goniometer the habit was rhombohedral.

The value for the length of the vertical axis, calculated from four good measurements, was found to be  $C = 1.2264$ . An examination in polarised light gave the interference figure of an uniaxial mineral, thus confirming the determination of hexagonal symmetry made by measurements with the goniometer. The author also directs attention to the fact that W. P. Schützenberger, in May, 1892, in a communication to the Academy of Sciences of France, described the manufacture of a new chemical compound of simple formula, the symbol being SiC. This was three months after Mr. Nikola Tesla had exhibited an electric lamp containing carborundum (silicide of carbon), the composition of which was not, however, known at that time.

The author states that the powder of carborundum has been successfully used in polishing diamonds, and he believes that in the form of a very fine powder it compares favourably in hardness and cutting qualities with diamond powder of equal fineness.—*Engineering and Mining Journal*.

## CONSPECTUS OF THE MOST USUAL METHODS FOR SEPARATING THE OXIDES OF THE CERIUM AND YTTRIUM GROUPS.

By Professor GERHARD KRÜSS.

### I. Drawn up Crystallising-out Double Salts.

A. POTASSIUM double sulphates used by Berzelius for separating the gadolinite and cerite earths. The substances precipitated are:—Scandium, terbium, cerium, lanthanum, didymium (Mosander, *Journ. Pr. Chemie*, 1843), dysprosium (Delafontaine), samarium (Bettendorf, *Liebig's Annalen*, 263), but also erbium (Nilson, *Ber. Deutsch. Chem. Ges.*, 1882; Krüss, *Liebig's Annalen*, 263).

a. As a modification, double sodium sulphates for the separation of philippium and terbium on the one hand (Delafontaine, (*Compt. Rend.*, 87), and of yttrium and cerium on the other (Erk, Naumann, *Jahrb.*, 1870).

B. Double ammonium nitrates for separating La and Di (according to Auer von Welsbach, *Monatshefte f. Chemie*, 1885); also for separating La and Di according to Schottländer (*Ber. Deutsch. Chem. Ges.*, 1892). Cerium is also precipitated, if present, as CeO<sub>2</sub>.

a. Double sodium nitrate was used by Auer von Welsbach for resolving didymium into praseodymium and neodymium.

C. Potassium double oxalate, used by Delafontaine and

Mosander for separating Er, Y, and Di, as the latter also forms an insoluble double salt (Krüss and Bröckemann, *Lieb. Ann.*, 265).

## II. Separation by Precipitation of Basic Salts.

This method is naturally available for all earths which separate out in the order of their basicity.

A. Fuming off the nitrates, Berlin's method, elaborated by Bahr and Bunsen. Thus Marignac obtained Tr; Nilson Yb and Sc (*Ber. Deutsch. Chem. Ges.*, 1879, 1880); Clève, pure Er (*Compt. Rend.*, 91; Clève, as also Damour and Deville, separate in this manner Ce, La, and Di. According to Krüss and Nilson (*Lieb. Ann.* 265; *Ber. Deutsch. Chem. Gesell.*, 1887, 1888) this method is inadequate.

Here must also be mentioned the method of Frerichs, who mixes the solution of La and Di with such a quantity of sulphuric acid that on evaporating down only a part of the nitrate is converted into sulphate. On gentle heating only the nitrates are converted into insoluble basic compounds (*Ber. Deutsch. Chem. Ges.*, 1874).

B. Mixture of the solution of nitrates with oxides of the same material, when basic nitrates are deposited on heating. Schottländer proceeds in the same manner for separating La and Di (*Ber. Deutsch. Chem. Ges.*, 1892). Hermann had previously used a similar method for separating La and Di, as had also Erk and Clève.

Here must be included the method of Frerichs, who separates La and Di by passing chlorine over the oxide. There are formed didymium chloride and lanthanum oxychloride, which in an aqueous solution are transformed into didymium oxide and lanthanum chloride.

C. Decomposition with excess of water. In this manner basic cerium salts are separated (Bunsen and Vogler, *Journ. Pr. Chem.*, 1858).

## III. Separation by Fractionated Precipitation of the Earths in various other Forms of Combination.

A. With ammonia, according to Mosander and Delafontaine. Clève (*Comp. Rend.*, 97) employed this method for purifying Sm, as also for separating La and Di (*Bull. Soc. Chim.*, 21). Crookes endeavoured, in like manner, to resolve yttria into five or eight constituents (*CHEMICAL NEWS*, liv.). Lecoq de Boisbaudran arrived partially in this manner at the discovery of his dysposium in Clève's holmium (*Comptes Rendus*, 1886); compare also Krüss (*Lieb. Ann.*, 265).

B. With aniline in alcoholic solution (Krüss, *Lieb. Ann.*, 265).

C. With oxalic acid, according to Mosander and Delafontaine. Bunsen and Zschiesche separate La and Di in this manner.

D. Formic acid, according to Delafontaine and Marignac, for obtaining terbia; also for obtaining philippium according to Delafontaine (*Comptes Rendus*, 87).

E. With excess of ammonium carbonate. According to Marignac and Krüss, Di alone is precipitated in this manner (*Lieb. Ann.*, 265).

## IV. Separation by Partial Solubility.

A. In water. La and Di as sulphates are placed in ice-water, and the solution heated to about 40°. Lanthanum sulphate separates out. Mosander, Holzmann, Krüss, and Bröckelmann (*Lieb. Ann.*, 265).

B. In alcohol. In the preparation of pure didymium nitrates (Bröckelmann, *Lieb. Ann.*, 265). For separating decipium and didymium sulphates (Delafontaine).

C. In acids. Mosander and Delafontaine employ for separation the partial solubility of the oxalates in nitric acid. Holzmann separates in this manner La and Di (*Liebig and Kopf. Jahrb.*, 1862); the former as oxalate is more readily soluble in nitric acid. Marignac proceeds similarly (*Ann. Chim. Physique*, [3], 27).

## V. Separation by Oxidation.

Cerium alone comes here into consideration.

A. In the dry way. On igniting the nitrates of the cerite earths CeO is oxidised to CeO<sub>2</sub>; La and Di remain unchanged, and dissolve in dilute nitric acid (Mosander). Debray (*Comptes Rendus*, 1883) melts the nitrates of the cerite earths with potash saltpetre, whereby CeO is oxidised. Bunsen (*Ann. Chem. Pharm.*, 105) ignites the oxides with magnesium oxide. ThCeO<sub>2</sub> thus formed is dissolved in concentrated nitric acid; the solution is poured into dilute nitric acid, when cerium dioxide is thrown down. This method, however, was abandoned by Bunsen himself. Auer von Welsbach converts CeO into CeO<sub>2</sub>, and allows it then to crystallise out as ammonium double nitrate (*Monatsh.*, 1884). Schöttlander proceeds in a similar manner (*Berichte*, 1882).

B. In the moist way. By introducing chlorine into the solution of earthy salts mixed with alkali in excess, Cer alone is precipitated as CeO<sub>2</sub>. The other hydroxides pass into solution as chlorides. Mosander (*Journ. Pr. Chem.*, xxx., 1843) arrived in this manner at the discovery of lanthanum. By passing Cl into the solution of the chlorides mixed with sodium acetate, or by boiling the solution of the neutral chlorides (mixed with sodium acetate) with sodium hypochlorite, CeO<sub>2</sub> is formed (Popp, *Ann. Chem. Pharm.*, 131). Winkler separates Ce, La, Di, by mixing the solution of chlorides with mercuric oxide, and adding permanganate until a red colour is obtained. Ce and Di are precipitated (*Journ. Pr. Chem.*, 1865). Stolba proceeds in like manner (*Bohm. Ges. d. Wissensch.*, 1878). According to Gibbs, the cerite earths are precipitated as nitrates with PbO<sub>2</sub>; according to Zschiesche, they are heated as sulphates with Pb<sub>3</sub>O<sub>4</sub> and nitric acid, when CaO<sub>2</sub> is thrown down.

If we look over the above large number of methods of separating we see that, in proportion to the number of earths to be separated, an unusual number of appliances is available. Nevertheless, we cannot yet separate even two of these earths quantitatively from each other without combination or a very frequent repetition of the single methods. This behaviour greatly impedes the examination of these bodies, especially when we have to decide whether an earth is single or compound. Perhaps the results of the following experiments will be of some use in this direction.

Finally, it is my agreeable duty to thank Dr. Karl Hofmann for his admirable assistance in carrying out the above experiments.—*Zeitschrift für Anorganische Chemie*.

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 165).

AMONG the lines enumerated various impurities may be represented, as I have indicated, at the passages in question. But this affects the here exclusively interesting fact relative to the profusion of rays in the region concerned in a vanishing degree only.

The appended numbers refer to the labels of the plates.

All the proofs were executed without a condenser, with a slit width of 0.040 mm. and of very sensitive plates (Zettnow's). The time of exposure varied, and is given specially for each spectrum.

*Cadmium*, No. 2039.—Exposure, six minutes. Twenty-two new lines, two of them beyond 1852; the most effective (4) in the immediate neighbourhood of the same length, mostly pale and moderately sharp.

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

**Antimony**, No. 2040.—Exposure, five minutes. Twenty-eight new lines, three of them beyond 185·2; the most effective (3) near wave-length 182·9. Except the three most refrangible all are distinctly shown, several very intense.

**Bismuth**, No. 2043.—Exposure, six minutes. Twenty new lines, three beyond 185·2; the most effective at  $\frac{1}{3}$  (Nos. 31 to 32). Most of them, especially the three most refrangible, pale and moderately distinct.

**Cobalt**, No. 2044.—Exposure, six minutes. Eighty-three new lines, twelve beyond 185·2; the most effective (9) near No. 31 towards No. 30. A large part of the lines intense and sharp; the remainder, including all beyond 185·2, very pale.

**Platinum**, No. 2045.—Exposure, six minutes. Eighty-one new lines, fourteen beyond 185·2; the most effective (15) nearly uniformly distributed over the spectrum, and surpassing in sharpness all the above-named spectra.

**Copper**, No. 2046.—Exposure, six minutes. Six new lines, one beyond 185·2; the most effective (2) near No. 30. All, even the palest, sharply drawn.

**Lead**, No. 2047.—Exposure, seven minutes. Six new lines, one beyond 185·2; the most effective close to the second component of No. 31; all the others very pale and indistinct.

**Iron**, No. 2048.—Exposure, ten minutes. Seventy-two new lines, four of them beyond 185·2; the most effective (4) between Nos. 31 and 32, but nearer to the former. The four most refrangible scarcely perceptible, the remainder more intense, but the less intense among them also imperfectly defined.

**Calcium**, No. 2049.—Exposure, seven minutes. Seven new lines, four of them beyond 185·2. Of the three most effective one coincides with the more strongly deflected component of No. 31, whilst the two others form the extremity of the entire spectrum. The less refracted of these two exceeds in efficiency all the lines situate beyond 185·2 of all the spectra here in question.

**Arsenic**, No. 2065.—Arrangement of experiment as in the foregoing proofs. Exposure, probably eight minutes. Twenty new lines, six beyond 185. Except these six all strong, but not clearly defined.

**Sodium**, No. 2103.—Exposure, twenty minutes. A single new line, scarcely deviating perceptibly from the second component of No. 31, moderately clear, but slightly intense.

**Silver**, No. 2107.—Exposure, three minutes. Twenty-eight new lines, six beyond 185·2. All the lines, except a single one situate near No. 31, and on its more refrangible side, very pale and chiefly indistinct.

**Gold**, on the same plate (No. 2107).—Exposure, seven minutes. Twelve new lines, three beyond 185·2. Of the five most efficient, three lie near No. 30, and a strong double line lies near No. 31, in both cases on the more refrangible side; all the others are very indistinct, even more so than with silver.

**Nickel**, No. 2108.—Exposure, seven and a half minutes. Twenty-six new lines, seven beyond 185·2; of the three most efficient two are near No. 30 and one a little less refrangible than No. 32. The entire region very pale, but well defined.

**Tin**, No. 2111.—Exposure, ten minutes. Eighteen new lines, three beyond 185·2. Except a single line, which lies in the middle between Nos. 31 and 32 and develops an enormous energy, all the lines seem melting away and are pale and very indistinct.

**Potassium**, No. 2112.—Exposure, five minutes. A single line, of faultless design and great intensity, coinciding exactly with the more refrangible component of No. 31.

**Tungsten**, No. 2113.—Exposure, ten minutes. Seventy-five new lines, twenty-one beyond 185·2; all nearly uniformly distributed, but forming distinct groups with single well-marked lines. The intensity of this band, so rich in lines, decreases uniformly towards its more refrangible end. The design of the lines is uniformly clear.

**Silicon**, No. 2114.—Exposure, ten minutes. Eleven

new lines, five beyond 185·2; one only intense and sharp, coinciding exactly with the more refrangible component of No. 31.

**Chromium**, No. 2132.—Exposure, seven minutes. Eleven new lines; only traces beyond 185·2, one only well-marked and coinciding with the more refrangible component of No. 31. All the rest very pale, and most of them perceptible only with difficulty.

**Thallium**, No. 2133.—Exposure, eight minutes. Eight new lines, three beyond 185·2; the four most efficient form a striking group between Nos. 31 and 32, the components of which decrease in intensity and mutual distance with the wave-length. Here again a line coincides with the repeatedly mentioned component of No. 31; but it is very pale, scarcely more than a trace. The design of the entire proof is very clear, even in the more refrangible lines.

**Molybdenum**, No. 2136.—Exposure, eight minutes. Forty new lines, four beyond 185·2; the six most efficient are between Nos. 30 and 31, all very pale, the most refrangible mere traces, design of all being clear.

**Mercury**, No. 2139.—Exposure, seven minutes. Twenty-six new lines, nine beyond 185·2; the most efficient of all is close before No. 31; two other lines, likewise very energetic, are close to Nos. 30 and 32. The lines beyond 185·2 are associated as a group of lines, rapidly increasing in intensity, and gradually decreases with the growth of their natural distance. The sharpness of the lines is moderate.

**Magnesium**, No. 2143.—Exposure, seven minutes (width and slit exceptionally only 0·030 m.m.). Three new lines are only distinct, coinciding with the more refrangible component of No. 31. Nothing visible beyond 185·2.

**Zinc**, No. 2144.—Exposure, thirty-two minutes. Seventeen new lines, one beyond 185·2. One of the two most efficient lines again coincides with the more refrangible component of No. 31; the other, more strongly deflected, lies closely to the same component. The entire region appeared very pale.

(To be continued.)

ON THE  
ACTION OF IODINE ON SOME  
PHENOLS AND ALLIED COMPOUNDS IN  
PRESENCE OF FREE ALKALI, AND  
A NEW CLASS OF DERIVATIVES  
RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 167).

ARISTOL.

THE article of modern materia medica known as aristol is taken by some to be a di-iodo-dithymol, by others a dithymol di-iodide, the latter being that now generally received. Aristol formed the subject of an abstracted note (*Pharm. Journ.*, May 2, 1891), in which free iodine was mentioned as an impurity. Pure aristol, according to Herr Reuter (*Apoth. Zeit.*, Jan. 28, p. 61), dissolves in ether with a yellow (not a brown) colour. He states that aristol of recent manufacture is probably less contaminated with free iodine than the earlier specimens.

Apart, therefore, from the details of its constitution, it is in all cases expected to be a thymol derivative. I propose to show in the following that this is not always the case, and to infer that it frequently is not so:—

A sample of aristol was procured through ordinary wholesale channels. It occurred as a pinkish, yellow-brown, light, pulverulent substance, with thymol-like odour. When heated in air oven at 100° C. for some time, it lost the greater part of its colour; and when

afterwards heated further, it melted to a brown sticky mass at about 156° C.

A quantity was dissolved in ether, filtered from extraneous matters, recovered, and then air-dried at ordinary temperature for two days. The total iodine was then estimated.

Quantity taken = 0.2128 gm.  
Silver iodide found = 0.1621 ,, = 41.16 p.c. iodine.

When deposited from ethereal solution it was found to hold water very tenaciously on account of its glutinous character. It was therefore further dried for ten days, and the iodine again estimated.

Quantity taken = 0.2527 gm.  
Silver iodide found = 0.1980 ,, = 42.33 p.c. iodine.

A quantity of the ether-purified aristol was heated in sealed tube with water and copper at about 130° C. for twelve hours. The substance, which on cooling had caked on the sides of the tube and acquired a much lighter colour, was rinsed out. It was collected, powdered moist, and rubbed down with water, then treated with weak solution of potash in order to dissolve out any "thymol" or true substituted "iodo-thymols" which might have existed in the original or been formed as the result of the treatment, and also any traces of free iodine, and finally it was slightly washed with alcohol. It was then dried, dissolved in ether, filtered, recovered, powdered, and treated with absolute alcohol (cold) as long as anything dissolved out; the alcoholic solution was then evaporated down, finally under the air-pump, as it began to show signs of free iodine at the dry edges. Colour, yellowish, and of somewhat sticky character.

Total iodine of the alcohol-soluble portion:—

Quantity taken = 0.1177 gm.  
Silver iodide found = 0.0897 ,, = 41.17 p.c. iodine.

Combustion of same:—

Quantity taken = 0.0780 gm.  
Water found = 0.0356 ,, = 5.07 p.c. hydrogen.  
Carbon dioxide found = 0.1454 ,, = 50.83 ,, carbon.  
By difference .. .. = 2.93 ,, oxygen.

Distinct ash.

The remaining portion insoluble in alcohol was dissolved in ether, recovered, powdered, and dried. It was of greyish white colour and pulverulent, melting with decomposition.

Total iodine of the alcohol-insoluble portion:—

Quantity taken = 0.1530 gm.  
Silver iodide found = 0.1192 ,, = 42.09 p.c. iodine.

Combustion of same:—

Quantity taken = 0.0886 gm.  
Water found = 0.0428 ,, = 5.37 p.c. hydrogen.  
Carbon dioxide found = 0.1685 ,, = 51.86 ,, carbon.  
Distinct ash, containing both copper and iron.

A quantity of the ether-purified aristol was treated with boiling alcohol as long as anything dissolved out, the alcoholic solutions being filtered off. As the united alcoholic solutions cooled, a whitish substance separated out, the solution retaining its yellowish red colour. This precipitate was filtered off, but when dried the quantity was so little that it was not further examined.

The alcoholic solution was evaporated down, and the residue, which was of a bright yellow colour, powdered and dried.

Total iodine of the alcohol-soluble portion:—

Quantity taken = 0.1930 gm.  
Silver iodide found = 0.1621 ,, = 45.38 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1125 gm.  
Water found = 0.0494 ,, = 4.87 p.c. hydrogen.  
Carbon dioxide found = 0.2006 ,, = 48.62 ,, carbon.

A quantity of the same alcohol-soluble portion was heated in sealed tube with copper and water at about 140° C. The product, after having been taken out and dried, was dissolved out by means of ether, recovered, and dried. Colour, greyish white, and of pulverulent character.

Total iodine of this product:—

Quantity taken = 0.1551 gm.  
Silver iodide found = 0.1169 ,, = 40.72 p.c. iodine.

The quantity of "extraneous" iodine in the original was therefore 4.66 per cent. Calculating the carbon and hydrogen in the real substance on the strength of this, we obtain the percentages—Carbon 50.99, hydrogen 5.11. The composition of the real substance was therefore:—

Carbon .. .. .	= 50.99
Hydrogen .. .. .	= 5.11
Iodine . . . . .	= 40.72
Oxygen .. .. .	= 3.18

Those figures agree with those found in the analyses of the alcohol-soluble portion obtained from the total aristol heated in sealed tube, and prove that the compounds then examined were not decomposition products.

The remaining portion of the aristol insoluble in boiling alcohol was dissolved in ether, recovered, powdered, and dried. Colour of a dirty yellowish white.

Total iodine of the alcohol-insoluble portion:—

Quantity taken = 0.1039 gm.  
Silver iodide found = 0.0806 ,, = 41.91 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1140 gm.  
Water found = 0.0518 ,, = 5.13 p.c. hydrogen.  
Carbon dioxide found = 0.2166 ,, = 51.81 ,, carbon.  
Ash .. .. . = 0.80 ,,

Another sample was procured at a later period, and after purifying by solution in ether and filtering, the recovered substance was air-dried for ten days and the total iodine estimated.

Quantity taken = 0.2000 gm.  
Silver iodide found = 0.1674 ,, = 45.20 p.c. iodine.

A combustion was also made of the same.

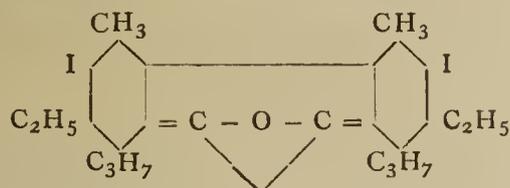
Quantity taken = 0.1389 gm.  
Water found = 0.0623 ,, = 4.98 p.c. hydrogen.  
Carbon dioxide found = 0.2459 ,, = 48.34 ,, carbon.

The physical properties and appearance of this sample were the same as those of the sample before examined. Those results show how variable the total iodine percentage of commercial samples is. This becomes the more important when we consider that the large differences depend on a portion of the iodine, which exists in a state relatively free, and therefore in a very active state relative to the animal economy.

It is quite apparent from the above analyses that those specimens of aristol were not prepared by the action of iodine on thymol in aqueous alkaline solution, and probably were not prepared from thymol in any form.

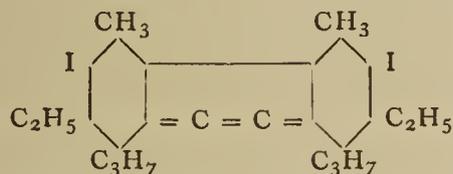
The alcohol-soluble portion may be represented by the formula  $C_{26}H_{30}I_2O$ , and the alcohol-insoluble portion by  $C_{26}H_{30}I_2$ , or constitutionally thus:—(see next column).

In a paper read at the Pharmaceutical Meeting of the Philadelphia College of Pharmacy, March 17, 1891, by George M. Beringer, Ph.G., and reprinted in the *Pharm. Journ.* of June 13, 1891, p. 1135, entitled "What is Aristol, and How is it Manufactured?" the author gives the results of an examination of a sample supplied by the Farben Fabriken Company, of Elberfeld. The physical characters of the substance there enumerated agree generally with those observed in the sample whose analyses I have submitted. The total iodine percentage reported by him (Carius's method), namely, 41.87, agrees with that given by me.



Theoretical .. .. .

{	50.98 = C = 52.35
	4.90 = H = 5.02
	41.50 = I = 42.63
	2.62 = O = 00.00



"Goldman states that aristol is di-iodo-dithymol,  $C_{20}H_{24}I_2O_2$ , containing 45.8 per cent of iodine. Accepting his formula, there should be by calculation 46.15 per cent of iodine. But the manufacturers drying the product at a low temperature to prevent decomposition, there must be some water retained, and the loss on heating on the water-bath, determined above as about 6.4 per cent, must be due mainly to water. Allowing two equivalents of water to be in combination, there would be present 6.14 per cent of water and 41.96 per cent of iodine, figures that closely agree with those results obtained by me. . . . From these experiments we are compelled to accept the statement that aristol is a biniodide of thymol, in which the hydrogen of the hydroxyl groups is replaced by iodine, and is represented by the formula  $C_{20}H_{24}I_2O_2 \cdot 2H_2O$ ."

The author repeated the reduction experiments of Messinger and Pickersgill, and obtained a product which corresponded fairly well with the properties assigned to dithymol, and possessed a peculiar odour of thymol almost phenol-like. (The method of reduction referred to—*Berichte*, xxiii., p. 2761—consisted in subjecting an ethereal solution to the action of an alcoholic solution of potash and zinc-dust at an elevated temperature).

The assumption as to the existence of 6.14 per cent of water, given as an explanation of the loss of weight on heating, is in all likelihood entirely erroneous; at all events, the assumption as to the existence of two molecules of water in the compound is. I have little doubt but that what was lost on heating was principally iodine. It is extremely likely that the sample was of the same ultimate composition as the one whose full analyses I have given, and that the reduction product was not dithymol.

(To be continued).

## NOTICES OF BOOKS.

*A Standard Dictionary of the English Language.* New York: Funk and Wagnall's Company.

THE matter before us is not the complete work, nor yet a volume or part, but a number of sample pages calculated to show the characteristic features of this great publication. Our opinion, founded on these specimens, is most favourable. It is, indeed, a bold undertaking to compress into a single volume such an extent and variety of knowledge on English words, their uses and their abuses. We naturally turn first to those departments in which our ordinary dictionaries have been the poorest—the terminology of the various sciences and of the industrial arts.

A very useful and gratifying feature is the exact definition of colours. A table will appear "containing the analysis of several hundred shades and tints now before

the public in various forms." This is an improvement the more needful since, in addition to the correct names used by physicists, chemists, colour-makers, biologists, and dyers, we are often perplexed by the terms invented by drapers and modistes.

The article "element" is most satisfactory, as all the different acceptations—chiefly scientific—in which the word can be used are clearly explained.

The table of chemical elements must meet with the approval of every competent judge. It is arranged on the periodic system, and gives in parallel columns the name of each element, its derivation, symbol, atomic weight, specific gravity, melting-point, valence, date of discovery, discoverer, and sources.

The illustrated articles on "bacteria," on "cells," and on bone are certainly all that can be reasonably expected where space is necessarily limited. From the passages mentioned we may conclude that scientific terms generally will be most ably dealt with.

But in other respects the "Standard" must command approval. We may particularly note the instances of "faulty pronunciation and diction" selected from different parts of the work. The Cockneyism of dropping the letter *r* or inserting it where it has no business, does not escape due censure. The use of "quite" as a synonym for "very," or as "awful" as a general emphasizing appendage is, we fear, increasingly common on both sides of the Atlantic. We are rather surprised to find "nasty" as a synonym for "disagreeable" objected to by the editor of that department.

In giving the meanings of any word, the "Standard" places *first* the acceptation which it generally bears at the present day. Then follow more meanings, and lastly such as are obsolescent or obsolete. This is certainly not the logical order, but it is the most practical. The quotations used to verify the meanings of words bear not merely the name of the author, but the volume, page, and edition whence they are taken. This is a decided improvement on the plan which has hitherto been generally followed.

Synonyms, autonyms, and the correct use of prepositions, so far as we can judge from the specimens before us, have been judiciously dealt with.

There is a singular impartiality shown in the selection and treatment of the subjects. Homœopathy, phrenology, the selective system of medicine, and socialism are assigned to special editors. We have every confidence that the work will tend to arrest a process which is already felt—the fractionation of the English language into a number of discordant dialects. If it can do anything to heal the cancer of slang so much the better.

*Alembic Club Reprints. No. 3. Experiments on Air.* (Papers published in the *Philosophical Transactions*). By The Hon. HENRY CAVENDISH, F.R.S. (1784—1785). Edinburgh: W. F. Clay. London: Simpkin, Marshall, Hamilton, Kent, and Co., Limited. 1893.

THE first of these two papers, as we learn from the preface, contains Cavendish's account of his investigations on the composition of water. All chemists are probably aware that prior to the year 1780 water ranked as an element. During the next decade it was proved to be an oxide of hydrogen. But both the exact date and the authorship of this capital discovery have been warmly contested.

In the "Elements of Chemistry" (Edition VII.), by Turner, edited by Liebig and Gregory, the composition of water is said to have been discovered by Cavendish, no date being given. In the English version of Gmelin's great work the discovery is said to have been made by Cavendish and Watt, in 1781. In the "Dictionary of Science, Literature, and Art," by Brande and Cox, we find the date of the discovery given as 1786 and 1787, and

its authorship ascribed to "Watt and Cavendish." The actual date of the paper read by Cavendish before the Royal Society is here given as 1784. We thus approach the once famous "Water Controversy," *i.e.*, the question whether Cavendish or Watt was the original and true discoverer of the nature of water? It is certain that these two savans were not working in concert, as the language of some of the text-books might lead the reader to suppose. Watt was certainly, as we see from p. 25 of the work before us, engaged with subjects bearing upon the composition of water. But no one who has formed an accurate idea of the ways of Cavendish can for a moment suspect him of seeking to appropriate any credit due to another. He took little pains to establish his own claims or to take date. Some of his researches have only been published late in the present century, and of others no record has been left, so that their existence is merely a matter of inference.

Two "interpolations" were made in the paper by Sir Charles Blagdon, Cavendish's secretary (p. 20 and p. 25), and Cavendish himself made an addition after the paper had been read, but before it had been printed (p. 35).

The phlogistian nomenclature used by Cavendish has been retained of necessity.

This little book will be very useful to all who are studying the history of præ Lavoisian chemistry.

*A Course of Practical Chemistry and Qualitative Chemical Analysis.* By the late W. G. VALENTIN, F.C.S. Edited and Revised by W. R. HODGKINSON, Ph.D., F.R.S.E., F.C.S., F.G.S., &c., Jodrell Scholar and formerly Senior Demonstrator and Lecturer in the Normal School of Science and Royal School of Mines; Professor of Chemistry and Physics in the Royal Military Academy and Artillery College, Woolwich. Eighth Edition. London: J. and A. Churchill. 1893.

THIS work is doubtless well known to many of our readers in its original form; but it now appears before us in a modified, and, in our opinion, a much improved state. It now brings forward the spectroscopic characteristics of the elements much more prominently than we find in ordinary analytical manuals.

A most important section is Appendix I., giving the reactions of the rare elements and directions for their separation into groups. This section will be the more welcome to the earnest student as in too many text-books the rare elements are either ignored altogether or at most considered in a very perfunctory manner.

Appendix II. contains a judicious selection of quantitative exercises.

Appendix III. treats of the non-metallic elements. Under Carbon we find the interesting remark, "There is just a doubt whether diamond is carbon only."

In Appendix IV. we find given the reactions of morphine, narcotine, quinine, cinchonine, strychnine, and brucine, with the divisions of the alkaloids into groups.

In looking over the list of reagents we find mention of methylated spirit. It is doubtful whether the passage was not written before the late mischievous tampering with this useful solvent. It can, of course, be obtained, theoretically speaking, in its old form, but no inconsiderable length of red tape has to be uncoiled, and the laboratory of the applicant is exposed to visits from the exciseman.

A peculiarity of this work is that in it formulæ are much more frequently used than in most analytical manuals. At the end of most of the sections and paragraphs we encounter a series of questions, in some cases as many as twenty-five.

The book ought, we think, to form one of the few elementary treatises to be recommended for a student's book-shelves.

*A B C Five-figure Logarithms for General Use.* By C. J. WOODWARD, B.Sc. London: E. and F. N. Spon. Birmingham: Cornish Bros. 1893.

SOME years ago the author published his "A B C Five-figure Logarithms," containing mantissæ of numbers only. The work was found useful, and met consequently with a favourable reception; but immediately after its appearance it was suggested that to many persons who have numerous calculations to make it would be a convenience to have logarithms of arc functions arranged on a similar principle. This task has been accordingly undertaken, and is now submitted to the public. There are subjoined examples referring to plane and spherical trigonometry, navigation, nautical astronomy, and crystallography.

We have no doubt that this handy volume will prove a boon to the increasing number of persons who have to make incessant use of calculations.

## CORRESPONDENCE.

### PREPARATION OF HYDROGEN.

*To the Editor of the Chemical News.*

SIR,—I have recently observed that, by the addition of a few drops of a solution of cobalt nitrate to the acid and zinc in a hydrogen apparatus, the rate of evolution of hydrogen is enormously accelerated, especially at the beginning of the reaction. The action is the same with either hydrochloric or sulphuric acid, and a couple of drops of solution of cobalt nitrate will suffice for a large quantity of acid.

This action does not seem to have been noticed before; it should be useful in the rapid preparation of hydrogen in the laboratory.

Most of the cobalt nitrate, if not all, is quite unaltered; there appears to be a very thin film of cobalt deposited on the zinc, which probably acts with the zinc as a voltaic couple, but the amount of cobalt deposited appears to be too small to weigh.

A solution of a nickel salt exerts a similar action.—I am, &c.,

JOHN BALL.

Royal College of Science,  
South Kensington, Oct. 6, 1893.

### ARRANGEMENT OF CHEMICAL LECTURES.

*To the Editor of the Chemical News.*

SIR,—There is no doubt that lectures on chemistry, in which the elements are treated of in the groups of the periodic system, so as to exhibit the characters connecting the members of a group and the points of difference and connection between one group and another, is an excellent plan, especially with students not exactly beginners.

It was tried with classes of science teachers attending the summer courses at South Kensington as early, I think, as 1879, and was continued in following years with undoubted success.

Even with students quite fresh to the subject I find it best to begin this systematic treatment of the elements after one or two preliminary lectures on the "ways" of chemical action and a very short historical outline.

The results with students who have received a proper mathematical training is very striking compared to when the "metals and non-metals" are treated of as disconnected things.—I am, &c.,

W. R. HODGKINSON.

Artillery College, Woolwich,  
Oct. 9. 1893.

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. cxvii., No. 13, September 25, 1893.

**Spectroscopic Observations made at the Observatory of Mont Blanc, Sept. 14 and 15, 1893.**—J. Janssen.—The chief object of the observations was the question of the presence of oxygen in the solar atmospheres. The instrument used—a Rowland's grating spectroscope—showed all the known details of group B. It is found that the double lines, the totality of which constitutes the group B, decrease progressively in intensity as their wave-length decreases. At the level of the sea the maps of B show, in addition to the head ray, thirteen or fourteen double lines. At Chamounix, at 1050 metres, the thirteenth is less easy to distinguish. At the Grand-Mulets (3050 metres), we can recognise only from the tenth to the twelfth, and on the summit of Mont Blanc the author could not go beyond the eighth. If we compare these results with tubes full of oxygen, we may infer the total disappearance of group B at the limits of the atmosphere.

**Action of the Electric Arc upon Diamonds, Amorphous Boron, and Crystalline Silicon.**—Henri Moissan.—As soon as the temperature is sufficiently high, the diamond sprouts without melting, and is covered with black masses entirely formed of graphite. After the experiment the graphite has the form of hexagonal laminæ, easily converted into graphitic oxide by treatment with a mixture of potassium chlorate and nitric acid. The stable form of carbon is graphite. If pure amorphous boron is placed in the electric arc, the boron becomes red and is surrounded with an extensive green halo, and then disappears without any phenomena of fusion. After the experiment we find at the extremity of the electrode black masses of a melted appearance presenting some crystalline points formed of a carbon boride. If crystalline silicon is placed between the two electrodes, it enters into fusion and then into true ebullition. When the electrodes are cold we find at their extremity, among the graphite which has been formed, pale green crystals of carbon silicide. Hence it is seen that boron and silicon readily combine with carbon at the temperature of the arc.

**Preparation and Properties of Crystalline Carbon Silicide.**—Henri Moissan.—This compound may be obtained either by direct combination at a temperature between 1200° and 1400° or by crystallisation in melted iron, or on reducing silica by carbon, or by allowing the vapours of the two elements to come in contact. Crystalline carbon silicide is a remarkably stable compound; it is colourless and reacts strongly upon polarised light. Its specific gravity is 3.12. It is hard enough to scratch ruby. It is not affected by oxygen or sulphur at 1000°. It is attacked by a current of chlorine at 1200°; potassium nitrate and chlorate in a melted state have no effect. It is the same with boiling sulphuric acid, hydrochloric acid, and nitric acid, aqua regia, and the mixture of monohydrated nitric acid and hydrofluoric acid. Caustic potassa in fusion disaggregates this compound, and ultimately dissolves it if heated to dull redness for an hour, yielding potassium carbonate and silicate. It yields on analysis 69.70 per cent silicon and 30 per cent carbon, corresponding to the formula SiO.

**A Glucoside of the Iris.**—F. Tiemann and G. de Laire.—The glucoside  $C_{27}H_{26}O_{13}$ , obtained from the roots of the iris, crystallises in fine white needles, which the authors name iridine. This substance, if heated

under pressure in sulphuric acid diluted with dilute alcohol, is split up into glucose and a crystalline body, which the authors name irigenine. This substance crystallises from absolute alcohol in yellowish white rhombohedra, melting at 186°. Iridine forms alcoholic ethers, and gives rise to two series of acid ethers. If submitted to the action of alkaline hydrates it takes up three molecules of water, and is then separated into three substances—formic acid, an acid phenol which the authors name iridic acid, and a phenol which they call iretol. Iridic acid has the composition  $C_{10}H_{12}O_5$ , whilst iretol is  $C_7H_8O_4$ .

*Zeitschrift für Analytische Chemie.*  
Vol. xxxii., Part 3.

**A Support for the Nitrometer.**—Foehr (*Chemiker Zeitung*).—This instrument cannot be intelligibly described without the accompanying illustration.

**A Modification of the Refrigerator with a Bulb-tube.**—Greiner and Friedrichs (*Zeit. für Angew. Chemie*).—The modification consists in substituting a Liebig-Mohr glass jacket for the bulb-tube, so that the apparatus approaches very closely to an arrangement recently patented by another inventor.

**Lamps for Sodium Light.**—H. E. J. G. du Bois (*Zeitschrift für Instrumentenkunde*).—The author uses a Linnemann burner, in the flame of which he introduces a soda rod. The rods are preferably 0.4 c.m. in diameter and 12 to 15 c.m. in length. They are made of sodium bicarbonate, sodium bromide, and tragacanth.

**Argand Lamp for the Alternate Production of White and Monochromatic Light.**—E. Pringsheim (*Wiedemann's Annalen*).—A T-tube is inserted in the flexible tube, connecting the gas pipe to the lamp and also communicating with a pulveriser containing solution of common salt. When the pulveriser is not in action the lamp gives a white light.

**Attackability of Platinum and its Iridium Alloys by Sulphuric Acid.**—Heraeus (*Zeit. Angew. Chemie*).—Already inserted.

**Durability of Standard Solutions of Permanganate.**—Bruno Grützner.—The author's experiments prove that a solution of 1:1000 underwent no change on exposure to diffused day-light for a year, and in one year and a half only to the extent of 2.61 per cent. In a blackened glass the loss in one year and a half was only 0.94 per cent. The results with a 0.3 per cent solution were still more favourable.

**Preservation of Sodium.**—W. Vaubel (*Zeitschrift für Angewandte Chemie*) and Merry (*CHEMICAL NEWS*).

**De-arsenising Chamber Acid.**—Le Roy W. McCay (*Chemiker Zeitung*).—The author proposes to treat the acid with sulphuretted hydrogen at 100° and under pressure.

**Test for Cerium Oxide.**—P. C. Plugge.—*Archiv. der Pharmacie*.

**Detection of Free Salicylic Acid in Salicylic Aldehyd and Salicylic Methyl Ether.**—A. Schneegans and J. E. Gerock (*Journ. de Pharmacie d'Alsace Lorraine*).—The authors have observed that the violet colour produced by solutions of salicylic aldehyd and salicylic methyl ether with ferric salts disappears on the addition of ethyl, chloroform, amylic alcohol, acetic ether, carbon disulphide, petroleum ether, paraffin oil, benzene, toluene, or xylene, whilst the same colour produced by salicylic acid is permanent.

**Determination of Creosote.**—A. Schlicht (*Pharm. Zeitung*).—The author shakes out the solution of the creosote with ether saturated with water, and calculates the proportion of creosote from the specific gravity of the ether-creosote solution.

**Examination of Ether.**—C. Traub (*Schweitzer Wochenschrift für Pharmacie*).—Good ether in contact with potassium hydroxide should undergo no change for twelve hours. The ether should be repeatedly examined for its odour upon blotting-paper. Pure ether dissolves in sulphuric acid without colour if added carefully and kept well cooled.

**Examination of Ammonium Chloride for Pyrogenous Substances.**—O. Schobert (*Pharm. Zeitung*).—According to the author, if 50 c.c. of a 5 per cent solution of ammonium chloride is mixed with 1 c.c. of a solution of permanganate, the red colour must not disappear within ten minutes.

**Determination of Cyanogen in Laming's Mass.**

**The Use of Sodium Nitro-prusside as a Reagent for Aldehyds and Ketones.**—Béla von Bittó (*Liebig's Annalen*).—The author draws from his experiments the general conclusion that the reaction in the aldehyds and ketones belonging to the fatty series always takes place when the aldehyd group CHO or the carbonyl group CO is directly connected with at least one group consisting only of carbon and hydrogen.

**Reactions of the Aldehyds and Ketones with Aromatic Nitro-compounds.**—Béla von Bittó.—The author reports with reference to the reactions with sodium nitro-prusside considered in the foregoing paper. Experiments with other nitrogen compounds, all of which had a negative result, rendered it probable that the reaction is occasioned by the nitroso-group (*Annalen der Chemie*).

**The Uses of the Calorimetric Bomb.**—M. Berthelot.—From the *Comptes Rendus*, cxv., p. 201.

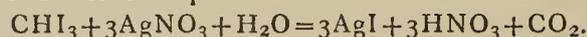
**The Elementary Analysis of Acetyl Fluoride.**—M. Meslans.—From the *Comptes Rendus*, cxiv., p. 1069.

**Determination of Sulphur in Organic Substances.**—A. Angeli (*Gazzetta Chimica and Journal of Chemical Society*).—Many organic substances if heated with nitric acid in a sealed tube, as in the method of Carius, are decomposed with much difficulty. The oxidation is much accelerated or completed by an addition of bromine.

**A Method for Determining Organic Substances by Oxidation with Potassium Chromate and Nitric Acid.**—H. Heidenheim (*Der Techniker*).—This paper requires the accompanying illustration.

**The Separation of Oleic Acid from Stearic and Palmitic Acids.**—Otto Hehner.—From the *Analyst*, xvii., 181.

**Determination of Iodoform.**—M. Greshof.—The author's method depends on the transformation—



Whilst Greshof worked on an aqueous solution, Ritsert (*Pharm. Central Halle*, xxxi., 610) modified the process by dissolving the iodoform in alcohol or ether-alcohol, acidulating with nitric acid, and titrating with silver nitrate at the heat of the water-bath. Greshof (*Pharm. Central Halle*, xxxii., 232) replying, considers it more advantageous to work according to his original method.

**Influence of Mouldiness on the Composition of Bread.**—Th. Dietrich.—The moulds grow at the expense of the carbohydrates of bread. Hence mouldy bread is relatively richer in proteine compounds.

## 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.

**Bleaching Oils.**—I read lately that silicate of soda was much used in the bleaching of oil. Could any of your correspondents tell me how it is so employed? Would it answer for bleaching fish oils?—J. D. JOHNSTONE.

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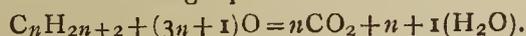
THE GASES "ENCLOSED" IN COAL DUST.\*

By P. PHILLIPS BEDSON, D.Sc.

THE investigations of Professor von Meyer (*Fourn. Prakt. Chem.*, [2], v., 146—183 and 407—416; also *Fourn. Chem. Soc.*, x., 798) and of Mr. W. J. Thomas (*Fourn. Chem. Soc.*, 1875 and 1876) have made us familiar with the fact that coal contains occluded or enclosed gases and with the general composition of the gases yielded by different varieties of coal. These gases consist, as a rule, of mixtures of carbon dioxide, oxygen, nitrogen, and marsh gas; in some cases von Meyer observed certain varieties of weathered coal to contain, in addition to marsh gas, some olefine hydrocarbons, and also denser members of the paraffin series of hydrocarbons, and further, the gases obtained by W. J. Thomas from cannel and jet were also found to contain similar hydrocarbons.

In a paper read some five or six years ago before the North of England Institute of Mining and Mechanical Engineers, I gave an account of the results of experiments made by applying Thomas's method of extracting the gases from coal, to coal dust. These experiments demonstrated that the coal dust under examination, when heated at 100° C. *in vacuo* for several hours, yielded from one-half to eight-tenths of its volume of gas. The gas obtained in this manner proved on analysis to contain carbon dioxide, oxygen, nitrogen, some olefines and hydrocarbons of the paraffin series. In analysing these gases I was, by reason of the lack of suitable laboratory accommodation, compelled to use the apparatus, &c., devised by Hempel, which, whilst admirably adapted for technical purposes, leaves much to be wished for in determining the nature and amount of the combustible gas left, after removal by absorbents, of carbon dioxide, oxygen, and olefines. Still, the results obtained showed conclusively that the combustible gas left after the absorption of the gases named was not simply marsh gas.

In determining the nature of this combustible gas, a measured volume of the residue left after the removal of the gases mentioned was mixed with oxygen and the mixture exploded. From the volume of carbon dioxide produced, the contraction resulting from the explosion, and the volume of oxygen used in the combustion, and the volume of nitrogen present, the proportion of combustible gas present was determined, and, assuming it to be a paraffin hydrocarbon, its probable composition was calculated by the aid of the following equation—



From which it is seen that 2 vols. of  $C_nH_{2n+2}$  would produce  $2n$  vols. of  $CO_2$ , give a contraction of  $(n+3)$  vols., and would require  $(3n+1)$  vols. of oxygen. The values found for "n" from the data provided by the explosions and the above relationships indicated the undoubted presence of higher members of the paraffin series; the values for n found for the gases from one sample of the dust being 2.78, and 2.42 in another case.

The coal dust with which these experiments were made was that collected on the screens at the Ryhope Colliery, in the county of Durham, and the investigation was undertaken with the hope of finding an explanation of the observation frequently made at this colliery that the cloud of dust produced in screening this special coal would often fire at the lamps used for lighting the screen, and in this manner produce a species of explosion.

\* Read before the British Association (Section B), Nottingham Meeting, 1893.

Since the publication of these results I have repeated the examination of this dust, and in the analysis of the gases have employed more exact and refined methods, using for that purpose the apparatus devised by the late Professor Dittmar. Further, in extracting the gases I attempted to effect a species of fractionation of the combustible constituents by performing the extraction at different temperatures. For this purpose, some 670 grms. of the dust were placed in a bottle and attached to the mercury pump, and after the air had been completely removed, the coal dust was heated by means of a water-bath for some twenty days at 30° C.; the gas produced was drawn off and measured. The temperature was then raised to 50° C., which was maintained for ten days; in this way a second quantity of gas was obtained. A third extraction was made by heating at 60° for another ten days, a fourth by heating at 60—80° C. for seven days, and finally a fifth by heating at 100° for some nine hours.

In this way the following volumes of gas were obtained:—

First extraction (30° C.)..	..	100.9	c.c. at N.T.P.
Second " (50° C.)..	..	160.6	" "
Third " (60° C.)..	..	116.3	" "
Fourth " (60—80° C.)..	..	286	" "
Fifth " (100° C.)	..	89.5	" "

753.3

This volume represents 112.4 c.c. of gas N.T.P. for every 100 grms of coal dust.

The following Table gives the results of the analysis of the several samples of gas:—

	I.	II.	III.	IV.	V.
Carbon dioxide .. ..	5.77	8.34	12.12	27.35	20.8
Oxygen .. .. .	9.33	7.31	5.35	0.56	4.16
Carbon monoxide ..	—	—	—	1.68	2.34
Olefines ( $C_nH_{2n}$ )..	—	0.39	0.77	2.14	4.74
Paraffins ( $C_nH_{m+2}$ ) ..	3.16	4.95	9.39	31.86	29.8
Nitrogen .. .. .	81.6	79.01	72.37	35.70	38.16
	99.86	100.00	100.00	99.29	100.00
Values for n in formula	2.1	2.2	2.1	2.3	2.8
$C_nH_{2n+2}$ .. .. n =	2.1	2.2	2.1	2.3	2.8

The changes to be observed in the composition of these gases given off at different temperatures are the gradual increase in the proportion of carbon dioxide and a diminution in the proportion of oxygen. This does not obtain with the gases produced at the highest temperature, and that is doubtless due to the fact that at this stage it was necessary to dismount the apparatus, by which the dust was brought into contact with the air. It will be further noted that whilst some combustible gas is given off at 30° C., the proportion increases with rise in temperature of the bath, the greater portion coming off between 80° and 100°, at which temperature the olefines and carbon monoxide make their appearance. The nature of the paraffin hydrocarbons, as shown by the value for n in the formula  $C_nH_{2n+2}$ , does not appear to suffer much change until at 100°, when the value corresponds very nearly to propane ( $C_3H_8$ ). Although the analysis of a mixture of such hydrocarbons does not enable us to determine the nature of the components, still there is in the above values for n a sufficient indication that the lighter gases of this series are the first to come away when the dust is heated *in vacuo*.

In this connection the question naturally arises—What is the nature of the gases enclosed in the coal from which this dust is produced? The solution of this question has been attempted by one of my students, Mr. W. McConnell, jun., who has examined the coal taken fresh from the same seam (the Hutton seam, Ryhope Colliery), and the results may be stated briefly as follows. 100 grms. of coal, heated *in vacuo* at 100° C., give 818 c.c. of gas at N.T.P. of the following composition.

	Volume.
Carbon dioxide .. .. .	0·7
Oxygen .. .. .	9·4
Carbon monoxide .. .. .	0·1
Olefines .. .. .	0·0
Marsh gas .. .. .	16·6
Nitrogen .. .. .	73·0
	<hr/>
	99·8

The paraffin hydrocarbon is here stated to be marsh gas, as the results of the analysis indicated this to be the case. The coal, after the gases had been extracted, was reduced to a fine powder, and the crushed coal again heated at 100° C. in an exhausted vessel attached to the air-pump. In this manner, from 208 grms. of the crushed coal, 109 c.c. of gas at N.T.P. were obtained, the analysis of which proved it to have the following composition:—

	Volume.
Carbon dioxide .. .. .	0·85
Oxygen .. .. .	6·95
Carbon monoxide .. .. .	trace
Olefines .. .. .	1·10
Paraffins (C <sub>n</sub> H <sub>2n+2</sub> ) .. .. .	17·90
Nitrogen .. .. .	73·20
	<hr/>
	100·00

The results of the determination of the composition of the paraffin give a value of 2·06 for *n*; showing the existence here of combustible gases similar to those obtained from the dust collected in the screens.

Further, Mr. McConnell has found that after heating the coal *in vacuo* at temperatures as high as 180° C., until it ceased to give off any gas, the coal, on crushing to a powder and heating again under reduced pressure at 100°, gave a further quantity of gas, which contained 39·7 per cent of paraffin hydrocarbons; the results of the combustion of which show the presence of some of the higher members of the paraffin series.

During the past two years Mr. McConnell (Royal Exhibition Scholar) has been engaged in the chemical laboratory of the Durham College of Science, in the examination of the gases "enclosed in" different coal dusts produced in the working of coal raised in the Northumberland and Durham coal fields. The detailed results of this investigation will be published shortly. I may, however, state that some of the dusts examined have been found to yield mixtures of carbon dioxide, oxygen, and nitrogen only. The coal from which these dusts were produced gave mixtures of a similar composition. Other varieties of dust were found to contain a small quantity of combustible gas in addition; whilst a third class was found to resemble the dust from the Ryhope Colliery, with the nature of the gases from which I have already dealt, and the chief point of interest in which is the existence among the combustible gases of such hydrocarbons as ethane and propane. The coals from which this third class of dusts are obtained have been proved to give occluded gases, similar in composition to the gas obtained from the Ryhope coal; the combustible constituent being marsh gas only. Further, these coals themselves, after the occluded gases had been removed by heating *in vacuo* at 100° C., gave, on crushing and heating the powdered coal at 100° *in vacuo*, a further quantity of gas containing some of the higher members of the paraffin series of hydrocarbons.

These results have an interest beyond the demonstration of the fact that the denser hydrocarbons are more firmly held by the coal substance than the lighter marsh gas; and that in the working of the coal the reduction to a fine powder, such as coal dust, must by free exposure to the air allow ample opportunity for a ready diffusion of the marsh gas; the denser hydrocarbons being retained by the particles of coal. Again, the existence of such enclosed gases in coal dust show that in considering the

part played by coal dust in forming explosive mixtures with air, we may have to deal with a variety of dust which might readily yield such hydrocarbons, as those found in the gases enclosed in the dusts examined by Mr. McConnell and myself. For these gases differ from marsh gas not only in the proportion required to form an explosive mixture with air; thus whilst 1 volume of marsh gas would require 10 volumes of air for its complete combustion, 1 volume of the hydrocarbons found in the Ryhope coal dust would require 23 volumes of air; or, in other words, whilst 9·3 per cent of marsh gas is required to form the most explosive mixture with air, about 4 per cent only of the combustible gas obtained from the Ryhope coal dust would be required. But the difference between marsh gas and its next homologues is seen again in the temperature required to ignite such explosive mixtures, for it has been recently shown by Victor Meyer that the temperature of ignition of explosive mixtures of oxygen and ethane is lower than that of marsh gas and oxygen.

These facts point to the ready inflammability and the sensitiveness of dusts containing such hydrocarbons—a conclusion borne out by the ignition of the coal dust on the screens at the Ryhope Colliery—a fact which led me originally to investigate this subject; and, further, the Austrian Fire-damp Commission has from the experiments with coal dust been led to the conclusion that the sensitiveness of dusts increases with the proportion of easily inflammable hydrocarbons, especially with the amount of ethane liberated at 100° C. and with the dryness of the dust.

There are doubtless other factors which contribute to the ready inflammability and sensitiveness of a coal dust, and one can easily understand how this would be contributed to by the fineness of subdivision and again by the air which the coal may absorb by long-continued exposure in an air current.

## THE APPLICATION OF ELECTROLYSIS TO QUALITATIVE ANALYSIS.\*

By CHARLES A. KOHN, Ph.D., B.Sc.,  
Lecturer on Organic Chemistry, University College, Liverpool.

THE first application of electrolysis to chemical analysis was made by Gaultier de Claubry in 1850, who employed the electric current for the isolation of poisonous metals, using platinum electrodes, on which the deposition of the metal took place.

Other early workers followed in this direction, and in 1861 C. L. Bloxam published two papers on "The Application of Electrolysis to the Detection of Poisonous Metals in Mixtures of Organic Matters" (*Journ. Chem. Soc.*, xiii., 12 and 338). The author appears to have made extensive use of the methods described in these papers, and which have reference to the detection of arsenic, antimony, mercury, bismuth, and copper. The electrolysis was effected in acidulated solutions, from which the arsenic was evolved as hydride, whilst the other metals were deposited in the metallic state upon the cathode and subsequently tested, after dissolving, by the usual reactions.

Since the publication of these results, the advances in electrolytic analysis have reference to quantitative methods only, and the advantage of these latter for qualitative work has been to some extent overlooked.

Within the last twelve years Classen and his pupils have placed a number of electrolytic methods for the determination and separation of metals in the hands of chemists—methods which have been added to by the labours of E. F. Smith, Vortmann, and others.

These methods are of special value when applied to qualitative analysis in cases of medical or medico-legal

\* A Paper read before the British Association (Section B), Nottingham Meeting, 1893.

inquiry. They are not supposed to supersede in any way the ordinary methods of qualitative analysis, but to serve as a final and crucial means of identification, and thus render it possible to detect very small quantities of the substances in question with great accuracy. As such, they fulfil the required conditions admirably, being readily carried out, comparatively free from contamination with impure reagents, and capable of being rendered approximately quantitative whenever desired.

The method devised by Bloxam for the detection of arsenic, in which all fear of contamination with impure zinc is avoided, has been elaborated by Wolff (*Journ. Soc. Chem. Ind.*, 1887, p. 147), who has succeeded in detecting 0.00001 grm. of arsenious acid by this means.

It is in connection with the most important of the remaining mineral poisons that I have examined the applicability of these electrolytic methods, viz., antimony, mercury, lead, copper, and cadmium.

#### Antimony.

The method employed in the case of antimony is that adopted in its quantitative estimation by means of electrolysis, a method which ensures a complete separation from those metals with which it is precipitated in the ordinary course of analysis, arsenic and tin. This fact is of considerable importance in reference to the special objects for which these methods have been worked out.

The precipitated sulphide is dissolved in potassium sulphide, and the resulting solution, after warming with a little hydrogen peroxide to decolourise any polysulphides that may be present, electrolysed with a current of 1.5–2 c.c. of electrolytic gas per minute (10.436 c.c. at 0° and 760 m.m. = 1 ampère), when the antimony is deposited as metal upon the negative electrode. One part of antimony (as metal) in 1,500,000 parts of solution may be thus detected—a reaction thirty times more delicate than the deposition by means of zinc and platinum. The stain on the cathode, which latter is best used in the form of a piece of platinum foil about 1 c.m. in diameter, is distinct even with a solution containing  $\frac{1}{25}$  m.grm. of antimony, and by carefully evaporating a little ammonium sulphide on the foil, or by dissolving the stain in hot hydrochloric acid and then passing a few bubbles of sulphuretted hydrogen gas into the solution, the orange-coloured sulphide is obtained as a satisfactory confirmatory test. The detection of 0.0001 grm. of metal can be fully relied on under all conditions, and one hour is sufficient to completely precipitate such small quantities.

#### Mercury.

Mercury is best separated from its nitric acid solution on a small closely-wound spiral of platinum wire. The solution to be tested is acidified with nitric acid and electrolysed with a current of 4–5 c.c. (c.c. refer to c.c. of electrolytic gas per minute). The deposition is effected in half an hour. The deposited metal is removed from the spiral by heating the latter gently in a test-tube, when the mercury forms in characteristic globules on the upper portion of the tube. As a confirmatory and very characteristic test, a crystal of iodine is dropped into the tube, and the whole allowed to stand for a short time, when the presence of mercury is indicated by the formation of the red iodide. 0.0001 grm. of mercury in 150 c.c. of solution can be clearly detected.

Wolff has applied this test under similar conditions, using a special form of apparatus through which the solution to be tested is allowed to pass slowly, and in which a silver-coated iron electrode is employed as the anode.

#### Lead.

Lead is precipitated either as  $PbO_2$  at the anode from a solution containing 10–20 per cent of free nitric acid, or as metal, at the cathode, from an ammonium oxalate solution. In both cases a current of 2 to 3 c.c. suffices to effect the deposition in one hour.

Here, again, 0.0001 grm. of metal in 150 c.c. of solu-

tion can be easily detected. With both solutions this amount gives a distinct colouration to the platinum spiral on which the deposition is best effected. As a confirmatory test, the deposited metal is dissolved in acid and tested with sulphuretted hydrogen, or the spiral may be placed in a test-tube and warmed gently with a small crystal of iodine, when the yellow iodide of lead is formed. The latter reaction is very distinct, especially in the case of the peroxide.

Of the above two methods, that in which an ammonium oxalate solution is used is the more delicate, although it cannot be employed quantitatively, owing to the oxidation that takes place on drying. An addition of 1 grm. of ammonium oxalate to the suspected solution is sufficient.

A great advantage of the electrolytic method as a crucial means for the detection of minute quantities of lead lies in the fact that, when the lead is deposited as peroxide from a nitric acid solution, it is completely separated from mercury, copper, cadmium, arsenic, antimony, and iron, none of which are deposited at the anode in this case. Manganese is the only commonly occurring element that behaves similarly.

This method is, therefore, of value for the determination of lead in water, citric and tartaric acids, baking-powders, &c.

If quantitative results for small quantities of lead are required, the best plan is to effect the electrolysis in nitric acid solution, as above, employing a small platinum dish as the anode, to which the deposited peroxide adheres well, and which can be weighed as  $PbO_2$  after washing and drying at 110° C. May has suggested (*Zeit. f. Anal. Chem.*, xiv., 344) the ignition of the  $PbO_2$  to  $PbO$  and final weighing of the latter; but a loss always occurs under these conditions, which increases with the quantity of the peroxide present. This loss amounts to 2–3 per cent of the weight of lead deposited.

#### Copper.

0.00005 grm. of copper can be very readily detected by electrolysing an acid solution in the usual way. A spiral of platinum wire is employed as the cathode, and the presence of the metal confirmed by dissolving it in a little nitric acid and testing with potassium ferrocyanide.

Quantitative results in solutions containing 0.001 grm. of metal are thus obtained with considerable accuracy, and the method, as in the case of lead, is of use for the detection of minute quantities of the metal in waters. The advantages of electrolysis over the colorimetric methods usually employed in such cases are twofold. In the first place, concentration is not necessary, owing to the delicacy of the test; and, secondly, the erroneous results that are obtained in all colorimetric processes, due to the influence of the varying constituents present in the solution tested on the accuracy of the reaction, are entirely obviated.

#### Cadmium.

Cadmium is deposited in the metallic state both from potassium cyanide and from potassium oxalate solutions, the former of which is preferable. A current of 0.2 c.c. is sufficient, and 0.0001 grm. of the metal can be thus detected. To confirm, the deposit is dissolved in hydrochloric acid, the solution diluted and treated with sulphuretted hydrogen.

#### Detection of Metallic Poisons in Urine by Means of Electrolysis.

To apply the above methods in cases of poisoning, the organic matter with which the metals are associated must first be destroyed in the usual way by means of hydrochloric acid and potassium chlorate, and the solutions or precipitates obtained in the ordinary course of analysis then subjected, at suitable stages, to electrolysis. In such cases the advantages of electrolysis lie, again, in the delicacy and reliability of the tests, and also in the fact that the small quantities of organic matter with which the solutions obtained in such cases are contaminated do not

interfere with the electrolytic tests as they do with the ordinary wet tests. By passing the current for a longer time than is required for ordinary aqueous solutions the organic matter is decomposed and thus prevented from affecting the reliability of the tests.

The detection of metallic poisons in urine can be directly effected by electrolysis.

The presence of mercury or of copper is detected by acidifying the urine with 2—3 c.c. of nitric acid (conc.) and electrolysis as described. 0.0001 gm. of metal can be detected thus in 30 c.c. of urine, or 1 part in 300,000 of urine.

Lead does not separate well as peroxide from urine acidified with nitric acid, but if ammonium oxalate be added the reaction is quite as delicate as in aqueous solution, and 0.0001 gm. of lead can be thus detected.

Antimony can be detected directly in urine, according to Chittenden (*Proc. Connecticut Acad. of Science*, viii.), by electrolysis after the addition of 2—3 c.c. of dilute sulphuric acid; but this process was not found satisfactory. The better plan is to first precipitate by sulphuretted hydrogen and then electrolyse as described.

In all these cases it is necessary to pass the current at least twice as long as when aqueous solutions are employed. In twenty-four hours a current of 1—2 c.c. completely decomposes urine, leaving a clear and colourless solution.

A comparison of the delicacy of these tests with the ordinary qualitative tests for antimony, mercury, lead, and copper by means of sulphuretted hydrogen showed that in the case of antimony and of copper the electrolytic tests were one and a half times more delicate; whilst with mercury and lead they were at least ten times more so. These comparisons were made in aqueous solutions.

In testing urine the value of the electrolytic method is still more evident; for here the colour of the liquid interferes materially with the reliability of the ordinary qualitative tests when only small quantities of the elements referred to are present. This was well instanced in a case of suspected lead poisoning in which the patient had been treated with potassium iodide. A direct test with sulphuretted hydrogen gave no reliable result, even after standing twenty-four hours; whilst the deposit obtained on electrolysis gave a distinct precipitate of lead sulphide after being dissolved in acid.

Other applications of the more reliable electrolytic methods of analysis to qualitative work can only offer attraction in special cases, and the data on the subject are to be found in the many electrolytic methods already published. It is by their judicious combination with the ordinary methods of analysis that a saving of time and labour, and, above all, an increased reliability and accuracy is effected.

## THE APPLICATION OF SODIUM PEROXIDE TO WATER ANALYSIS.\*

By Dr. S. RIDEAL and H. J. BULT.

Now that sodium peroxide can be obtained commercially its use in analysis seems desirable. W. Hempel (*Zeit. Anorg. Chem.*, iii., 193) has already shown that it is a useful oxidising agent for the detection of chromium and manganese, and that it forms a very convenient reagent for opening up tungsten minerals and for effecting the decomposition of titaniferous iron ores. Since the commercial sodium peroxide is free from sulphur, it can be used quantitatively for estimating the sulphur in sulphides. It occurred to us that an alkaline oxidising agent of this character, if used as a substitute for alkaline permanganate, in water analysis, might throw some light upon the

character of the organic nitrogen in waters. Hitherto either methods for determining the total nitrogen, *e. g.*, Frankland's and Kjeldahl's, or Wanklyn's well-known process, in which only a portion of the nitrogen present in the organic matter is discovered, have been employed. In this latter process very different quantities of ammonia are obtained from the different classes of nitrogenous organic bodies. Only when the nitrogen is present as some simple amido-compound like urea, aspartic acid, or leucine, does this process yield the whole of the nitrogen present.

Preusse and Tiemann (*Berichte*, xii., 1906) have shown, in their review of the various processes for determining organic substances in water, that no reliance can be placed upon this process for estimating the absolute quantity of nitrogen in many substances, and that therefore, when used as a method of water analysis, the quantities of ammonia obtained are only relatively true for waters of the same type. A comparison of the quantities of ammonia evolved from a water when treated with alkaline permanganate and with sodium peroxide, might therefore possibly afford a means of differentiating the nitrogenous constituents. With this purpose in view we have compared, in the ordinary course of analysis, the amounts of ammonia given off under these two treatments. In one case, when using 1 gm. of sodium peroxide per  $\frac{1}{2}$  litre of water, the total ammonia evolved was equal to 0.027 part per 100,000, while with alkaline permanganate 0.050 part per 100,000 is obtained. On repeating this experiment, with the same water and under similar conditions, 0.026 part per 100,000 was yielded by the peroxide and 0.048 by the permanganate. The addition of a further quantity of the sodium peroxide and further distilling did not increase the quantity of ammonia produced, and it was therefore evident that the sodium peroxide had failed to break down the organic nitrogenous substances present to the same extent as had the alkaline permanganate. In fact, we have since found it possible to obtain a fresh quantity of ammonia from a water after treatment with sodium peroxide by the addition of the alkaline permanganate.

The following table gives the results obtained in parts per 100,000 with four samples of water.

		Free NH <sub>3</sub> .	NH <sub>3</sub> from Peroxide.	NH <sub>3</sub> from Permanganate after Peroxide.
Water .. ..	A.	0.01	trace	0.007
" .. ..	B.	0.001	0.004	0.011
" .. ..	C.	0.012	0.011	0.015
" .. ..	D.	0.021	0.024	0.057

		Free NH <sub>3</sub> .	NH <sub>3</sub> from Permanganate.
Water .. ..	A.	0.01	0.008
" .. ..	B.	0.001	0.013
" .. ..	C.	0.012	0.027
" .. ..	D.	0.019	0.078

From these figures it will be seen that the sodium peroxide in no case oxidises the organic matter present to the same extent as does the permanganate. The peroxide seems to liberate a portion of the nitrogen which is included in that set free by the alkaline permanganate, as the total ammonia obtained by the action of the peroxide followed by permanganate is in most cases about equal to that obtained when the water is distilled with alkaline permanganate alone. There appears to be no ratio between the quantities of ammonia evolved by the two reagents, and therefore the nitrogenous organic matter present in waters might be divided into two classes, *viz.*, that which is oxidised by the sodium peroxide and that which resists such treatment. The results obtained by Wanklyn's process, as compared with the total nitrogen present in a water, also show a differentiation in the organic nitrogen substances present in waters; but this knowledge has hitherto not been of any

\* Paper read before the British Association (Section B), Nottingham Meeting, 1893.

value, owing to the complex nature of the problem. Further experiments alone can decide whether the limited oxidation of the nitrogenous matter in water will throw any fresh light on the condition of these organic constituents of water. We have, however, noticed that in some cases a water which has been partially oxidised by the peroxide yields the remainder of its ammonia to the alkaline permanganate with much greater rapidity than when the water has not been so treated. We suggest that the explanation of this phenomenon may be due to the presence in waters of organic nitrogenous substances, which when partially oxidised are then in a condition to be completely broken up by the stronger reagent. This result has been obtained with waters containing fresh sewage; but we hope, by taking solutions containing nitrogenous compounds of known constitution, to confirm this suggestion, and hope thereby to show that in this reagent we have an oxidising agent which will be useful in establishing the constitution of the nitrogen in complex organic substances.

A NEW METHOD FOR  
THE RAPID ESTIMATION OF SULPHUR  
IN STEELS, PIG-IRONS, &c.

By H. A. HOOPER.

THE sulphur in steels, pig-irons, &c., is determined, in the following process, by evolving the sulphur in the form of sulphuretted hydrogen by the addition of dilute hydrochloric acid. The sulphuretted hydrogen is absorbed in sodium hydrate solution, and the quantity of sulphur is ascertained by adding a standard solution of lead nitrate until no further precipitate of lead sulphide is formed.

A standard solution of lead nitrate is made by dissolving 3.2265 grms. of pure lead in as small a quantity of nitric acid as possible, and then making this up to 1000 c.c. with distilled water. One c.c. of this solution is equal to 0.0005 grm. S. The following is a description of the process as actually carried out:—Five grms. of steel are dissolved by dilute hydrochloric acid in the apparatus generally used for the determination of sulphur by the evolution process, the absorption-tube being charged with about 10 c.c. of sodium hydrate solution, of about 1.20 sp. gr., and free from sulphide. When the steel is completely dissolved, the contents of the absorption-tube are transferred to a large beaker without any more dilution than is absolutely necessary, and the standard lead nitrate is added in small quantities at a time, agitating the fluid after each addition until it is quite clear) until a drop of the solution gives no further brown colouration. The number of c.c.'s of standard solution used, divided by 100, gives the percentage of sulphur present in the steel.

A single drop of the solution is sufficient to show when the reaction is complete. If a sheet of white paper is placed under the beaker, the final traces of colour are more easily seen.

The delicacy of the above process can be judged from the fact that the sulphur in Swedish pig-irons, &c., can quite easily be determined.

A great advantage of the process is, that the standard solution is quite permanent. The presence of a small quantity of free nitric acid is quite harmless, as it is neutralised by the soda solution, and alkaline nitrates have no immediate action on alkaline sulphides in the cold.

After the substance has been dissolved, the assay can easily be completed within five minutes.

The process has been in use for some time past, and has been proved to be most satisfactory.

Newburn Steel Works, Newcastle-on-Tyne.

NOTE ON THE  
COMPOSITION OF THE FEN AND MARSH  
SOILS OF SOUTH LINCOLNSHIRE.

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

VERY little having been published on this subject it has been suggested to me that the results of analyses of soils of this district would prove of interest. In no case have samples been selected from any supposed superiority, but rather every care has been taken to obtain specimens representative as far as possible of their particular district. Each sample was taken to the depth of six inches, being about the average depth cultivated. A partial analysis of a sample of peaty matter dug up in the fen is appended, being of interest as showing what was the composition of the land before it had been clayed.

The first series of analyses gives the absolute composition of the soil, the solvent used being hydrochloric acid (specific gravity 1.16).

Peaty Matter from the Fens.

Organic matter and combined water .. .. .	67.93
Silica and insoluble matter .. .. .	18.53
Ferric oxide and alumina .. .. .	8.51
Lime .. .. .	2.23
Phosphoric acid .. .. .	0.25
Sulphuric acid .. .. .	1.04
Alkaline salts, &c. .. .. .	1.51
	<hr/>
	100.00

Fen Soil.—No. 1.

Organic matter and combined water .. .. .	26.47
Silica and insoluble matter .. .. .	55.88
Ferric oxide.. .. .	11.56
Alumina .. .. .	1.18
Manganous oxide .. .. .	0.13
Lime .. .. .	1.44
Magnesia .. .. .	0.28
Potash .. .. .	0.42
Phosphoric acid .. .. .	0.26
Sulphuric acid .. .. .	0.76
Carbonic acid, soda, &c. .. .. .	1.62
	<hr/>
	100.00

Fen Soil.—No. 2.

Organic matter and combined water .. .. .	22.78
Silica and insoluble matter .. .. .	59.53
Ferric oxide.. .. .	8.66
Alumina .. .. .	4.48
Manganous oxide .. .. .	0.05
Lime .. .. .	1.50
Magnesia .. .. .	0.34
Potash .. .. .	0.43
Phosphoric acid .. .. .	0.21
Sulphuric acid .. .. .	0.41
Carbonic acid, soda, &c. .. .. .	1.61
	<hr/>
	100.00

Fen Soil.—No. 3.

Organic matter and combined water .. .. .	16.13
Silica and insoluble matter .. .. .	75.34
Ferric oxide.. .. .	3.45
Alumina .. .. .	1.85
Manganous oxide .. .. .	0.02
Lime .. .. .	1.02
Magnesia .. .. .	0.42
Potash .. .. .	0.28
Phosphoric acid .. .. .	0.16
Sulphuric acid .. .. .	0.32
Carbonic acid, soda, &c. .. .. .	1.01
	<hr/>
	100.00

## Marsh Soil.—No. 1.

Organic matter and combined water ..	4'63
Silica and insoluble matter .. .. .	85'49
Ferric oxide.. .. .	4'95
Alumina .. .. .	0'84
Manganous oxide .. .. .	0'08
Lime .. .. .	2'16
Magnesia .. .. .	0'40
Potash .. .. .	0'16
Phosphoric acid .. .. .	0'16
Sulphuric acid .. .. .	0'15
Carbonic acid, soda, &c. .. .. .	0'98
	100'00

## Marsh Soil.—No. 2.

Organic matter and combined water ..	4'54
Silica and insoluble matter .. .. .	84'03
Ferric oxide.. .. .	4'22
Alumina .. .. .	2'70
Manganous oxide .. .. .	0'02
Lime .. .. .	2'12
Magnesia .. .. .	0'28
Potash .. .. .	0'20
Phosphoric acid .. .. .	0'21
Sulphuric acid .. .. .	0'30
Carbonic acid, soda, &c. .. .. .	1'38
	100'00

A second series of analyses was then made with a view of showing the amount of plant food in a readily available condition. In this case the solvent used was acetic acid (specific gravity 1'04). The results are percentages calculated on the dry soil.

## Fen Soil.—No. 1.

Ferric oxide.. .. .	1'326
Alumina .. .. .	0'579
Lime .. .. .	0'944
Magnesia .. .. .	0'231
Potash .. .. .	0'112
Phosphoric acid .. .. .	0'015

## Fen Soil.—No. 2.

Ferric oxide.. .. .	0'481
Alumina .. .. .	0'781
Lime .. .. .	0'824
Magnesia .. .. .	0'165
Potash .. .. .	0'242
Phosphoric acid .. .. .	0'113

## Fen Soil.—No. 3.

Ferric oxide.. .. .	0'298
Alumina .. .. .	0'873
Lime .. .. .	0'843
Magnesia .. .. .	0'089
Potash .. .. .	0'036
Phosphoric acid .. .. .	0'022

## Marsh Soil.—No. 1.

Ferric oxide.. .. .	0'309
Alumina .. .. .	0'248
Lime .. .. .	1'823
Magnesia .. .. .	0'290
Potash .. .. .	0'034
Phosphoric acid .. .. .	0'040

## Marsh Soil.—No. 2.

Ferric oxide.. .. .	0'199
Alumina .. .. .	0'333
Lime .. .. .	1'001
Magnesia .. .. .	0'155
Potash .. .. .	0'121
Phosphoric acid .. .. .	0'013

High Bridge, Spalding.

AN INTERNATIONAL INDEX TO  
CHEMICAL LITERATURE.

OPENING ADDRESS TO THE SECTION OF BIBLIOGRAPHY,  
CONGRESS ON CHEMISTRY, HELD AT CHICAGO,  
AUGUST 21ST—26TH, 1893.

By HENRY CARRINGTON BOLTON,  
Chairman of the Section.

DURING one of my bibliographical tours in Europe, an eminent librarian of a German university remarked:—"You Americans are doing more and better work in bibliography than all the nations of Europe taken together." And this he said not in flattery, but as the expression of an earnest conviction. Later I expressed surprise that Germans, with such splendid collections of books and other advantages, should leave it to Americans to cross the Atlantic and wrest from Europe materials for general and special bibliographies. To this he promptly replied: "Ach, mein Freund, das Geld fehlt."

I shall not attempt to demonstrate the accuracy of the gentleman's statements, as it would involve comparisons, and these are said to be odious. A basis for his enthusiasm is, however, found in such monumental works as "Pool's Index," "Fletcher's Index," Billing's "Index Catalogue of the Medical Library of the Surgeon General's Office," the "Index-Medicus" (edited by Dr. Robert Fletcher), the Catalogue of the Boston Athenæum, as well as the bibliographies of science published by the Smithsonian Institution, by the U.S. Department of Agriculture, and in independent journals. Many other notable works will suggest themselves to the chemists present, who will understand that this is only a passing reference.

The production of special and general bibliographies in the United States goes forward with the multiplication of public and endowed libraries, now increasing in number and value with gratifying rapidity throughout the land. Some of these are publishing bibliographies of specific subjects in addition to their library catalogues; in this direction Harvard University takes the lead.

Unfortunately, much good work done by Institutions does not get beyond the M.S. stage, as, for example, the subject-index in preparation at the Scientific Library of the United States Patent Office, and the chemical bibliographies compiled by the Students of the University of Michigan as appendages to theses in science.

There are at least three organisations in the United States which promote the preparation of bibliographies; these are the American Library Association, the Committee on the Bibliography of Geology appointed at the International Congress of Geologists, and the Committee on Indexing Chemical Literature, of the American Association for the Advancement of Science. The work of the American Library Association is familiar to everyone; through the journal it reaches all librarians and bibliographers in sympathy with its enterprises. Its scope is, however, almost entirely literary, and science finds little place in its admirable plans.

The Secretary of the Committee on the Bibliography of Geology appointed at the International Congress of Geologists, held September 1st, 1891, at Washington, has issued a circular, dated November 20, 1891, which sets forth its plans for work. These comprise the preparation of (1) a list of the geological bibliographies already in existence; (2) new bibliographies of special topics; and (3) the periodic registration of the current bibliography of geology. Their work has been so recently begun that no great results can as yet be expected.

The work of the Committee on Indexing Chemical Literature, of the American Association for the Advancement of Science, now in the eleventh year of its existence, is familiar to most persons present. This Committee has endeavoured to direct attention to the importance of compiling bibliographies, catalogues, and indexes to the voluminous literature of chemistry. While little

systematic work has been undertaken, duplication of labour has been prevented and independent efforts have accomplished much. Thus a collection of special bibliographies has been gradually forming, which now number more than fifty; the list was printed in the tenth annual report of the Committee, published in the *Proceedings of the A. A. A. S.* for 1892, as well as in the *CHEMICAL NEWS* (London). While the Committee feels that their labours have not been in vain, the proportion of the completed bibliographies to the number of authors publishing chemical papers is still unhappily small, and the average of five bibliographies per annum is rather lower than expected. The Committee expresses the hope that the number will grow much faster in the future.

In England, the British Association for the Advancement of Science has done something towards fostering the object under consideration by appointing Committees on Indexing Solutions and other topics, but their work progresses slowly.

The Chemical Societies of Berlin, Paris, and London give to their members and subscribers laboriously prepared abstracts of papers published in countries other than their own. For persons whose linguistic attainments are limited to their mother tongue these abstracts are undoubtedly useful, perhaps invaluable; but it rarely happens that they can be entirely relied upon for the details needed by chemists practically interested, and the originals must eventually be consulted. It has seemed to me that if the same amount of energy expended by abstractors of the Societies named could be exerted in indexing, greater practical results would be obtained, and at far greater economy of space. Moreover, these Societies generally confine their abstracts to publications issued in other countries than their own, and consequently a large amount of good material published at home in Government reports, Transactions of learned Societies, and periodicals devoted to general science escapes the eyes of all except a few industrious readers.

It has further occurred to me that the chemical societies of Germany, France, Italy, Russia, England, and the United States, instead of filling their official organs with abstracts of papers foreign to each, might well devote their energy to indexing the wealth of material produced each in its own nation.

And this brings me to the statement of a plan which I have the honour to propose to this Congress, for a Co-operative International Index.

I suggest that this Congress, in which are representatives of the six leading Chemical Societies of the world, recommend to these Societies the preparation of an annual index to current chemical literature, each Society to care for the productions of the country in which it is situated. These annual indexes to chemical literature could be published in the journals (*Berichte*, *Bulletin*, *Journal*, &c.) of the respective Societies; which fortunately for our purpose are all in octavo form; and when all the indexes are issued for a given year, they could be bound together for convenience. The bibliographies would, of course, be compiled on the same or similar plans; this uniformity being secured by conference between the Index Committees of the several Societies. This plan would necessitate the consultation of six alphabets at least in each annual volume, but this inconvenience would be counterbalanced by the greater accuracy and fulness attained by the sub-division of labour proposed.

What reception this plan may receive by the several societies is uncertain; but I believe that no more important work can be undertaken by the American Chemical Society. This newly re-organised association now numbers over seven hundred members, and is a truly national society; the *Journal* could not present to its members and subscribers a more welcome contribution than a subject-index to the publications of American chemists. This might be done half-yearly—or, better, quarterly—and should embrace the widest range of pure and applied chemistry. Perhaps the American Chemical

Society will lead in this enterprise, and then the older and more conservative societies of Europe might follow. One stimulus that would eventually influence them is national pride.

So far, this plan relates only to current literature, and some provision must be made for indexing the enormous accumulation of material already in print. Probably there is no better way to attack this problem than to prepare a subject-index to the chemistry contained in the catalogue of scientific papers published under the auspices of the Royal Society. This monumental work loses much of its value owing to the lack of a subject-index, and it is deeply to be regretted that there is no prospect of one being compiled, if at least one may judge from the correspondence on this subject printed in the pages of *Nature*.

And here allow me to place on record a fact bearing on the question. A few years ago a member of the Committee on Indexing Chemical Literature of the American Association for the Advancement of Science, already known to the scientific world by his labours in bibliography, decided to undertake the preparation of a subject-index to the chemistry and physics in the eight quarto volumes of the work named; but before doing so wrote a courteous letter to the secretary of the Royal Society announcing his scheme. In that letter the gentleman explained that he planned to compile the subject-index and to print it entirely without expense or liability on the part of the Royal Society. After a long lapse of time the gentleman received a note from the secretary of the Royal Society stating that the matter had been laid before the Council, and they had refused permission to have such an index prepared! Thus rebuffed, my friend abandoned his scheme and turned his attention to another task.

In spite of this attitude of the Council of the Royal Society, I believe a regularly constituted Committee of chemists could secure permission, if indeed any be necessary.

Details of methods to be pursued cannot here be considered; they could be formulated by a Committee.

A general bibliography of chemistry has been recently attempted by the writer of this communication; the results form a volume of over twelve hundred pages just issued by the Smithsonian Institution as No. 850 of the series entitled *Miscellaneous Collections*. This "Select Bibliography of Chemistry" (1492—1892) embraces about twelve thousand titles in twenty-four languages, yet makes no claim to completeness. It is, moreover, a bibliography, not an index.

In conclusion, I have the honour to propose the appointment of an International Committee on Chemical Bibliography, to consist of one member from each country represented in this Congress. That this Committee have unlimited power to add to its number, provided, however, that no country have more than two representatives. That this Committee, through the European and American Chemical Societies, report a scheme for an International Co-operative Index to Chemical Literature.

University Club, New York City,  
August, 1893.

This paper was referred to a Committee, who then reported as follows:—

TO THE CONGRESS ON CHEMISTRY:

Your Committee, having considered the suggestions of Dr. Bolton, recommend that a communication be addressed from this Congress to the national chemical societies of England, France, Germany, Italy, Russia, and America, reporting the following action by this Congress:—

"Whereas, Some activity has been shown of late years in the compilation of bibliographies of various subjects, but without the uniformity and system which are desirable.

*Resolved*, That we recommend the annual publication of classified bibliographies by the chemical societies of

England, France, Germany, Italy, Russia, and America, for these several countries.

*Resolved*, That we recommend each of these societies to appoint one representative upon an International Committee to confer together and report to the several societies a scheme for an International Co-operative Index to Chemical Literature."

Respectfully submitted,  
(Signed) EDWARD HART,  
ROBT. B. WARDER, } Committee.  
WM. L. DUDLEY. }

### ON ERBIA.\*

By GERHARD KRÜSS.

Continued from p. 178).

In order to render this result certain and to raise the objection that the true erbia might perhaps have not been brought, by an unsuitable arrangement of the above experiments, into the materials which we called Nos. 1 to 7,† both the more feebly basic and the more strongly basic oxides were examined for the presence of  $Er=166$ . The elaboration of the stronger bases coincides with an investigation of holmia which is also already concluded. According to those experiments, no  $Er_2O_3$  with a constant  $Er=$  about 166 could be isolated from the holmia earth. The examination of the more feebly basic earths which approached nearest to the erbia earth gave the following results:—

As the material, there were used fractions 1 and 2 of Series 10. They stand on the side of weaker basicity nearest to the erbia material No. 6, which is identical with fraction 3 of Series 10.

To the fractions 1 (172.4) and 2 (172.9) of Series 10 there were further added as a precaution the feeblest bases of the thulium material fraction 1 (171.6), Series 8; this also was a material in which a little erbia might be present.

From these three united fractions precipitations of solutions were alternately effected with aniline hydrochlorate, so that we obtained—

Series 15.			
Weaker bases ←—.			
Aniline precipitates.			
1	2	3	Middle
173.4	—	173.0	172.0
—→ Stronger bases.			
Aniline solutions.			
4	3	2	1
167.5	168.8	166.9	165.3

We have here the same phenomenon as in working up the above-mentioned erbia materials in general; the ytterbia earth can be relatively easily and well separated from the erbia earth; further, there remains in the fractions of Series 15 obtained by the aniline solutions Nos.

4, 3, and 2 the  $R$  for the earth approximately constant  $=167$  to  $168$ . The last three fractions (167.5, 168.8, 166.9) were united, and were now resolved by aniline hydrochlorate into three fractions and a residue—the precipitate remaining from the third solution.

Stronger bases ←—.		—→ Weaker bases.	
1	2	3	4. Remnant.
Series 16. 161.8	164.5	168.9	171.1

\* *Zeitschrift für Anorganische Chemie*.

† It is certain that these materials, according to their spectrum and to the determination of their equivalents, must contain  $Er=166$  to  $168$  if it exists.

There existed, therefore, no unitary erbia earth in the earths which were adjacent to the erbia materials Nos. 6 to 8. The last-mentioned experiments even confirm the result obtained in Series 14, that the erbia is relatively easily decomposed by aniline hydrochlorate when certain

quantities of earths having values  $R > 168$  and  $< 166$  are eliminated from the erbium material.

The above experiments were executed with erbiferous earths derived from 5 kilos. of gadolinite. But as the object was to obtain pure  $Er_2O_3$ , and not to prepare large quantities, the erbia material No. 6 represented a quantity of only about 2 grms. of earth. I had therefore great pleasure in obtaining from Herr L. F. Nilson considerable quantities of erbia earths, which served to repeat the above experiments and confirm or modify their results. I obtained from L. F. Nilson—

1. 98 grms. erbia earth, according to Nilson about  $=165$ ; my own determination gave  $R=164.7$ .
2. 24 grms. erbia earth, according to Nilson  $R=164$  to  $165$ ; my own determination  $=165.3$ .
3. 22.5 grms. erbia earth, according to Nilson  $R$  probably greater than  $165$ ; my own determination  $R=166.9$ .

The earths Nos. 1 and 2 were obtained from the same material from which L. F. Nilson, in 1879 and 1880, obtained pure ytterbia and scandia. Both oxides had an equally fine rose colour, and the solution of the chlorides gave an absorption-spectrum with lines at  $\lambda=669.0'$ — $654.7^3$ ;  $Er\alpha$ ,  $640.0^1$ ;  $X\alpha$ ,  $558.6^1$ ;  $Sm\beta$ ,  $543.0^1$ ;  $X\beta$ ,  $539.9^2$  (?)— $523.1^3$ ;  $Er\beta$ ,  $488.8^1$  (?)— $485.5^2$ ;  $X\delta$ ,  $474.5^3$ ;  $X\epsilon$ ,  $428.5^2$   $X\eta$ .

Nilson's third erbiferous earth was obtained from materials of a different origin, and had a similar colour to the preparations 1 and 2, but with a lilac cast. The lilac-rose coloured solution of chlorides yielded an absorption-spectrum like the two other preparations, but besides the above-named lines, it displayed bands at  $\lambda=542.6^3$ ;  $X\beta$ ,  $539.9^1$  (?) ;  $\lambda$  428.8  $X\eta$  was absent in the spectrum of this substance. (The exponents placed after the wave-lengths of the bands are to show approximately the intensity, increasing with magnitude of the exponents).

(To be continued.)

### ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 181).

*Hydrocarbon*, No. 2152.—Luminous in an electric discharge tube closed with quartz; pressure = a mercurial column of 3 m.m. Exposure, twenty-five minutes. Ten new bands, decreasing very regularly in efficacy and intensity with its wave-lengths; the last band appears as a faint shadow between the two components of line No. 32.

Another proof with the same tube (No. 2153) gave, with a double width of slit (0.080 m.m.) and  $2\frac{1}{2}$  hours' exposure, the entire spectrum stronger, but still very clear, and traces of two new bands beyond 185.2.

All these spectra, I must add, like the spectrum of aluminium, have acted much more feebly in their more refrangible half than in the rest of the ultra-violet. As

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

far as the region of the most refrangible cadmium rays they consist of a deep black band, interrupted at most by single, solarised lines, which stand clear as glass. In the other part, even on the most prolonged exposure, I have never seen such a confluence of the lines, still less solarisation.

As results from the above conspectus, it is common to all the proofs that they develop a greater or less abundance of rays in the most refrangible part of the spectrum, where hitherto only the few lines of aluminium had been known; that most of them overstep the previous limit of the ultra-violet; and, further, that they finish with almost the same wave-length.

I next hoped to attain more by prolonged exposure, and by sparks of still greater energy. I increased the number of the immersed elements, as also the number of the Leyden jars; substituted for the inductorium an influence machine, which, in combination with the Riess battery, gave very energetic sparks; altered the composition of the coating of my plates, increasing the proportion of iodine, so as to heighten the sensibility; sensitised my plates by fuming with ammonia;—in short, I sought, by all means to penetrate further into the ultra-violet. But what I gained was scarcely worth mentioning. In some spectra there was a slight increase in length, but beyond the wave-length,  $182\ \mu\mu$ , not the trace of a line.

It is a phenomenon universally observed in spectral photography that the photography of greatly enfeebled rays involves extraordinary difficulties, and that exposure, however prolonged, does not yield clear images. I have regularly encountered this evil at the limit of the transparency of the material of the prism: in heavy flint-glass at the very beginning of the ultra-violet, in light flint-glass near the Fraunhofer line O, and in crown-glass near R. It is the same at the limit of the transparency of the air, the position of which, as appears sufficiently from the foregoing, depends on the thickness of the stratum of air. That the result, at any rate to a small extent, depends also on the degree of sensitiveness of the photographic plate is proved by the fact that I obtained the spectrum of the June sun (from my laboratory, about 120 metres above the level of the Baltic), beyond the Fraunhofer line U, upon Zettnow's plates, whilst the same line could not be obtained upon other plates at the same time. Still the photographic result in the most refrangible ultra violet would have fallen out far better if the light which originates on the refractive phases and in the interior of the prisms and lenses had not regularly illuminated the visual field so strongly that on prolonged exposure the whole plate is coloured more strongly than the spectrum itself. We might indeed, as I observed in 1888, with the photographic spectrum apparatus of Simony, considerably reduce the diffused light by shortening the slit length to a minimum ( $0.2\ \text{m.m.}$ ); but even here, on prolonged exposure, it overpowered the delicate impression of the most refrangible rays to total invisibility.

The contraction of the length of the slit was the last expedient which had opened up the prospect of better results as long as I was limited to the apparatus employed.

If we collate the results of the proofs obtained with a short focal distance, it follows:—

1. That on sufficient diminution of the absorption of the rays by the air, nothing further stands in the way of the exploration of the spectral region between the wave-lengths  $200\ \mu\mu$  and  $185\ \mu\mu$ , and that the existing means of observation are fully sufficient.

2. That nearly all the electrodes tried emit photographically effective light beyond the limit of the ultra-violet, as hitherto observed.

The appearance of rays beyond the wave-length  $185.2\ \mu\mu$  gave an altered direction to my work; instead of the known spectrum it now referred to the opening up of the unknown luminous region between the wave-lengths  $185.2\ \mu\mu$  and zero.

The following portion of my report treats of the means for this purpose and the present position of the solution of this problem.

(To be continued.)

ON THE  
ACTION OF IODINE ON SOME  
PHENOLS AND ALLIED COMPOUNDS IN  
PRESENCE OF FREE ALKALI, AND  
A NEW CLASS OF DERIVATIVES  
RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 183).

SALICYLIC ACID ( $\text{C}_6\text{H}_4\text{OH.CO}_2\text{H}$ ).

A SOLUTION was prepared containing 2 grms. salicylic acid and 3 grms. caustic soda in 150 c.c. of water. 15 c.c. of this solution was made up to 300 c.c. with water, the whole heated to  $60^\circ\ \text{C.}$ , and the iodine solution run in to large excess. This process was repeated until a sufficient quantity of the product was obtained. The precipitate was of a violet-red colour, and of similar appearance to that obtained with simple phenol.

The precipitate, after drying, was boiled with alcohol, but the soluble portion being so slight was neglected. The remainder was treated with warm ether, but here again only a small portion dissolved out. The remainder was boiled with chloroform, which dissolved out a rather larger quantity. The remainder was then collected and dried, when it appeared as a pinkish red pulverulent substance, which did not melt, but decomposed at a high temperature (about  $370^\circ\ \text{C.}$ ). It was cautiously heated on a mercury bath at a temperature of about  $350^\circ\ \text{C.}$  until it had lost its red colour, that is, until the "enclaved" iodine had been dissipated. The product, which was of a dirty white colour, was practically insoluble in carbon disulphide.

Total iodine of this product:—

Quantity taken =  $0.1636\ \text{gram.}$   
Silver iodide found =  $0.2120\ \text{,,}$  =  $70.03\ \text{p.c. iodine.}$

Combustion of same:—

Quantity taken =  $0.1334\ \text{gram.}$   
Water found =  $0.0117\ \text{,,}$  =  $0.97\ \text{p.c. hydrogen.}$   
Carbon dioxide  
found =  $0.1009\ \text{,,}$  =  $20.63\ \text{,, carbon.}$   
By difference .. .. =  $8.37\ \text{,, oxygen.}$

Those results may be formularised thus,  $\text{C}_{12}\text{H}_5\text{I}_4\text{O}_4$ .

Another batch was prepared from salicylic acid with a total dilution, prior to the addition of iodine, equal to about a half that used in the last case, under otherwise similar conditions.

The precipitate, which was of similar appearance, was treated with the various solvents in the same order as before. The quantities dissolved out by alcohol and ether were little more than traces, but the quantity taken out by chloroform was rather greater than in the previous case. The remainder of the precipitate from the chloroform treatment was treated with carbon disulphide, in which it almost wholly dissolved, forming a fine violet-red coloured solution. The solution was filtered and the solvent evaporated off. The residue was quite similar in appearance and properties to that similarly obtained from the simple phenol precipitate. It was powdered and heated for about two days at a temperature of about  $345^\circ\ \text{C.}$ , at the end of which time it had almost entirely lost its red colour. It was then taken for analyses.

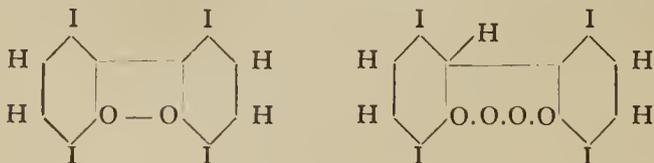
Total iodine:—

Quantity taken =  $0.1664\ \text{gram.}$   
Silver iodide found =  $0.2274\ \text{,,}$  =  $73.83\ \text{p.c. iodine.}$

Combustion of same:—

Quantity taken	= 0.1086	grm.
Water found	= 0.0078	" = 0.79 p.c. hydrogen.
Carbon dioxide found	= 0.0852	" = 21.39 " carbon.
By difference .. ..	= 3.99	" oxygen.

Those results may be represented by the formula  $C_{12}H_4I_4O_2$ . This and the substance previously examined being represented respectively, thus:—



It is apparent, therefore, that the products derived from salicylic acid are essentially the same as those from simple phenol as the result of this iodine reaction, the group COOH being wholly removed, as might have been premised.

The total iodine percentages for the precipitate obtained with salicylic acid, reported by M. and V., are 61.01, 59.73, and 60.56. It is evident from those results that they had obtained a precipitate containing on the average only one atom of iodine in each benzene nucleus (granting that the precipitate was otherwise practically the same as that examined by me). This is somewhat remarkable when compared with the case of phenol. They consider it to be the potassium salt of the iodine derivative of salicylic acid. When they digested it with acid it let fall a red powder, and when boiled with caustic potash solution it retained its iodine as the di-iodo-phenol-iodide, and passed in great part into solution. When they acidified this there fell out a white crystalline precipitate which contained iodine and melted about 165° C.; this they thought was probably the di-iodosalicylic acid already known. They represented the original precipitate thus—



Taken alongside the results found by me, it is difficult to reconcile some of those statements made by M. and V., but without fuller evidence of the essential identity of the two precipitates it would be useless to criticise them. At all events, however, it would be exceedingly unlikely that they had obtained the potassium salt of di-iodo-salicylic acid as a precipitate. Further, since they state the colour of the precipitate as being dark red, this is conclusive evidence in itself that the precipitate contained a relatively large proportion of the oxidised products, which colour is mainly due to "enclused" iodine, and such "enclused" iodine is peculiar to such products, confining those remarks to the substituted phenols and their allies.

The principal incongruities may very probably be explained away by assuming that M. and V. had only used a meagre excess of iodine in preparing the precipitate.

(To be continued).

**Examination of Lanoline.**—The method given by Helbing and Passmore (*Zeit. Anal. Chemie*, xxxii., 115) has been repeatedly examined and pronounced useless. W. Graff (*Pharm. Zeitung*) finds lanoline more or less attacked by aqueous potassa-lye. On working according to Helbing and Passmore with alcoholic potassa moderately constant results may be obtained; but the lanoline is not entirely split up at the temperature of the water-bath in two hours, so that the constant of saponification given by the above-named authors (8.536) is too low. According to Kremel 9 parts KOH are required for the saponification of anhydrous lanoline. If a hydrocarbon (vaseline) is present along with glycerin fat, the method of saponification gives utterly worthless results.

## NOTICES OF BOOKS.

*Methods of Practical Hygiene.* By Prof. K. B. LEHMANN, Wurzburg. Translated by W. CROOKES, F.R.S. In Two Volumes, with numerous Illustrations. London: Kegan Paul, Trench, Trübner, and Co., Ltd. 1893. 8vo., pp. 433 and 468.

WE have here a very comprehensive work on the methods employed in sanitary inquiries. The author has more especially kept in view the requirements of the physician, whether in private practice or as medical officer of health. But much of the instructions here conveyed will be valuable to scientific chemists, pharmacutists, and lawyers.

The author's point of view is throughout moderate and judicious. He eschews sensational and alarmist statements, and suggests no sweeping measures. Where our present knowledge is insufficient to warrant a decided opinion, he admits the difficulty. Sanitary experts who adopt his principles, which are substantially those of the late Dr. Angus Smith, will never bring Science into disrepute by contradicting each other in Court.

The present version is founded on a copy revised, corrected, and extended by the author according to the most recent investigations. The text, as may be found on a careful examination, has been literally followed. In the many cases where the differences of laws and customs in Britain and in Germany rendered it necessary, and where the views of the editor slightly differed from those of the author, footnotes have been added. The comparison of German laws and decisions on the pollution of drinking-waters, and on the sophistication of food, with those existing or proposed in Britain, should render this work especially interesting to the legal profession and to legislators.

The author begins with general methods, chemico-physical and bacteriological, followed by general indications on hygienic toxicological inquiries. Here dietetic experiments on animals are recommended as necessary, which, as the editor does not omit to inform his readers, are practically speaking illegal in Britain.

In the "special part" we have instructions for special investigations, *i. e.*, the examination of air in its physical relations and its chemical composition, and as to the quantity of corpuscular matter. This section, like most other parts of the work, is plentifully and judiciously illustrated.

The examination of soils is next entered upon, to decide whether any plots of land are suitable for human habitations, for cemeteries, or for irrigation fields. Especial attention is given to the bacteriological examination as throwing light on the occurrence of malaria. We note the interesting remark that "the Bavarian moor-lands which suffer from malaria have a striking immunity from cholera."

We agree with the editor that Prof. Lehmann seems disposed to under-estimate the dangers of grave-yards. We cannot find that he refers at all to cremation.

Water meets with elaborate treatment. Its examination—chemical, microscopic, and bacteriological—is very fully described. There are also chapters on river-pollution, on sewage, and on filters. The suitability of a water for technical purposes is merely sketched.

Next we arrive at the general methods for the examination of foods. The "chemical preservatives" now often added to foods very rightly find here little favour. The reasons against the use of such additions are given in a manner which must commend itself to every person able and willing to judge.

Following on the general examination of foods come the special sections on the scrutiny of meat, including the detection of animal and vegetable parasites, poisons, and incipient decomposition. Preserved meats are similarly scrutinised.

Next follows milk. We are glad to note that the lactoscope, the lactometer, and the cremometer meet here with little countenance. For the determination of fat the Adams and the Soxhlet methods are recommended. The microbia commonly found in milk—some of them pathogenic—are duly noticed. Of these the most important is the bacillus of tubercle. The "cow-house test" is described in full.

Butter and cheese, with their alleged adulterations, follow next, though some reported sophisticants are considered as not proven.

Under flour and bread come instructions for detecting diseased grains of cereals and the seeds of weeds, such as corn cockle and—above all—ergot. The last-mentioned product contains *three* poisons,—the paralyzing ergotic acid, sphacelic acid (which occasions gangrene), and the highly poisonous cornutine. Concerning the physiological action of the seeds found accompanying grain, the statement of observers are often discordant. "Panin-meal" consists of dirty crusts collected in hotels, &c., slightly roasted, ground up and mixed with flour, or used to thicken soups. We have not yet acclimatised this unpleasant fraud in Britain.

In preserved fruits and vegetables the addition of copper is shown to be undesirable, but less dangerous than it is commonly supposed.

Our knowledge of fungi is insufficient. Their value as foods is much lower than a mere determination of their nitrogen might seem to prove, since much of this nitrogen is present in the form of non-assimilable amido-compounds.

A section is devoted to sugar, honey, and Fahlberg's saccharine, which the author pronounces non-poisonous.

Coffee seems to have been selected as the especial notion of fraudulent ingenuity—witness the spurious coffee-beans made on the Continent. Here very drastic legislation is urgently needed.

As regards cocoa and chocolate, the Association of German Chocolate-makers have done much to discourage fraud. Any addition of starch must be shown on the packages. Spices seem to be grossly falsified abroad. Factories exist in Austria for preparing so-called matta-powder—an abominable mixture with sometimes lead chromate, and which is used for sophisticating pepper, cassia, pimento, &c.

The various fermented and distilled liquors are discussed at great length. The attempt to counteract the "plastering" fraud by the addition of barium chloride may lead to serious consequences.

Clothing and its materials are next considered from a hygienic point of view, and with especial reference to different climates.

An important section is taken up with the sanitary examination and decision on dwelling-houses. Here we have notice of cellar-dwellings, roof-dwellings, walls, windows, artificial lighting, coal gas, petroleum, the electric light, ventilation, heating, water-supply, house-sewage, and closets. Next we have the hygienic examination of household appliances by which poisons or infections may be introduced. Disinfection is finally judiciously considered.

To all the more important sections there are appended very full references to the literature of the subject.

Prof. Lehmann's book must form an invaluable work of reference for medical officers of health, public analysts, town clerks, and in general to all medical men, chemists, and engineers, who ever have to concern themselves with sanitary questions.

*Agricultural Journal.* Published by the Department of Agriculture of the Cape Colony. Vol. vi., Nos. 15 and 16.

IN an article borrowed from the *Melbourne Weekly Times* we find the following sensible caution:—"The secret of

successful irrigation is only to apply the water as often as in your judgment the plants or trees seem to require moisture." How different is this from the practice of our sewage irrigationists.

The prickly pear, invaluable for fences, but now becoming—both at the Cape and in Australia—a very troublesome weed, is now being combated with sodium arsenite! We fear that without due care and judgment the remedy may become as bad as the disease.

The banana crop is now threatened by the "banana blight," but spraying with "Bordeaux broth" (copper and lime) seems to be an effectual remedy.

The fruit trade seems to have a great future before it. The Union and Castle lines of steamers enter thoroughly into the spirit of the trade.

The name wire-worm, generally applied in the old country to the larvæ of certain Elaters so destructive to root crops, is now extended to *Strongylus contortus*, recently known as *Filoria hamata*, which is as dangerous to sheep as the other wire worm is to vegetation.

The farmers and gardeners are much exercised by the inroads of the spring hare (*Pedetes capensis*), a burrowing species.

We hope that the *Agricultural Journal* may be duly appreciated as it undoubtedly deserves.

## CORRESPONDENCE.

### PREPARATION OF HYDROGEN.

*To the Editor of the Chemical News.*

SIR,—Referring to Mr. John Ball's letter on the "Preparation of Hydrogen," which appeared in the *CHEMICAL NEWS*, vol. lxxviii., p. 184, your readers may be interested in knowing that I used a solution of cobalt nitrate for the rapid evolution of hydrogen for laboratory and lecture room use when I was lecture-assistant to the late Prof. W. Dittmar, of the Anderson's College, in 1876, not considering at the time it being anything new.—I am, &c.,

G. C. MACDONALD.

4, Roslea Terrace, Kelvinside, Glasgow,  
October 14, 1893.

### BIARIUM SULPHATE IN SANDSTONE.

*To the Editor of the Chemical News.*

SIR,—In reference to the above it may be of interest to Prof. Clowes to know that barium sulphate occurs in the millstone grit at Houghton's Quarry, near Skelmersdale, in Lancashire. The rock is a fine-grained white sandstone, the cementing material being largely carbonates of lime and magnesia (dolomite in joints), and containing also a little barium sulphate, which may be found compact in crevices. The actual amount in the rock was not determined quantitatively.—I am, &c.,

H. T. MANNINGTON.

Flint, North Wales,  
October 16, 1893.

**Medal.**—Dr. A. B. Griffiths has been awarded a bronze medal by the Committee of the Gardening and Forestry Exhibition (Earl's Court) for his books on Manures and "in testimony of the appreciation in which the Committee hold his valuable aid in contributing to the Exhibition."

**Distinction between Natural Butter and Margarine.**—F. Gantter.—The author concludes that pure butter fat, with the sulphuric acid test, must take merely a straw or reddish yellow colour, but not a deep brown. Its iodine number must not exceed 16.—*Zeit. Anal. Chemie*, xxxiii., Part 4.

## 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. cxvii., No. 14, October 2, 1893.

**Fixation of Iodine by Starch.**—G. Rouvier.—The author has obtained the following results:—The weights of starch remaining the same, as well as the other conditions of the experiment, if we increase the percentage of iodine employed the quantity of iodine fixed increases at first progressively. If we employ iodine in sufficient quantity we obtain a compound the percentage of iodine in which differs very little from 19.6, corresponding to the formula  $(C_6H_{10}O_5)_{16}I_5$ . He has never obtained a larger proportion. The weights of iodine and of starch remaining the same, as well as the other conditions of the experiment, if the volume of the mixture continually increases, the quantity of iodine fixed decreases, though on condition that we do not use a quantity of iodine much greater than that necessary for obtaining the proportion of 19.6 per cent.

*Zeitschrift für Analytische Chemie.*

Vol. xxxii., Part 3.

**Examination of Paper.**—M. Stockmeier (Eleventh Congress of Bavaria Technical Chemists).—The author extends previous researches on the injurious action of certain papers on leaf-metals. He tests the papers on Kämmerer's principle for their behaviour with leaf-silver by stratifying five samples of the papers to be examined with leaf-silver, folding the packets together, and letting them lie for twenty hours at 50° between watch-glasses in a place free from acids and hydrogen sulphide. If the metal is visibly attacked or discoloured, the paper is unfit for wrapping objects of metal. For the detection of sulphurous acid (which renders papers unfit for packing steel wares) the author distils 50 grms. of the sample in a current of steam in an apparatus filled with carbonic acid, and receives the distillate in iodised potassium iodide. Papers containing chlorides or alums are not suitable for packing articles of steel. Sulphurous acid or sulphites may be detected in papers by conversion into hydrogen sulphide by means of zinc and phosphoric acid. The absence of substances which give off hydrogen sulphide with acids must first be ascertained. For the detection of free sulphuric acid the author (in concert with Wurster) finds Congo paper too sensitive. He extracts 10 grms. of the paper in question with alcohol in an Erlenmeyer flask, concentrates the extract to a minimum with the addition of water, and tests the drop of liquid thus obtained with methyl violet. A simultaneous blank experiment must give a negative result.

**Analysis of Iron.**—This and the following paper are too voluminous to be inserted in full.

**Determination of Phosphorus in Steel and Iron.**—A. von Reis (*Stahl und Eisen and Zeit. f. Angew. Chem.*).

**Examination of Salipyrine.**—J. Altschul (*Pharm Central Halle*).—The author dissolves 3.26 grms. of the specimen in a little alcohol diluted with half its volume of water, heating on the water-bath, and titrates with normal alkali until redness appears, using phenolphthalein as indicator. The tenths of a c.c. consumed give at once the percentage of antipyrine salicylate in the sample. Antipyrine has no action upon phenolphthalein.

**Determination of Alkaloids.**—Ledden Hulsebosch.

**Determination of Resinous Matter in Jalap.**—F. H. Alcock.—From the *Pharm. Journ.*, 1892, 1154, p. 107.

**The Atomic Weight of Nickel.**—G. Krüss and F. W. Schmidt.—The authors conclude that purified nickel of the atomic weight 58.6 still contains small quantities of a substance of a high atomic weight.

## MISCELLANEOUS.

**The Glasgow and West of Scotland Technical College.**—The secretary of this establishment has kindly sent us a syllabus of the lectures to be delivered before its members during the ensuing winter session. Most of the subjects selected seem to belong rather to mechanical engineering than to chemistry or its applications. We may, however, call attention in particular to the lectures by Dr. G. G. Henderson, F.C.S., on the "Evolution of the Lucifer Match," and that by Dr. E. J. Mills, F.R.S., on "Water and Water Supply," a subject which during the past summer has been forced somewhat unpleasantly upon the notice of the public. One lecture, to be delivered by Dr. John Young, Professor of Natural History, Glasgow University, entitled "The Medallie Art of Renaissance," seems, if we understand its title aright, to have been more suited for discussion by a Royal Academician than by a professor of natural history. Mr. A. Humboldt Sexton's survey of a century's technical education in Glasgow must doubtless have proved highly suggestive.

**The Stas Memorial.**—The following announcement has been circulated among the subscribers to the Stas Memorial Fund:—"The Committee formed to do homage to the memory of Jean Servais Stas was definitely constituted on December 13, 1892, the anniversary of the death of the illustrious *savant*. During the following month the list of subscriptions was circulated; the money received was deposited in the State Saving's Bank till required. The subscription will remain open till May 1, 1894. The chief object the Committee had in view in appealing to the public was to reprint the works of Stas. This work, from which the Executive Committee does not assume the right to eliminate any important matter, forms three quarto volumes of from 500 to 600 pages each. The first volume includes the memoirs and work specially devoted to the atomic weights; the second volume contains notes and notices, reports, and discourses; the third volume contains posthumous works, especially relating to spectroscopic researches. The edition will be published under the direction of MM. Spring and Depaire. Arrangements have been made to enable the work to be finished within a year. The resources actually at the disposal of the Committee have enabled them to entrust this part of their work in the hands of a competent publisher. What ultimately remains from the subscribed money will go towards the erection of a monument. It will not be disposed of till after the publications are issued. The three volumes of the complete works of Stas will be published simultaneously at the price of thirty francs. Every one who has subscribed a sum of at least twenty francs will receive a copy gratuitously. Subscribers whose contributions are below that amount may increase their subscriptions up to the above sum. The Committee will be obliged if you will communicate this decision to those who may be interested in it. Names of subscribers will be published in an appendix to the last volume."

## 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.

**Books.**—Could any correspondent tell me the best books, editors, and publishers on Coal Gas Analysis and Roman and Portland Cements Analysis?—ENQUIRER.

## MEETINGS FOR THE WEEK.

FRIDAY, 27th.—Physical, 5. "On Air-Core Transformers," by E. C. Rimington. Two Experiments by W. B. Croft, M.A., on the Rings and Brushes in Crystals, and Electrical Radiation in Copper Filings.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1770.

FERMENTATION IN THE LEATHER INDUSTRY.\*

By JOSEPH T. WOOD.

THE science of Bacteriology touches upon the leather industry in the following important points:—

1. Putrefaction.
2. The soaks.
3. Changes in lime liquors.
4. Bating or "puring."
5. Drenching.
6. Fermentation of tan liquors.

I only propose to give a short *resumé* of our present knowledge of the "drenching" process, as this closely resembles ordinary fermentations.

Skins from the bate after washing are placed in vats containing an infusion of bran in water (0.4 to 1 per cent of bran) at a temperature of 30° to 35° C. This ferments vigorously for 18 to 24 hours, with evolution of considerable quantities of gas and the formation of weak organic acids, which have a slight swelling action on the skin, cleanse the pores, and make it in a fit condition to receive the tannin. On examination with a high power of the microscope the liquid is found to be swarming with active bacteria. They are mostly in the form of pairs or dumb-bells, each cell 0.75  $\mu$   $\times$  1.25  $\mu$ ; some form chains. I described (*Journ. Soc. Chem. Ind.*, ix., 27) a method by which the organism causing the fermentation was separated, as it refused to grow in ordinary nutrient gelatin; and lately, in conjunction with Mr. W. H. Willcox, B.Sc., have made a complete examination of the products of the actual fermentation, previous to carrying out a similar research with the pure ferment.

We found the following gases evolved:—

Gases.	A.	B.	C.
CO <sub>2</sub> and H <sub>2</sub> S .. ..	21.9	25.2	42.4
O <sub>2</sub> .. .. .	1.0	2.1	3.6
H <sub>2</sub> .. .. .	53.1	46.7	28.2
N <sub>2</sub> .. .. .	24.0	26.0	25.8

- A is from a vat containing no skins, 1—2 days.  
B from a vat containing skins, 2—3 days.  
C from a vat containing skins, 3—4 days.

The H<sub>2</sub>S is present only in small quantities (1—2 per cent).

The principal acids found were acetic and lactic, accompanied by small quantities of formic and butyric acids.

The following Table shows the quantities found in an experimental drench per 1000 c.c.:—

	Grms.
Formic acid .. .. .	0.0306
Acetic acid.. .. .	0.2402
Butyric acid .. .. .	0.0134
Lactic acid.. .. .	0.7907
Total .. .. .	1.0749

We find in actual work that the quantity of acid produced varies from 1 to 3 grms. per litre. We found that an unorganised ferment, "*cerealin*," changes the starch of the bran into glucoses and dextrin; the bacteria then ferment the glucoses, splitting them up with evolution of gases and formation of acids.

The bacteria causing the fermentation have no action on the cellulose of the bran nor on the skins, as some bacteria in the bate have; in every case where the skin is attacked it is by putrefactive or gelatin liquefying bacteria introduced from the bate, or in specially favourable circumstances (hot sultry weather) developing from germs always present in the atmosphere. The gases evolved have only a mechanical action on the skin, floating and distending them, and so enabling them better to take up the acids. In carrying out this work we discovered a delicate test for lactic acid.

The presence of lactic acid was shown in the following manner:—10 c.c. of the liquid were placed in a small distilling flask along with 2 c.c. strong H<sub>2</sub>SO<sub>4</sub> and about 0.5 gm. potassium chromate in a little water. This was distilled and the vapours received in a test-tube surrounded by cold water; on adding magenta solution decolourised by SO<sub>2</sub> to the liquid in the test-tube, a red colour was produced by the aldehyd formed from the lactic acid; aldehyd was also recognised by its smell. We find this an exceedingly delicate test for lactic acid, and as far as we know it is quite new in this form.

For 10 c.c. of liquid to be examined we find 2 c.c. strong H<sub>2</sub>SO<sub>4</sub> and 1 gm. of potassium chromate to be the best proportions. Formic, acetic, propionic, butyric, valerianic, succinic, malic, tartaric, and citric acids do not give the reaction.

In conclusion, there are no doubt other organisms capable of fermenting a bran infusion in a somewhat similar way, and the work of isolating and separately examining their life history and products yet remains to be done.

THE VOLATILITY OF PYROPHOSPHORIC ACID.

By GEORGE WATSON, F.C.S.

ORTHOPHOSPHORIC acid, according to the text-books, is dehydrated into pyrophosphoric acid at a temperature of 215° C., and into metaphosphoric acid at a red heat, at which temperature the latter is slowly volatilised, but no statements regarding the volatility of pyrophosphoric acid have, to my knowledge, been recorded.

The possibility of the latter being volatile suggested itself to me from noticing the behaviour of a strong solution of orthophosphoric acid during concentration. About 2 kilos. of the "ortho" acid, having a specific gravity of 1.750, was being heated in a platinum basin, in order to expel a trace of nitric acid which it contained. The basin was heated by means of a Fletcher's small ring radial burner; the temperature, obviously, never at all approaching redness. Nevertheless, when all the free water had been driven off (which could be approximately told from the bubbles of evolved steam becoming very much smaller in size) a bluish white smoke began to rise from the acid. On holding a test-tube, wetted externally, in this smoke for a few minutes (having first turned off the gas in order to prevent the projection of any drops of acid on the tube) the film of water was found thereafter to contain a very perceptible quantity of phosphoric acid. A warmed thermometer on being plunged into the acid indicated a temperature of 290° C. at the surface; while on being thrust to the bottom, the mercury rose to 330° C., upon which the thermometer was withdrawn. From this observation it was evident either that metaphosphoric acid was formed at a temperature of 290° C. and was volatile at that temperature, or that the acid volatilising was the "pyro" one.

Before proceeding to examine the question systematically, a tentative experiment was made by exposing 19.362 grms. of phosphoric acid, of 1.750 sp. gr., in a platinum capsule to a moderate heat over a radial burner, the gas being turned down till the flame was about 2 c.m. from the bottom of the capsule. The amount of orthophos-

\* Abstract of a Paper read before the British Association (Section B), Nottingham Meeting, 1893.

phoric acid contained in the acid used was 90.20 per cent, from which it is calculated that the weight of "pyro" acid obtainable from the 19.362 grms. taken should be 15.860 grms. After one and a half hour's heating the weight of the residue was found to be 14.450 grms. and after other two hours heating 14.295 grms., thus showing a loss of about 1.5 grms.

A series of experiments was then performed as follows:—

A small quantity, usually about 0.5 gm., of the syrupy phosphoric acid mentioned above was weighed into a platinum capsule, which was then placed in a Rammelsburg air-bath. A thermometer, wound with a strip of asbestos cloth, was fixed into one of the holes in the bath lid, the bulb resting on the tray close to the capsule, while the other hole was plugged with a roll of asbestos cloth. The bath was then placed in a large tin can (a phosphorus tin) and the whole heated by means of a radial burner. With this arrangement the temperature could be kept fairly steady, a few degrees only of variation taking place, but an eye was kept on the thermometer pretty constantly as well during each experiment. Undernoted are the particulars:—

*Experiment 1.*—1.363 grms. of phosphoric acid, heated to 215° C. for five hours, gave a residue weighing 1.172 grms. The calculated weight of "pyro" acid being 1.116 grms., dehydration was therefore incomplete.

*Experiment 2.*—Acid taken, 0.4645 gm.; heated for five and a half hours to 215° C., residue weighed 0.391 gm.; heated next day for another six hours to 225° C., residue weighed 0.389 gm.; calculated weight, 0.3805 gm. Dehydration still incomplete.

*Experiment 3.*—0.5565 gm. phosphoric acid, heated for ten hours for 220–225° C., residue weighed 0.470 gm.; heated other three hours next day to 215° C., residue weighed the same; heated following day for other seven hours to 215° C., weight of residue unchanged. The residue was then converted into magnesian pyrophosphate, which was found to weigh 0.5655 gm.; this is equal to 0.4534 gm. of "pyro" acid, or 0.4992 of the "ortho" form. As the residue weighed 0.470 gm., it follows that the conversion into the "pyro" modification was again incomplete, while the calculated weight of "ortho" acid in the 0.5565 gm. taken being 0.5019 gm., it is evident that no volatilisation had taken place, the slight loss of 2.7 m.grms. being probably due to errors of experiment.

*Experiment 4.*—0.448 gm. acid, heated for seven hours to 230–235° C., residue weighed 0.3735 grms.; heated next day for other seven hours to the same temperature, residue weighed 0.3755 gm. It was then converted into magnesian pyrophosphate, and gave a precipitate of 0.4587 gm.; this is equal to 0.3678 gm. of pyrophosphoric acid, which on subtraction from 0.3735 leaves 5.7 m.grms. of water still present. Calculating the magnesian salt into orthophosphoric acid, we get 0.4049, while the weight contained in the 0.448 gm. taken is 0.4041 gm. This shows no loss by volatilisation.

*Experiment 5.*—0.535 gm. acid, heated to 255–260° C. for six and a half hours, residue weighed 0.427 gm., which on conversion into magnesian salt gave a precipitate of 0.5340 gm. This is equal to 0.4281 gm. of "pyro" acid, or 0.4715 gm. of "ortho" acid, which on deduction from 0.4825 (the weight of H<sub>3</sub>PO<sub>4</sub> in the 0.535 gm. of acid taken) gives a loss of 0.011 gm.

*Experiment 6.*—0.4 gm. acid, heated to 280–285° C. for seven hours, residue weighed 0.3055 gm.. After heating next day for other seven hours it weighed 0.2905 gm.; other seven hours' heating gave 0.2755 gm. The magnesian pyrophosphate obtained from this weighed 0.3458 gm., which is equal to 0.2766 gm. of "pyro" or 0.3053 gm. of "ortho" acid. The weight of "ortho" acid in the 0.4 gm. taken being 0.3608 gm.; this indicates a loss of 0.0555 gm.

*Experiment 7.*—0.433 gm. acid, heated to 280–285° C. for seven hours, residue weighed 0.3315 gm. The weight of magnesian pyrophosphate obtained from this was

0.4151 gm., which is equal to 0.3328 gm. of "pyro" acid, or 0.3665 gm. of "ortho" acid. The weight of "ortho" acid taken being 0.3905 gm., a loss of 0.024 gm. is shown.

*Experiment 8.*—0.5087 gm. of acid, heated to 285–290° C. for the following periods of time:—

3 hours.	Residue weighed	0.4002 gm.
6 "	" "	0.3702
7 "	" "	0.3610
3 "	" "	0.3442
7 "	" "	0.3150

On conversion into magnesian pyrophosphate, a precipitate weighing 0.3915 gm. was obtained. This equals 0.3139 gm. of "pyro" acid, or 0.3456 gm. of "ortho" acid. Deducting this from the weight of "ortho" acid taken (0.4588 gm.), a loss of 0.1132 gm. is indicated.

An experiment at a temperature of 290–300° C. was also made, and the residue tested for "meta" acid by dropping a solution of baric chloride on it and allowing to stand. A small quantity of "meta" was indicated.

From these experiments I conclude—

(a) That orthophosphoric acid is not completely dehydrated into pyrophosphoric acid at temperatures below 230–235° C.

(b) That orthophosphoric acid is completely converted into the "pyro" modification at a temperature of 255–260° C., the pyrophosphoric acid being volatile at the same temperatures. Hence it is probable that the temperatures of complete formation and of volatility may be identical; in which case orthophosphoric acid will be analogous to orthoboric acid, which is dehydrated into metaboric acid and slowly volatilised at a temperature of 100° C. (see Roscoe and Schorlemmer, "Treat. on Chem.," vol. i., p. 552).

(c) That metaphosphoric acid is on the verge of formation at temperatures about 290–300° C.

## BORON-EISEN.

By H. N. WARREN, Research Analyst.

SILICON-EISEN, chromeisen, alumin-eisen, zinc-eisen, and various other ferro-compounds, are all familiar names, either in the works or laboratory; there still, however, remain gaps to be filled, as in organic regions; one of which, namely, the boron compound, which has lately been successfully procured, is now being further experimented with by the writer, and to which the name boron-eisen has been given, signifying boron-iron.

Boron, unlike most other elementary substances, presents so much difficulty in its estimation that, when present in small quantities, it is too often entirely overlooked; its slight affinity also for other elements presents a grave difficulty in obtaining a regulus; not unfrequently have the buttons procured from the dry assay of iron ores that have been performed under my notice, when subjected to analysis, revealed a total of one or two per cent wanting, and in most cases where borax had been employed as a flux the difference has been found to be boron.

The first preparation of this substance of a definite character was brought about by the addition of a solution of borax to one of ferrous chloride; the white precipitate of ferrous borate thus obtained being pressed to free it from adhering water, and after thoroughly drying, reducing it with an equivalent proportion of carbon in plumbago crucibles. In this way boron from 4 to 5 per cent enters into union with the iron, producing a compound breaking with the fracture of metallic manganese, and presenting sufficient hardness to readily scratch glass, at the same time being with difficulty soluble in acids; the melting-point of the compound approaching that of cast-iron.

A more economical method has since supplanted the former—by reducing ferric carbonate, or oxide, in admixture with boron oxide and charcoal. In this, as in the former method, a number of minute precautions are necessary in order to obtain the desired compound, which if performed dexterously results in the boric oxide gradually reducing and alloying with the iron. The most peculiar property of this compound is its great predominancy when in admixture with large quantities of iron; one ounce of the boride thus melted with about two pounds of iron causes the whole to break with almost an analogous fracture of the boron compound itself, whilst at the same time it contains but the fraction of a percentage of boron. The boron iron thus produced casting more soundly, expanding slightly, and being free from blow-holes.

The average of several analyses of the compound prepared at high temperatures are the following:—

Iron .. .. .	94.08
Boron .. .. .	4.02
Combined carbon . . . .	1.50
Phosphorus .. .. .	0.09
Sulphur.. .. .	0.31
Silicon .. .. .	trace
Manganese .. .. .	trace
	100.00

Several other curious compounds of boron not hitherto dealt with will shortly appear.

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18, Albion Street, Everton, Liverpool.

### ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 195).

#### *The Photograph of the Spectral Region beyond the Wave-length 185.2 μ.*

ACCORDING to the foregoing proofs the most refrangible rays of aluminium had entirely lost their energy in a stratum of air of 17 metres in thickness; at 2 metres of air they had left upon the plate an impression capable of being developed, and at a distance of the spark from the plate a good photograph. Their photographic action and its intensification were not in consequence of a heightened intensity of the spark, but of the diminished resistance which the rays encountered on their way to the plate. The spark was quite sufficient, but the energy of the rays was defective. When they had passed through a great length of air, their photographic efficacy at its entrance into the silver particles of the plate was no longer strong enough to set up its decomposition to a sufficient degree. The preservation of the energy of the rays was therefore the point upon which a better result must be founded.

In all probability, even at the smallest focal distance which I have employed, the loss of energy of the rays was very considerable in consequence of various hindrances which they encountered on their way. If this loss could be diminished further success was in view. That such diminution was possible was beyond all doubt. Even the removal of the air which still intervened between the spark and the plate (though only in a stratum of moderate thickness) promised appreciable advantages. But the air was not the sole obstructive absorbent which

the rays encounter on their way. Quartz absorbs the most refrangible rays to a perceptible extent (L. Soret, *Arch. des Sciences Phys. et Nat.*, lxi., 332—334, 1878); also glycerin (W. A. Miller, *Phil. Trans.*, clii, 871, 1862), with which the halves of my quartz prism were corrected; and also gelatin, even in a thin stratum, obstructs them visibly (Soret, *Arch. des Sc. Phys. et Nat.*, III. period., x., 453—455, 1883).

If these hindrances existed, and if their renewal or their great reduction was possible, a further increase of photographic energy would be secured.

The photographic effect is not merely a function of the energy of the rays—it depends above all on the behaviour of the sensitive plate. The more unstable the chemical combination of the sensitive constituents of the coating of the plate, the more its loosening during the action of the rays is assisted (Sensitiveness, H. W. Vogel, "Handbuch der Photographie," iv. edition, 1897, pp. 172, 193, 208), the more rapid is its decomposition on exposure. If it were possible to assist in this manner the more refrangible rays, the prospect of success would become more favourable.

Delicate details in a photograph, faint luminous impressions, require a plate quite free from any veil. They become turbid, doubtful, and often disappear again if the ground issues from the developing-bath not clear as glass, but covered with a grey layer.

As already mentioned, this case occurred regularly in my proofs on prolonged exposure. The dispersed light from the interior of the apparatus, the cause of this veil on the plates, is composed of rays of all degrees of refrangibility; but only those for which the plate is most sensitive have a veiling action. These, with gelatin plates and spark light, are the rays of less refrangible ultra-violet,—those, therefore, which are not wanted for my purposes. If I could keep them out of my apparatus my proofs would be still further the gainers. Not merely was there secured greater clearness for the more delicate impressions, but the design of the entire proof was improved.

This consideration led to a series of researches which had to precede the resumption of my original work. These preliminary operations consisted in:—

1. In ascertaining the influence of all absorbents which come into play in the photographic action of the most refrangible rays of spark light.
2. In the utilisation of the results thus obtained for the creation of better means of observation for the spectral region in question.

The only exception here was glycerin, which could be disregarded, since the double prism of the apparatus works correctly without being cemented together. The glycerin was only to prevent the loss of light occasioned by the reflexion which arises on the planes of the two single prisms if left uncemented.

The absorptive behaviour of quartz and gelatin with the most absorptive rays of aluminium has certainly been very carefully determined by Soret. But he has only employed the eye-piece. His results do not, therefore, necessarily agree with those of the photographic plate.

The relations of brightness of the wave-lengths, as ascertained by Soret, according to the fluorescence have always a relative value.

(To be continued.)

**Influence of Organic Solvents upon the Rotatory Power of the Tartaric Ethers.**—P. Freundler.—All the solvents, except carbon disulphide, act in the same direction upon the chemical molecule of the tetra-substituted tartaric ethers. Hence Biot's law is confirmed, and the variations of the rotatory power furnished by certain solvents are due to a dissociation.—*Bull. de la Soc. Chim. de Paris.*

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

## ON ERBIA.\*

By GERHARD KRÜSS.

(Continued from p. 194).

ALL the preparations were excellent erbia materials, as appears from the values obtained for R. Nilson's preparations Nos. 1 and 2 were united as—

*Erbia Material No. 9.*

This material fractionated in the state of hydroxide by successive treatments with aniline hydrochlorate gave—

Series 17.

← Stronger bases.				
"Aniline solutions."				
1	2	3	4	5
164·8	165·1	166·1	167·2	—
Weaker bases →.				
"Aniline solutions."				
6	7	8	9	10 (Residue).
167·9	168·1	168·6	166·4	161·5

Fraction 10 of this series was the precipitate remaining from the solution No. 9. It was selected small in weight (about 2 grms.). It is remarkable that there was no increase of the R value in the direction of Yb = 173, but a decline, so that I tested for scandia, but without result.

Fraction 10, in the state of a neutral sulphate, was treated by suspending in it crystals of  $K_2SO_4$ . There appeared a slightly flocculent precipitate, like an earthy hydroxide, which, after gentle ignition, appeared reddish, and was insoluble in hydrochloric acid. The nature of this body could not be determined on account of its small quantities. But this substance has perhaps occasioned the decrease of the R value in fraction 10, Series 17; for after filtering off this deposit, the liquid was concentrated until  $K_2SO_4$  was separated out. It contained an earth, R = 166·7, and its filtrate, R = 168·6.

For the further elaboration of fractions 1 to 9, Series 17, 1 and 2 were united as substantially identical. Then the most feebly basic portion of a fraction is first eliminated by treatment with aniline hydrochlorate and transferred to the nearest fraction on the side of weaker basicity; that is, the aniline precipitate from fraction (1+2) can be transferred to fraction 3, the precipitate from the present fraction 3 to fraction 4, and, lastly, the aniline precipitate from fraction 8 to fraction 9,

The reverse was now taken in order to bring the more strongly basic constituents of one fraction into the adjacent fraction on the side of stronger basicity, *i.e.*, the aniline solution from fraction 9 was brought over to fraction 8, and that of fraction 4 to fraction 3, &c. The analysis of the fractions then showed—

Series 18.

Stronger bases ←.									
→.									
(1+2)	3a	3b	4	5	6	7	8	9	—
162·9	163·3	164·7	—	165·9	167·2	166·8	168·3	—	—

Fractions 1+2 and 3a of Series 18 were excluded in the further elaboration of the material for Er = 166 or 167, as being too strongly basic. It must be remarked that the determinations of the equivalents of fractions 5 to 8 (Series 18) had given values which in fact might lead us to conjecture the non-existence of an erbium with R = 166 or 167 to 168. This is the same phenomenon to which attention was called above on the decomposition of the erbia materials Nos. 6 and 7.

In order in the fractions 3b—9 (Series 18) to bring from

every fraction small quantities of the more strongly basic oxides to the corresponding side, and more feebly basic oxides to the other side of the series of fractions, these earths were worked up by aniline precipitations and aniline solutions on the same system as fractions 1—9 (Series 17), After carrying out these operations the analysis of the earths gave the following values:—

Series 19.

← Strong bases.					
8 (dissolved)	3b	4	5		
165·5	167·4	165·1			
Weak bases →.					
6	6/7	7	7/8	8	9
170·2	172·5	168·3	—	167·1	168·5

If in the fractions 5 to 8 of Series 18 there had been present an erbium with a constant R between 166—168, this must have come in evidence still more in the values found for the fractions of Series 19 than in Series 18. Here, also, as on working up the material No. 8, it was found that as other earths are approximately removed from the erbia material the earth with R = 166—168 becomes relatively unstable in contact with aniline hydrochlorate. The fluctuations in the values of the so-called atomic weights which could not be ignored appear considerably stronger in Series 19. To this point we shall return in the sequel.

(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 SEPTEMBER 30TH, 1893.

By WILLIAM CROOKES, F.R.S.,

and  
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,  
Professor of Chemistry at the University of Oxford.

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

London, October 9th, 1893.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the 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 September 1st to September 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 182 samples three were recorded as "clear, but dull," the remainder being clear, bright, and well filtered.

The meteorological conditions during the month of September have been of an entirely abnormal character. An excess of bright sunshine and high temperature have stimulated the fluviate vegetation on which the purity of running streams in great measure depends, and have promoted the oxidation of the traces of organic matter always present in river and lake water. The rainfall, as registered at Oxford, has been remarkably small. The

\* *Zeitschrift für Anorganische Chemie.*

mean rainfall of September, from an average of twenty-five years, is 2.66 inches, whereas the actual rainfall has only been 0.57 inch, showing a deficiency in the month of over 2 inches, and of no less than 3.64 inches for the four months June to September. This deficiency of rain has tended to increase the organic purity of the river, as little or no peaty colouring matter has been washed into it from the collecting area.

How little impurity has been present will be seen from the following table, in which a comparison is shown between the average composition of the five Thames-derived waters for last month with that of the same waters in September, 1892, on which occasion we spoke of the composition and purity of the waters as being "entirely satisfactory."

Comparison of the Averages of the Five Thames Supplies for the Months of September, 1892 and 1893.

	Common salt per gallon.	Nitric acid per gallon.	Oxygen required per gallon.	Organic carbon per gallon.	Colour.
	Means.	Means.	Means.	Means.	Means.
Sept., 1892	2.195	0.947	0.043	0.083	15.1 : 20
„ 1893	2.163	0.570	0.026	0.057	12.2 : 20

It is not probable that so exceptional a state of things will last much longer, and as cold, wet weather comes on, a slight increase of vegetable organic matter and peaty colouring matter may be expected.

We are, Sir,  
Your obedient Servants,  
WILLIAM CROOKES.  
WILLIAM ODLING.

ON THE  
ACTION OF IODINE ON SOME  
PHENOLS AND ALLIED COMPOUNDS IN  
PRESENCE OF FREE ALKALI, AND  
A NEW CLASS OF DERIVATIVES  
RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 196).

RESORCINOL (C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>).

A QUANTITY of the precipitate obtained by the action of iodine on resorcinol was prepared under conditions similar to those set up in the case of the red-violet phenol precipitate (60° C.). In this case only a small proportion of the precipitate was obtained until after acidification. The precipitate was of a dark purple red colour, and of brittle character when dry. It was powdered and boiled direct with chloroform as long as anything dissolved out. The portion dissolved out by the chloroform was very little, and was neglected.

The remainder of the precipitate from the chloroform treatment was almost entirely insoluble in carbon disulphide. It was therefore cautiously heated at a temperature of about 350° C. until it was deemed to have lost all its "enclined" iodine. It was then taken for analysis.

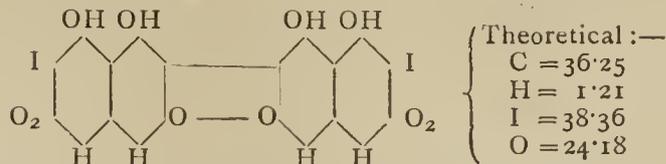
Total iodine:—

Quantity taken = 0.1580 gm.  
Silver iodide found = 0.1105 „ = 37.78 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1309 gm.  
Water found = 0.0172 „ = 1.46 p.c. hydrogen.  
Carbon dioxide found = 0.1762 „ = 36.70 „ carbon.  
By difference .. .. = 24.06 „ oxygen.

Those results may be represented by the formula C<sub>20</sub>H<sub>8</sub>I<sub>2</sub>O<sub>10</sub>, or constitutionally thus:—



The high percentage of carbon found was no doubt due to slight decomposition, as the result of heating.

A second batch was prepared with the following proportions:—1 gm. resorcinol, 1.2 grms. caustic soda in 600 c.c. of water at 60° C. The precipitate was similar in appearance to the one just treated of. It was boiled with chloroform in successive portions till nothing more dissolved out. The portion soluble in chloroform, which was very small, was recovered, dried, and the iodine estimated.

Total iodine of the chloroform-soluble portion:—

Quantity taken = 0.1059 gm.  
Silver iodide found = 0.1560 „ = 79.66 p.c. iodine.

The remainder of precipitate, insoluble in boiling chloroform, was cautiously heated until the "enclined" iodine was driven off. (This portion was also insoluble in carbon disulphide). It was then taken for analysis.

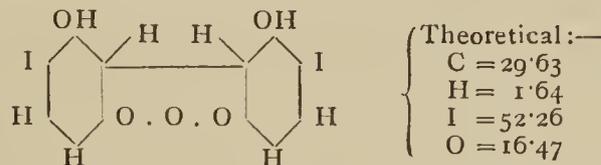
Total iodine:—

Quantity taken = 0.1072 gm.  
Silver iodide found = 0.1034 „ = 52.11 p.c. iodine.

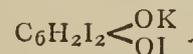
Combustion of same:—

Quantity taken = 0.0844 gm.  
Water found = 0.0138 „ = 1.81 p.c. hydrogen.  
Carbon dioxide found = 0.0908 „ = 29.33 „ carbon.  
By difference .. .. = 16.75 „ oxygen.

Those results may be represented by the formula C<sub>12</sub>H<sub>8</sub>I<sub>2</sub>O<sub>5</sub>, or constitutionally thus:—



This latter batch would agree fundamentally with that obtained by M. and V., who reported a total iodine percentage for the resorcinol precipitate of 72.48, and assumed it to be the potassium salt of di-iodo-resorcinol-iodide, which they represented thus:—



It is evident from the analyses I have submitted that the precipitate consisted of a mixture of a mono- and tri-substituted compound.

The first batch, whose total iodine percentage was 52.67, probably contained a di-substituted molecule, together with the compound whose full analyses I have given.

(To be continued).

Chaloner Testimonial.—Mr. George Chaloner, F.C.S., having resigned the position of Lecturer on Chemistry at the Birkbeck Institution, which he has held for a quarter of a century, it is thought that many of his old students and friends will be glad to combine to present him with some mark of good-will and esteem on the occasion of his retirement. With this view a Committee is being formed to consider the form of the Testimonial, to receive subscriptions, and to make arrangements for the presentation. It being the desire to make the Testimonial as largely representative as possible, it is suggested that the subscriptions should be limited to sums not exceeding one guinea. A preliminary meeting will be held on Tuesday, October 31st, 1893, at 43 and 44, Holborn Viaduct, E.C., at 7 p.m.—E. GODWIN CLAYTON; HERBERT TREWBY.

## LAWS AND NATURE OF COHESION.

## PART II.

By REGINALD A. FESSENDEN, Lafayette, Ind.

IN a previous note (*Science*, July 22, 1892, and *CHEMICAL NEWS*, lxxvi., 206), a number of reasons were advanced for believing that cohesion is due to an electrostatic force, and it was shown that the results predicted by such a theory agree very closely with the results of experiment.

This theory was, however, only extended to the phenomena of rigidity, elasticity, and tensile strength. It was purposed to follow it with another note on the phenomena of conductivity, surface tension, solution, refraction of light, and compression of gases. Pressure of other work and the necessity of making experiments to determine some doubtful points will prevent such publication for some time, and it was therefore judged best to give a short preliminary statement of a few of the results so far obtained.

1. *Relative Closeness of the Atoms.*—It appears to be generally considered that the atoms are at distances from each other which are large in comparison with their diameters, even in the solid state. As an example of the extent of this belief may be mentioned the fact that in a recent article on magnetism Mr. Steinmitz made the statement that Professor Ewing's theory could not be correct, unless the atoms were close together, but as they were far apart, his theory must be wrong. This conclusion has not been attacked up to the present time. But the facts are that all our evidence points the other way, and it is almost absolutely certain that in the solid state the distance between the centres of two neighbouring atoms is almost the same as their diameters.

For instance, from Van der Waals's equation we have, at the critical point:—

Volume of gas = 12 times the volumes of the atoms themselves, or, the distance between the centres of two atoms is 2.3 times the diameter of a single atom. And this is just at the critical point, so that from the curves of volume, pressure, and temperature, the solid elements must have a volume of, at the most, six times that of the atoms themselves, reducing the distance between centres to 1.8 times the atomic diameter.

Again, when a body is at absolute zero it is extremely difficult to conceive why the atoms, having no kinetic energy and the cohesive force still in existence, should not join together as closely as is possible, *i. e.*, till they touch. (We may discard the old "force point" atom as obsolete and without reason for existence, all modern research and theory being in favour of the idea that atoms have most exact and well-defined boundaries).

If, then, the atoms of silver in the solid state at 0° C., say, were very far apart, then, since we know its change of volume is very slight down to about -200° C., there must be a most remarkable and sudden change at some point in the last 73°. But this is not to be believed, for it is impossible for any such violent change in the space occupied by the atoms to take place without some change in the conductivity of the metals. And we know from the researches of Dewar and others that the curve of resistance is a straight one, and cuts the axis of temperature at absolute zero, if produced.

On the other side, after considerable search, there does not appear to be any reason for believing that the atoms are widely separated in a solid, and the writer would be glad to know of any such reason, other than the fact that certain mathematicians have seen fit to make the supposition because it renders some of the work on surface-tension, &c., a little easier to handle.

There is, it is true, one class of facts which has hitherto been looked upon as evidence of this nature, but which must, by all the laws of evidence, be considered as proof of the comparative closeness of the atoms instead of the opposite. For if, according to two theories, a certain

effect should follow certain conditions, and according to one theory there is no assignable limit to the effects, while according to the other there is a well-defined limit, then if out of a great number no effect is found to pass the well-defined limit, all the evidence is in favour of the latter theory.

The phenomena referred to are the facts that some of the elements can combine with other elements to form compounds having a less atomic volume than the element itself. For instance, 45.5 c.c. of potassium combine with one equivalent grm. of chlorine to form one equivalent grm. of KCl, having a volume of only 37.4 c.c. But if we suppose, as we have every reason for believing is the fact (witness the great advances which have been made in organic chemistry, due to the theory that the carbon atom has the form of a tetrahedron, and the still more recent work on nitrogen), that the atoms have regular geometric forms, then it is inconceivable that the facts should be otherwise than they are.

For, suppose that the potassium atom has the form of a sphere, then, when in the free state, as it is homogeneous, every atom must be similarly situated with respect to every other atom, *i. e.*, the atoms must have the position shown in fig. A. It is easily shown that by

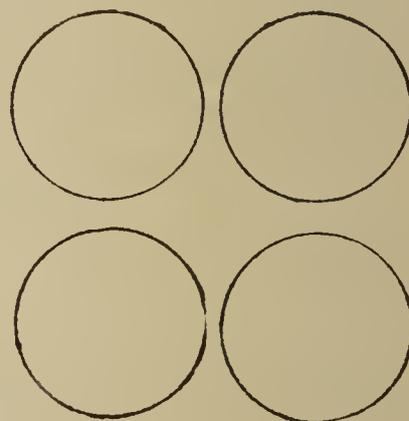


FIG. A.

the combination with the potassium atoms of an element whose atomic volume is less than 3.4, the resultant volume would fall to 32, the atoms taking the position shown in fig. B (shown in two dimensions only, it should be in three), the original volume of the potassium alone being 45.4.

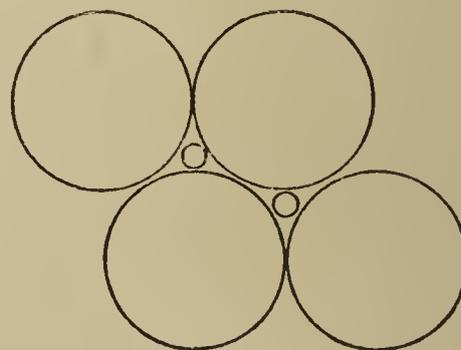


FIG. B.

Similarly, it may be seen that the potassium atoms can combine with an element of atomic volume 18 without any increase in bulk beyond the 45.5 of the potassium alone. Any combination with an element of less atomic volume than 18 would be followed by a diminution in volume. All this is on the supposition that the atoms of the combining element are spherical. If they are of any other form the diminution in bulk on the combination of an element of a given atomic volume would be greater. For instance, potassium could combine with an element whose atoms are of cubical form, and be reduced in bulk to an atomic volume of 32 if the volume of the combining

element were 4.33 instead of 3.4, as would be the case if the element were spherical.

It is to be noticed, moreover, that this diminution of bulk occurs only when elements of large atomic volume combine with the elements of small atomic volume, *i. e.*, in the case of sodium, potassium, caesium, and rubidium, and that in no case is the contraction greater than that given by these purely geometric conditions, so that we may discard all theories based on elements having two or three atomic volumes according to the element they combine; it will also be evident that by combining crystallographic data with those derived from volume measurements we have a means, possibly, of working out the stereotomy of all the atoms.

(NOTE.—In passing it is curious to note that the number of "space nets" into which an infinite number of points (each point similarly situated to every other point) may be arranged is sixty-six, or just the number of the well-defined elements. So that imagination may picture Spencer's homogeneous cloud of atoms splitting up into these different "space nets" arrangements, each kind of net being a different element).

2. *Solution.*—The chief opponent of the disassociation theory of solution is Professor Pickering; and his chief argument against it (for of course the disassociation theory allows the formation of hydrates as well as Professor Pickering's own hydrate theory does) is the fact that while disassociation almost always takes place with absorption of heat, solution generally emits it. This anomaly can be explained very satisfactorily by the electrostatic theory of cohesion. For whether a substance is a solid (or fluid) or a gas depends on whether the fraction

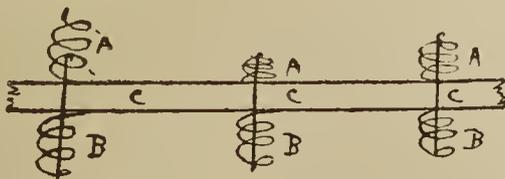
cohesive force of atoms

I.  $\frac{\text{repulsive force due to kinetic energy of atoms} + \text{attraction of atoms for other atoms}}$

is greater or less than unity. We can thus turn a substance into a gas by either decreasing the numerator or increasing the denominator. The numerator we cannot change. The first term of the denominator we can increase by heating the substance, the second term by placing the substance in contact with a solvent.

In the last case the atoms of the solid part company with each other. But their cohesive force is not lost; it is simply added to that of the solvent, as shown by the increase of surface tension and of boiling-point of a solution over that of the solvent. Since the solvent takes up the stress there is no necessary evolution or absorption of heat. A mechanical simile will make my meaning clear: suppose a spiral spring, A, fixed on a board, C, which when compressed gives out heat from some reversible cause, so that it will absorb the same amount of heat in expanding. This is similar to the behaviour of a gas—when compressed it gives out heat, when it expands again it absorbs heat.

But now suppose a second spring, B, placed beneath the board, C, similar in every respect to the first spring, and its axis a prolongation of that of A. Suppose an iron rod fastened to the bottom of C, extending up the centre of both springs, the rod being somewhat longer than one of the extended springs, and having a hoop on the end of it.



In Fig. 1 both springs are extended. In Fig. 2 the spring A is compressed, heat being given out.

If it is now allowed to expand, the same amount of heat will be absorbed. This latter represents the turning of a solid into a gas by heating it.

But suppose, being compressed, the iron rod is hooked

over the top of it. Then when it is let go it will expand and assume the position of Fig. 3. But no heat will be generated in the system, for it is evident that B will give out just as much as A absorbs. If the amount of heat given off by unit contraction of A were greater than that given off by B, the resultant effect would be a cooling of the system. If it were less, the resultant would be a heating. So we see that while the expansion of A by itself would always absorb heat, when it is joined to B the resultant effect depends on B.

Now this is a very fair simile of what goes on when a solid is dissolved in a solvent. The solid loses its stress, which is taken up by the solvent, the result being an increase of cohesion between the molecules of the solvent, producing as a natural consequence increase of surface tension, lowering of the freezing-point, and raising of the boiling-point.

If the added electrostatic strain produces a greater amount of heat in the solvent than the loss of strain in the solid would absorb heat, the resultant would be a heating of the whole solution. Since, when a dissolved substance is plated out by electrolysis, the result resembles the cutting of the iron rod, D, in Fig. 3, there is an absorption of energy or cooling, so that work must be done to plate the dissolved substance out, and the electromotive force necessary to do this, since the ampères are constant for all equivalents, must depend on the rate at which the surface tension varies per withdrawal of unit weight of the electrolysed substance, allowing also for any heating or cooling during the electroplating. It will be noticed that this theory differs in many respects from the ordinary theory of disassociation, but gives in general the same results.

3. *Compression of Gases.*—The ordinary formula for the compression of gases is that of Van der Waals, *i. e.*,—

$$I. \quad \left( p + \frac{a}{v^2} \right) (v - b) = RT.$$

If the electrostatic theory of cohesion is correct, the equation should read—

$$II. \quad \left( p + \frac{a}{v^{\frac{4}{3}}} \right) (v - b) = RT.$$

for reasons evident to those who have read the previous note (*Science*, Aug. 22, 1892).

This is no longer a cubic, and it is pretty certain that the equation for the compression of gases should be one on account of the shape of the pressure-volume curves of carbonic acid gas. But we can transform the above equation, II., into a cubic by putting *a* no longer as a constant, but equal to a constant multiplied by  $v^{\frac{2}{3}}$ . The equation then reads—

$$III. \quad \left( p + \frac{c \times v^{\frac{2}{3}}}{v^2} \right) (v - b) = RT.$$

in which *c* is the same for all gases. The experimental data agree with this modified equation, as shown by Table I.

TABLE I.

Substance.	$a \times 10,000.$	$v (ab).$
Diethylamine .. .. .	355	58
Ethyl. acet... .. .	348	55
Ether .. .. .	324	57
Benzine .. .. .	(438)	51
Ethyl. form.. .. .	304	48
Chloroform .. .. .	287	44
Acetone .. .. .	273	44
Methyl. acet. .. .. .	248	39
Alcohol.. .. .	236	37
Ethyl. chlor.. .. .	227	40
CS <sub>2</sub> .. .. .	219	33
SO <sub>2</sub> .. .. .	123	24
NO <sub>2</sub> .. .. .	(74)	19

as closely as can be expected.

TABLE II.

Substance.	$\pi$ .	$a$ .	$b^2$ .	$27b^2$ .	$\frac{a}{27b^2}$ .
Ether .. ..	36.9	324	3249	87.723	36.9
CS <sub>2</sub> .. ..	74.7	219	1089	29.403	74
SO <sub>2</sub> .. ..	78.9	123	576	15.552	79
Alcohol .. ..	62.1	236	1369	36.963	63.8
Eth. chl... ..	52.6	227	1600	43.200	52.5
Benzene .. ..	49.5	438	2601	70.227	62.3
Acetone .. ..	52.2	273	1936	52.272	52.2
Eth. acet. ..	42.6	348	3025	81.675	42.6
Chloroform ..	54.9	287	1936	52.272	54.9
Eth. form. ..	48.7	304	2304	62.208	48.8
Meth. acet. ..	57.6	248	1521	41.067	60.3
Diethylam. ..	38.7	355	3364	90.828	39
Nitrous oxide..	37.1	74.2	376.4	10.116	73

This Table shows that  $a$  varies as (volume) <sup>$\frac{2}{3}$</sup> . Two substances do not agree with this theory—benzene and NO<sub>2</sub>. This is owing to the fact that the data are given wrongly in the Table from which this is copied (*i.e.*, that in Ostwald's "Outlines of General Chemistry"). This is seen by the following facts:—From the cubic equation we find that at the critical point,  $\pi$ , the critical pressure—

$$= \frac{a}{27b^2}.$$

Table II. gives the results of this calculation, and it will be seen that the values for benzene and NO<sub>2</sub> do not coincide with the values for  $\pi$ . As the values of  $a$  and  $b$  were originally calculated from  $\pi$ , it is evident that some misprint has crept into the tables, and there is little doubt but that if the correct values for  $a$  and  $b$  were substituted, they would fall into line, and that in all cases the quantity  $a$ , in Van der Waals's equation, must be taken as equal to a quantity  $c$ , which has the same value for all gases, multiplied by the atomic volume to the  $\frac{2}{3}$  power.

4. *Electrical Conductivity.*—As before mentioned, linked atoms cannot conduct. If we examine the enclosed cube of the elements, we see that the non-conducting elements are found on sides E and W of the cube, and these are the elements whose atoms are linked or plexed. We can tell this in the following ways:—

1. By their low specific heats. Those who are acquainted with chemical physics will recognize this fact, and the necessary deduction. Briefly, if the kinetic energies of all molecules are the same at the same temperature, then if the sulphur molecule in solid sulphur is triatomic, or has its mass three times that of one atom; then, since all the  $\frac{1}{2}mv^2$ s are equal, solid sulphur will only have  $\frac{1}{3}$  the specific heat it would have if the molecule were monatomic (provided that no work is spent in disassociating the molecule).

The standard atomic heat is 6.4. The following substances have low specific heats, and are all insulators or poor conductors:—Sulphur, 5.4; phosphorus, 5.4; fluorine, 5; silicon, 3.8; carbon, 1.8.

2. By their vapour densities. If a substance has a biatomic vapour it is not likely that it will be a monatomic solid. The following substances have two or more atoms to the molecule when in the state of vapour:—Sulphur, iodine, bromine, chlorine, selenium, tellurium, phosphorus, arsenic. And these are all insulators or poor conductors; while mercury, cadmium, zinc, and sodium have monatomic vapours and are good conductors.

As regards metals in the allotropic state. Allotropic is a word which has been used to cover a multitude of sins. Every time an erring element goes wrong and misbehaves itself by emphasizing some of its previous peculiarities, or develops some new ones, it is stigmatised as "allotropic." For instance, we see it stated that when iron-amalgam is strongly heated the iron left behind is allotropic because it takes fire in the air. But such an action does not show that any new property has been developed, it merely emphasizes a fact already well known, *i.e.*, that

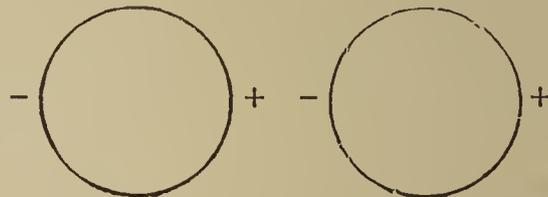
iron oxidises when exposed to air. A fine cambric needle will catch fire when held in the flame of a Bunsen burner for a second, and will continue to burn like a match after it is withdrawn. When the iron is in a finely divided state, the surface exposed is greater, and, the oxidation per unit mass being much greater, the temperature of the iron is raised much more, thus favouring oxidation still more.

If, then, we are to use the word allotropic in this sense, we should logically speak of kindling-wood as an allotropic form of timber; for, as fire underwriters know, heavy timber is one of the most fireproof of substances. We might also speak of that form of conscience which large corporations are supposed to possess, as an allotropic conscience.

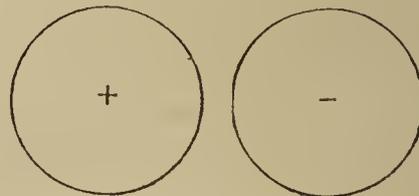
If, however, we do apply the word allotropic to such forms as Joule's iron, Carey-Lea's silver, &c., then we need another word to express the changes in the physical behaviour of metals which are not due merely to the accenting of known properties, but to the development of new properties, due to the joining of two or more atoms of a metal into one molecule. Polymerism might do, but it does not lend itself easily to use, and for myself I prefer to use the word plex, and to speak of diplexed iodide, triplexed sulphur, and of an element in a plexed form; though I have no doubt that if Clifford were still with us he would say that two-linked and three-linked are good enough for any honest Anglo-Saxon.

As regards the conductivity of "allotropic" elements, there is no reason to suppose that the conductivity of Joule's iron is different from that of ordinary iron. But when the elements are plexed, as we have seen above, the resistance will be much increased and the temperature sufficiently lowered, because heating increases disassociation nearly as fast as it lessens rigidity, or even in the case of those alloys or elements with negative temperature coefficients, faster.

(NOTE.—With regard to the previous paper, it may be noted that the explanation of the difference between cohesion and chemical combination, that in cohesion the atoms are charged similarly in every way except as regards position, thus—



while if any third substance short circuits the atoms they are left chemically combined, thus—

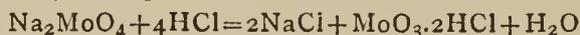


is also an explanation of a law which will probably be found true in the near future, *i.e.*, no two substances can combine with each other without the presence of a third, thus making all chemical action the result of catalysis, plexed forms of the substances being capable of acting third substances. As regards the shortening of stretched rubber by heating, it is, of course, not to be supposed that the two parts of indiarubber are literally contained one inside a sphere of the other, but that rubber rather resembles a tangled reel of silk embedded in jelly. If we consider any element of the jelly, and we see that it is bounded on all sides by threads of silk, and that these will act as the cell-wall of the previous paper,



(*Annalen*, clxix., 344) in their analyses of the chlorides  $\text{MoCl}_2$ ,  $\text{MoCl}_3$ ,  $\text{MoCl}_4$ ,  $\text{MoCl}_5$ . The chlorine in each was determined as silver chloride and the molybdenum as disulphide. Clarke ("A Re-calculation of the Atomic Weights," Washington, 1882) expresses the opinion that the most reliable results are those that have been obtained by the reduction of the trioxide. Of the work of Liechti and Kemp, he remarks:—"Traces of oxychlorides may possibly have contaminated the chlorides and augmented their atomic weight." Rammelsberg (*Berichte d. D. Chem. Gesellschaft*, x., 1776) made one experiment in the reduction of the trioxide, from which he calculated the atomic weight of molybdenum to be 96.18.

Thinking that additional light could be thrown upon the magnitudes of this constant by proceeding in a different direction, we utilised a reaction first observed by Debray (*Comptes Rendus*, xlvi., 1098; *Ann. Chem. Pharm.*, cviii., 250), which, in the hands of others (Péchar, *Compt. Rend.*, cxiv., 173; *Zeit. f. Anorg. Chem.*, i., 262; Smith and Oberholtzer, *Journ. Am. Chem. Soc.*, xv., 18; and *Zeit. f. Anorg. Chem.*, iv., 237) has proved to be a most excellent means of determining molybdenum and separating it from its intimate associate—tungsten. We refer to the action of hydrochloric acid gas upon molybdic acid and molybdates, whereby the molybdic acid is volatilised with ease in the form of an hydroxychloride— $\text{MoO}_3 \cdot 2\text{HCl}$ . Numerous trials have demonstrated that the reaction expressed by the equation—



is quantitative. We exposed pure anhydrous sodium molybdate (at 150–200°) to the action of hydrochloric acid gas, volatilised the molybdenum trioxide, and from the weight of the residual sodium chloride calculated the atomic weight of molybdenum.

The sodium molybdate employed by us was Merck's purest preparation. We re-crystallised it many times and then by a careful examination satisfied ourselves that it did not contain silica, sulphates, tungstates, or alkaline carbonates—substances that might have been present. The purified salt was dried with extreme care until no further loss in weight was observed. In this anhydrous condition it was preserved in clean weighing bottles, which were kept in desiccators to exclude dust and moisture. The specific gravity of the anhydrous salt was determined, alcohol being used for the purpose. The value found was 6.9780. The balance employed by us was of the Sartorius design.\*

The weights of brass and platinum were of Westphal make and had been previously carefully adjusted for this purpose.

Tared porcelain boats were used to carry the anhydrous sodium molybdate, which was exposed in hard glass tubes, to the action of pure and dry hydrochloric acid gas. This was prepared from salt and pure sulphuric acid. The gas as it was evolved was first conducted through a U-tube half filled with damp silver chloride; it next passed through two flasks containing sulphuric acid, then through a tower of dry calcium chloride, and finally through clean cotton, after which it was admitted to the combustion-tube, where it came in contact with the sodium molybdate. A very gentle heat was applied to the latter and gradually increased to from 150–200° C., beyond which the temperature was not permitted to rise. Moisture was excluded as much as possible. The volatilised  $\text{MoO}_3 \cdot 2\text{HCl}$  was collected in water. The boats containing the residual sodium chloride were allowed to cool in a slow current of hydrochloric acid gas, then transferred to vacuum desiccators, and the vapour repeatedly exhausted. The weights were taken after the boats had stood one hour. Second weighings were made after the boats had remained overnight in the dry desiccators, and showed no appreciable alteration. Barometric pressure and temperature

were carefully observed, and all weighings reduced to the vacuum standard. Our results are as follows:—

$\text{Na}_2\text{MoO}_4$ in grms.	$\text{NaCl}$ in grms.	Atomic weight of Mo.
1.14726	0.65087	96.130
0.89920	0.51023	96.094
0.70534	0.40020	96.108
0.70793	0.40182	96.031
1.26347	0.71695	96.087
1.15217	0.65367	96.126
0.90199	0.51188	96.067
0.81692	0.46358	96.077
0.65098	0.36942	96.073
0.80563	0.45717	96.078
Mean .. .. .	=	96.087
Maximum .. .. .	=	96.130
Minimum .. .. .	=	96.031
Difference .. .. .	=	0.099

In our calculations we used the following values:— $\text{Na}=23.05$ ,  $\text{Cl}=35.45$ , and  $\text{O}=16$ . These have been taken from a revised table of atomic weights, published by Clarke, October, 1891.

The sodium chloride in five of the determinations just given was converted into silver chloride. From the calculated silver contained in the chloride we deduced the atomic value of molybdenum to be 96.10—the mean of five determinations. This figure we regard as confirmatory of the rest of our work.

The sodium chloride which we obtained dissolved readily and to a clear solution in water. Molybdic acid was not found present in it. This was one of the points that we watched very closely, although its presence would have tended to diminish rather than to augment the atomic value found. Another cause of a like result would have been moisture absorbed by the sodium chloride. Against this source of error we likewise took every precaution, and consequently feel that the result 96.08 obtained by us approaches very closely to the true atomic magnitude of molybdenum.

## NOTICES OF BOOKS.

*Catalogue of Physical Apparatus, &c., Manufactured and Sold by Philip Harris and Co., Ltd.* Edmund Street, Birmingham. 1893.

THE authors remark in their Preface that, since they issued a Catalogue of Chemical and Physical Apparatus in 1889, the demand for the appliances needful in technical education has increased to such an extent that they have found it necessary to issue their present special Catalogue of Physical Apparatus. The catalogue extends to 168 pages, and is furnished with 2704 well and clearly drawn illustrations.

Electricity evidently claims the largest share of space. Wimshurst electrical machines are supplied with twelve plates of 26 inches diameter. Almost every form of apparatus required for the study and the application of electricity is duly figured and described, save the appliances of the electric charlatans who now form so numerous and thriving a body. Various forms of calorimetric apparatus are here mentioned, but we do not find Berthelot's calorimetric bomb.

In the section on light several forms of spectrosopes appear; but we see no microscopes, except a model of a compound microscope.

Lanterns have received prominent attention, on account of their increasing use for the illustration of lectures.

Harris and Co. make a speciality of the supply of

\* We would here acknowledge our indebtedness to Dr. John Marshall, of the Medical Department, for the privilege of using this excellent instrument

oxygen, hydrogen, and coal gas, in patent weldless steel cylinders, and give several useful hints for their safe application.

## CORRESPONDENCE.

### BARIUM SULPHATE IN SANDSTONE.

To the Editor of the *Chemical News*.

SIR,—I have to thank Mr. H. T. Mannington for the information communicated by his letter in the *CHEMICAL NEWS*, vol. lxxviii., p. 197. I am in some doubt whether the barium sulphate which he refers to occurs wholly in crevices in the sandstone or partly also in the cementing material which holds the sand-grains together. Perhaps Mr. Mannington can inform me more precisely on this point which I hold to be of some importance. If other gentlemen who have local information to impart on this matter would be so good as to communicate with me, and especially if they would supply me with fully-labelled specimens for analysis and examination, I should feel grateful.—I am, &c.,

FRANK CLOWES.

University College, Nottingham,  
October 21, 1893.

## 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. cxvii., No. 15, October 9, 1893.

**Relation Between the Precipitation of Chlorides by Hydrochloric Acid and the Lowering of the Point of Congelation.**—R. Engel.—At the congelation-point of a saturated solution of the alkaline and alkaline-earthly chlorides, and the alkaline bromides and iodides, there is a relation between the solubility and the atomic weights of the elements of the molecule. This relation the author purposes to expound in a future paper.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. viii., No. 91.

This number contains merely the *éloges* of the members deceased during the past year,—among whom figures the honoured name of Henry Peligot,—and notices of the prizes awarded to inventors.

*Bulletin de la Société Chimique de Paris.*  
Series 3, Vols. ix. and x., Nos. 17 and 18.

**Assay of Manganese Oxides by means of Oxygenated Water.**—Adolphe Carnot.—Will be inserted in full.

**Natural Manganese Oxides (Part 3), Acerdeses, Hausmannites, and Braunites.**—A. Gorgeu.—The author has examined four samples of acerdeses, obtained from Ilfeld-in-the-Hartz, hausmannites from Ilmenau, in Thuringen,—which constantly contain zinc oxide in proportions varying from 1 to 8.6 per cent,—and braunite from Saint-Marcel and Schwarzenburg. The specimens from Saint-Marcel are the only manganese ores which contain CoO in a notable quantity.

**Cuprous Phosphide.**—A. Granger.—This compound,  $\text{Cu}_2\text{P}_2$ , is obtained in the form of a grey crystalline compound, easily attacked by chlorine and bromine, and readily soluble in nitric acid. In contact with air, it dissolves in ammonia, with the formation of copper phosphate and phosphite.

**A Contribution to the Study of the Salts of Chromium Sesquioxide.**—T. Klobb.—The author describes the double sulphate (chrome and ammonia) and the anhydrous chrome alum. He examines the action of ammonium sulphate upon potassium-chrome alum, and finds that the alkaline chromosulphates or the anhydrous chrome alums crystallise together in all proportions, forming hexagonal tables. The chromotrisulphates crystallise in prismatic needles. The red chromium sulphate appears of a greyish rose colour by day, but green by gas-light.

**Action of Nitrogen Peroxide upon Metals and Metallic Oxides.**—Paul Sabatier and J. B. Senderens.—Manganous oxide ( $\text{MnO}$ ) of a greenish yellow colour, prepared by the action of hydrogen upon the peroxide, is oxidised in nitrogen peroxide at about  $350^\circ$ , yielding manganese sesquioxide. Blackish brown titanium sesquioxide,  $\text{Ti}_2\text{O}_3$ , is slowly oxidised at  $300^\circ$ , yielding white titanitic acid. Tungstic bi-oxide,  $\text{WO}_2$ , obtained by the prolonged action of hydrogen upon tungstic acid at dark redness, reacts with incandescence below  $300^\circ$ . The product, like that obtained in air, is yellow tungstic acid,  $\text{WO}_3$ , mixed with a little of the blue oxide,  $\text{W}_2\text{O}_5$ . Vanadium sesquioxide,  $\text{V}_2\text{O}_3$ , is oxidised at from  $300^\circ$  to  $400^\circ$ , and entirely converted into brownish yellow vanadic acid,  $\text{V}_2\text{O}_5$ . Cuprous oxide,  $\text{Cu}_2\text{O}$ , is transformed at  $300^\circ$  into the black oxide,  $\text{CuO}$ . **Metals.**—Metals in the state of filings or reduced by hydrogen are oxidised if heated in nitrogen peroxide almost as in air. With zinc the oxidation begins at  $300^\circ$ . Magnesium filings do not react below dull redness, when a very brisk combustion is set up. Aluminium filings are scarcely attacked at  $500^\circ$ . Lead is slowly oxidised at  $200^\circ$ , and yields a white basic nitrate. Sodium does not oxidise in the cold, and in heat the oxidation is very slow. Copper reduced by hydrogen is converted into black oxide at  $250^\circ$ . Reduced nickel, cobalt, and iron burn with incandescence at the common temperature in nitrogen peroxide, where they are more pyrophoric than in air. The products are  $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ , and nickel protoxide slightly mixed with sesquioxide. On operating at the ordinary temperature upon reduced copper, and in special conditions upon cobalt, nickel, and iron, we obtain totally different results, which form the subject of the next paper.

**A New Class of Compounds—the Nitro-metals.**—Paul Sabatier and J. B. Senderens.—Nitrogen peroxide, pure and dry, may be fixed in the cold upon certain metals recently prepared by the reduction of their oxides, forming compounds which the authors name *nitro-metals*. These formations have been observed in the cases of copper, cobalt, nickel, and iron. The copper compound has the composition  $\text{Cu}_2\text{NO}_2$ . It is a maroon-coloured mass, permanent in dry air in the cold. The reactions of this compound take place as if the nitrogen peroxide were merely in juxtaposition with the copper, each acting on its own account. This neutrality of chemical properties approximates to that of the metallic carbonyles obtained from iron and nickel. Nitro-cobalt,  $\text{Co}_2\text{NO}_2$ , is a black powder. The composition of nitro-nickel is similar. Nitro-iron is obtained with much more difficulty, and the authors can merely affirm its existence.

**Polarimetric Observations.**—J. A. Le Bel.—This paper does not admit of useful abstraction.

**Certain Derivatives of Methyl-gallate and Dibrom-gallate.**—Alex. Biatrix.—The author has obtained the bismuth methyl-gallate, the lead methyl-gallate, the lead methyl dibrom-gallate, and the triacetylic methyl dibrom-gallate.

**Certain Symmetrical  $\beta$ -diketones of the Aromatic Series.**—A. Béhal and V. Auger.—This extensive paper does not admit of useful abstraction.

**Bismuth Sub-gallate (Dermatol).**—M. Causse.—This compound,  $\text{C}_7\text{H}_3\text{O}_5\text{Bi} \cdot 2\text{H}_2\text{O}$ , is obtained in small lemon-yellow crystals insoluble in water, but soluble in the mineral acids. It is little affected by air and light.

**A Process for the Synthesis of the Benzenic Carbides.**—A. Brochet.—To effect the combination of the carbides the author proceeds as follows:—A quantity of crystalline benzene is mixed with hexylene, and agitated with 10 per cent of sulphuric acid at specific gravity 1.767. The two liquids blacken strongly. When the first reaction is completed, and after cooling, we add successively fresh portions of the ethylenic carbide, constantly stirring. We may thus introduce into the hexylene half the weight of the benzene employed. Care must be taken to renew the acid at least once at the end of the operation to ensure the total disappearance of the hexylene. There must be no further rise of temperature. We decant off the upper stratum, which is washed first with water and then with caustic soda. The benzene is easily expelled by reason of the great difference between the boiling-points of this liquid and of the product obtained. We obtain, thus, hexylbenzene equal in weight to the hexylene employed. The yield is about 50 per cent.

**Preparation of the Amides in General.**—A. Verley.—The author distils a mixture of the sodium or potassium salt of the acid the amide of which is required, and of the hydrochlorate of the base which is to enter into the reaction. The ammoniacal base which takes rise is at once split up into water and the corresponding amide. The yield is theoretical.

#### 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.

**Margarate of Ammonia.**—I shall feel greatly obliged for any particulars as to how I can make anhydrous margarate of ammonia. Kindly say if it is soluble in cold water. I need it for purposes of experiment. I have read in some work on the human body that it is contained in the sweat exuded from the system and can be made artificially by the action of ammoniacal vapour on olive oil, that it melts at 140°, and is soluble in alcohol, but not in water.—W. PAGE.

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THE CHEMICAL NEWS.

Vol. LXVII., No. 1771.

THE VOLUMETRIC ESTIMATION OF LEAD.

By A. P. LAURIE, M.A.

IN the course of some experiments for the Home Office I found it necessary to determine rapidly the amount of lead present in a large number of solutions containing free hydrochloric acid.

The amount of lead to be determined was small, varying from about 0.05 to about 0.005 gm. I determined after several trials to use the direct estimation by titration with bichromate of potash, using nitrate of silver as an indicator, which is described on page 348 of Crookes's "Select Methods in Chemical Analysis" (Second Edition).

In the first place, I found that the behaviour of the indicator was affected by the presence of chlorides. On adding a drop of the solution to a drop of nitrate of silver, on a white plate, before the bichromate is in excess, a white precipitate of chloride is formed. As soon as a little excess of bichromate is present, the white precipitate of chloride is dyed yellow, so that the end of the reaction is indicated, not by the usual pinky colour, but by the yellow tint of the chloride.

The sensitiveness of this indication is affected by the amount of chloride present in the liquid to a certain extent. If very little chloride is present, the amount of precipitate formed is too small to show the colouration distinctly, and if too much chloride is present the large quantity of the precipitate conceals the effect of the dye.

To obtain the most sensitive reaction, the amount of chloride present should be equivalent to from 0.5 to 0.2 gm. of sodium chloride in 100 c.c.

Under these conditions, 3 parts of bichromate in 1,000,000 parts of water will produce a perceptible change of tint in the chloride of silver precipitation. In fact, the reaction is, I think, more sensitive than the pink colouration, where no chloride is present.

In estimating the lead I made use of a solution of bichromate which was made up to approximately precipitate 0.002 gm. of lead per 1 c.c. of solution, and I standardised it against pure lead.

One serious practical difficulty is the obstinate way in which the lead precipitate remains floating in the liquid. This is fatal to the method, as any lead chromate taken up with the drop of liquid seems at once to stain the silver chloride, and so render the indicator useless. The best way to get over this difficulty is to add most of the bichromate necessary to precipitate the lead, and gradually raise the liquid to boiling with frequent stirring. This will cause most of the chromate of lead to settle, merely leaving a little floating on the top. On touching the surface of the liquid this floating precipitate is repelled in all directions, and a little liquid can be withdrawn by means of a capillary pipette (made by drawing out a piece of glass tubing), and blown out into the drop of silver. The fresh precipitate formed on adding more bichromate will usually settle on stirring without much difficulty. The precipitate ceases to form just a little before the yellow reaction appears.

In order to obtain results which agree one with another, certain precautions must be taken. The presence of large quantities of other salts in the liquid should be avoided; the liquid, if acid, must be carefully neutralised; and sodium acetate must be added before titration. In standardising the solution, I dissolved the pure lead in as little nitric acid as possible, added ammonia till a slight permanent precipitate was produced, and then added a little sodium chloride and some potassium

acetate. The amount of potassium acetate added was about twice the weight of the lead present. I then titrated in the way already described.

The following figures and ratios, the result of four consecutive titrations, made after I had determined the best conditions, serve to show that the method is fairly trustworthy, and sufficiently accurate for ordinary purposes:—

Weight of lead taken. Grms.	Ratio between weight of lead and No. of c.c. used.
0.1105	2188
0.1058	2186
0.1070	2189
0.1063	2183
	8746

Mean ratio .. .. . 21865  
Widest difference from mean .. +25 or -35

These results are quite within the errors due to the burette readings, and are, I think, fairly satisfactory, and seem to show that this method may be safely used for rapidly estimating small quantities of lead.

On adding the acetate to the neutral solution, basic salts usually separate, and the addition of the chloride causes a slight cloudiness as well. The long heating evidently converts these precipitates completely into chromate, and the result does not seem to be affected by the varying amounts of precipitate that may be formed.

The method might doubtless be used for estimating larger quantities of lead by adding a weighed quantity of pure bichromate of potash, heating, and then finishing the precipitation with the standard solution.

ON A SOURCE OF ERROR IN EVAPORATING  
OVER SULPHURIC ACID.

By GEORGE STILLINGFLEET JOHNSON.

IN the CHEMICAL NEWS (vol. lxxiii., p. 151) is published a paper which was read at the Chemical Section of the Franklin Institute, Jan. 20, 1891. The title of this paper—"Is Sulphuric Hydrate Volatile at the Ordinary Temperature of the Air?"—indicates that it deals with a question of the greatest importance to all chemists. After reading it, I at once set a number of experiments on foot with the object of throwing light upon the point at issue. As the results of these experiments are of some interest I have recorded them here.

Before entering upon a description of my own experiments, I will briefly summarise the observations and conclusions of the author of the paper mentioned above.

After keeping some pure iron in an ordinary desiccator over sulphuric acid (pure) for nine months, he found the metal coated with an anhydrous ferrous sulphate. The lid of the desiccator was kept tight by means of vaseline. From this observation the conclusion is drawn that sulphuric hydrate is volatile at the ordinary temperature of the air.

It happened that just before I read the above, a student in King's College Chemical Laboratory had been puzzled to account for reduction of a silver salt, which had been dried in an ordinary desiccator over sulphuric acid in a partial vacuum. I suggested that the reduction might be due to gases from the grease used to keep the receiver air-tight acting upon the sulphuric acid, and to avoid such action I recommended the addition of some chromic anhydride to the sulphuric acid. This was done, and the next sample of silver salt escaped reduction altogether.

It occurred to me, therefore, that reducing-gases from the vaseline might, in like manner, have been the cause of the formation of ferrous sulphate in the experiment quoted above; sulphur dioxide being generated and attacking the metal.

The method I adopted in examining this question was to take solutions of a compound stable in common air, but very easily deoxidised by reducing agents, and evaporate these solutions under varying circumstances, noting the results in each case. In order to accelerate matters the evaporations were generally carried on in a partial vacuum. The pump which I used (Fleuss's) gave a vacuum the residual tension in which was represented by one-fiftieth of an inch mercurial column.

My first experiments were made with potassium permanganate.

*Experiment 1.*—30 c.c. of a solution of potassium permanganate, saturated at 67° F. (19.5° C.), weighed 31.0601 grms. Evaporated in a vacuum desiccator, kept air-tight by grease, over sulphuric acid containing CrO<sub>3</sub> in solution. A mercury gauge left in the desiccator maintained a constant level throughout the experiment. The residue left in the dish weighed 1.7514 grms.; its weight remained constant at 100° C. Hence solubility of K<sub>2</sub>Mn<sub>2</sub>O<sub>8</sub> = 1 in 16.734 parts of water at 67° F.

*Experiment 2.*—The most perfect crystals were picked out from the residue from Experiment 1; their weight was 1.3306 grms. These crystals were re-dissolved in water and evaporated in precisely the same conditions as in Experiment 1. The weight of crystals left on evaporation was exactly the same as the weight taken, viz., 1.3306 grms.

From this it appears that potassium permanganate undergoes no decomposition when its aqueous solution is evaporated *in vacuo*.

*Experiment 3.*—30 c.c. of the same potassium permanganate solution as in Experiment 1 weighed (in a covered dish) 31.0570 grms. The dish was uncovered, and the solution was evaporated in a vacuum desiccator kept air-tight by grease which had been previously washed until quite free from acid reaction. To avoid spirting from the rapid evaporation, the exhaustion was stopped as soon as the tension was reduced to 1 inch of mercury. Fresh sulphuric acid was used for absorbing the water-vapour, but no CrO<sub>3</sub> was dissolved in it. The residue obtained weighed 1.7167 grms. This gives the solubility of permanganate of potassium 1 in 17.091 parts of water. This residue contained a brown deposit (Mn<sub>3</sub>O<sub>4</sub>), was deliquescent, and gave an alkaline solution in water. Hence every indication of reduction was obtained.

In all these experiments, the presence of metallic supports for the dishes, &c., was rigidly avoided. The vessels were placed on a ground-glass plate, covered with a glass receiver with ground welt, and glass tripods were used for supporting the upper dishes. The only possible source of the reducing agents which acted upon the permanganate was therefore the grease (mutton fat) used to keep the receiver air-tight.

On examining the sulphuric acid which had been used in the above experiment it showed evidence of reduction. 100 c.c. of the used acid decolourised 5.2 c.c. of a solution of potassium permanganate containing 0.2 gm. of K<sub>2</sub>Mn<sub>2</sub>O<sub>8</sub> in 500 c.c. 100 c.c. of the unused sulphuric acid (from the same bottle) decolourised only 1.9 c.c. of the same permanganate solution.

*Experiment 4.*—In this experiment a covered dish was again used, the glass lid overlapping and turned down at the edges, but, of course, not fitting air-tight. 20 c.c. of the same saturated permanganate solution was weighed in this dish (weight = 20.7725 grms.). The solution was evaporated *in vacuo*, with the lid on, over sulphuric acid with no CrO<sub>3</sub> dissolved in it, the apparatus being kept air-tight by grease, as before. The weight of dry permanganate crystals obtained was 1.790 grms. This gives the solubility of permanganate as 1 in 16.61 parts of water at 19.5° C. The crystals were perfectly pure, since the reducing gases had no access to them until the evaporation ceased. These crystals were now re-dissolved, and the solution evaporated with the lid off, spirting being carefully avoided by regulating the degree of exhaustion; other conditions the same as before. The weight of

residue obtained was 1.732 grms., and there was distinct evidence of reduction—brown deposit in the dish, &c.

*Experiment 5.*—A natural suggestion was to employ some material other than grease for keeping the desiccating apparatus air-tight. I am indebted to my friend and colleague, Mr Herbert Jackson, for preparing a substance which answers the purpose admirably in excluding air, and at the same time is free from the objection of yielding reducing vapours. The proportions of the ingredients are as follows:—

Melted vaseline .. .. .	1½ fluid ozs.
Vulcanised indiarubber.. ..	¾ oz.
Solid paraffin-wax .. .. .	1 drachm.

These ingredients are heated together in a porcelain crucible until the greater part of the volatile matter is expelled. The product is a dark brown sticky mass, which does not alter in any way on being kept. 20 c.c. of the same permanganate solution (weight = 20.733 grms.) was evaporated in an open dish over sulphuric acid containing no CrO<sub>3</sub>, but instead of grease the apparatus was kept air-tight by Mr. Jackson's lubricant. The weight of dry crystals was 1.1735 grms.; this gives the solubility of permanganate 1 in 16.66 parts of water. The crystals were pure.

The general conclusion from the above experiments is that—

1. Reduction of permanganate takes place during its evaporation over sulphuric acid in presence of vapours from common grease.

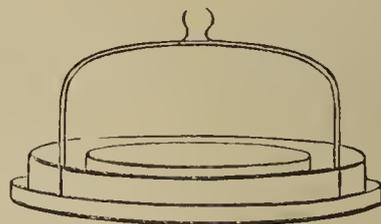
2. This reduction may be avoided by evaporating in a covered vessel, or by dissolving CrO<sub>3</sub> in the sulphuric acid, or by employing a substance which yields no reducing vapours instead of grease.

The determinations of the solubility of potassium permanganate at 19.5° C. agree well when precautions are taken to avoid reduction. Thus.—

Experiment 1 .. .. .	1 in 16.734
" 4 .. .. .	1 in 16.61
" 5 .. .. .	1 in 16.66
	3)50.004
Mean .. .. .	1 in 16.666

It will be observed that the figure indicating the greatest solubility was obtained from the experiment in which the dish was covered during the evaporation.

So far, my experiments have proved that a reducing atmosphere is produced by the interaction of vapours from fatty substances and sulphuric acid, and that the sulphuric acid itself suffers reduction in these circumstances (Experiment 3). The following experiments were conducted in a large desiccator constructed entirely of glass, the receiver of which has a glass ring both inside and outside it.



By pouring mercury into the space between the outer ring and the receiver, we can ensure the complete exclusion of the outer air. The exhaustion is effected by means of a glass tube in the centre of the glass plate. The dishes, &c., were supported on glass tripods.

*Experiment 6.*—In this experiment I tested incidentally the veracity of a statement which has been recently made to the effect that evaporation takes place more rapidly when the vessel containing the absorbent for the vapour is above the evaporating liquid. Three glass

dishes of equal diameter and capacity were employed. The lowest and the uppermost dish each contained 200 c.c. of a solution of  $\text{CrO}_3$  in sulphuric acid; the middle dish contained a cold saturated solution of potassium hydroxide, perfectly free from sulphur compounds. The desiccator was then exhausted until a mercury gauge within it showed one-fiftieth of an inch of gaseous tension. This exhaustion was maintained for four months. The opaque residue in the middle dish was then dissolved, acidulated with pure hydrochloric acid, and mixed with a solution of barium chloride. No trace of barium sulphate was formed. The volume of liquid in the upper and lower dishes was exactly the same, viz., 250 c.c., and the specific gravity of the two liquids was exactly equal, viz., 1.725. It appears, therefore, that in a good vacuum the evaporation of the absorbent—whether above or below the evaporating liquid—is a matter of no importance. We have also a negative result as regards volatilisation of sulphuric acid.

There is, however, an obvious objection to the above experiment as a test of the possible volatilisation of sulphuric acid, inasmuch as the dilution of the acid by the condensed water from the potash solution might have hindered volatilisation. Therefore the following experiment was performed.

*Experiment 7.*—The same large desiccator was employed. Mr. Jackson's lubricant was used to keep it airtight. Sulphuric acid containing  $\text{CrO}_3$  in solution was used, and above it was placed a porcelain dish containing the liquid alloy of potassium and sodium. The vacuum was made as before, on April 25, 1893. The air was readmitted on July 15, 1893. The metal still in the dish was oxidised and hydrated by leaving it under a glass shade with a dish of water near it. The contents of the dish were dissolved, acidulated with  $\text{HCl}$ , and treated with barium chloride. Not a trace of  $\text{BaSO}_4$  was formed.

*Experiment 8.*—In this experiment common grease was used to keep the desiccator airtight. Sulphuric acid without chromic anhydride was employed. The sodium and potassium alloy was placed as before, and the exhaustion was maintained for a month. On dissolving and acidulating the sodium and potassium compounds and adding barium chloride, precipitation took place, and I collected and weighed 17 m.grms. of barium sulphate.

My conclusion is that sulphuric acid is certainly not volatile at ordinary temperatures, even in a good vacuum, but that it is liable to vitiate the results of our experiments if exposed to reducing vapours.

Chemical Laboratory, King's College,  
London, October 14, 1893.

## SEPARATION OF BARIUM, STRONTIUM, AND CALCIUM.

By Prof. Dr. FRESENIUS.

I AM now in a position to recommend trustworthy methods for the separation of barium, strontium, and calcium, when the three alkaline earths are jointly present. I will first speak of a process which appears particularly suitable for the recognition of the three alkaline earths when they exist together without the aid of spectroscopic analysis. It is a combination of known methods which have been mostly described in my former memoirs. I can recommend the method as simple in execution, and as successful even when only a very small quantity of barium, strontium, or calcium is present along with larger quantities of each of the other alkaline earths, as I have satisfied myself by repeated experiments.

In qualitative analysis, if we separate baryta, strontia, and lime from magnesia, we obtain the three former as carbonates. After washing we dissolve them in dilute

nitric acid, evaporate the solution to dryness in a small porcelain capsule, heat it for ten to fifteen minutes very strongly on an iron plate (the temperature may be safely allowed to rise to  $180^\circ$ ) until the residue no longer smells of nitric acid, and until a cold glass plate—placed as a cover over the capsule for a few seconds—is no longer bedewed with water-drops. The contents of the capsule when cold are immediately ground up, first dry, and then with the addition of 5 to 10 c.c. of a mixture of equal vols. of ether and absolute alcohol. After a few minutes the solution is filtered off, and the residue washed four times with small quantities of the mixture of ether and alcohol. We have now in the residue the barium and strontium nitrates, to which small portions of calcium nitrate may still adhere; and in the filtrate the calcium nitrate in which, without due care in working, demonstrable traces of strontium nitrate may be present.

To the ether-alcoholic solution there are now added two drops of dilute sulphuric acid. If there appears any appreciable precipitate it can only be calcium sulphate, and there can be no occasion to test further for calcium. If the precipitate is very slight it may be due to traces of strontium which have possibly passed into the ether-alcoholic solution. In this case we mix the solution with 4 c.c. of water, evaporate away the ether and alcohol, add a few drops of ammonia and about 1 grm. of ammonium sulphate. Heat to ebullition, filter through a small filter, add to the filtrate a drop of acetic acid so that it just reddens litmus-paper, and then a few drops of ammonium oxalate. If lime is present there appears at once (or in case of very small quantities after standing) a precipitate of calcium oxalate. It cannot be mistaken for the minute quantities of strontia possibly present, because the traces of strontium sulphate which dissolve in a concentrated solution of ammonium sulphate are not precipitated by ammonium oxalate in presence of a trace of free acetic acid.

The barium and strontium nitrates are dissolved with heat in about 100 c.c. of water, filtered if necessary, acidulated with 3 to 4 drops of acetic acid, heated to ebullition, gradually adding neutral potassium chromate until the solution has a yellow colour, and allowed to boil again. If the odour of acetic acid is still felt we add a little more potassium chromate. If barium is present there appears at once (or in case of very small quantities after a short time) a light yellow precipitate. The liquid is allowed to stand for an hour, filtered, and to a portion of the filtrate there is added ammonia, and then ammonium carbonate. If there appears any appreciable precipitate it can be nothing but strontium carbonate, and there is then no need to test further for strontium. If there is no precipitate, or merely one extremely slight, we add to the bulk of the filtrate one or two drops of nitric acid, concentrate to from 10 to 20 c.c., and add then ammonia and ammonium carbonate. If still no precipitate is formed, strontium is not present; but if a slight precipitate appears it may be strontia, or possibly traces of lime. The small precipitate is filtered off, washed, dissolved in a few drops of dilute hydrochloric acid, and the solution is evaporated to dryness. The slight residue of the neutral chloride, or neutral chlorides, is dissolved in 1 or 2 c.c. of a mixture of 3 parts of water and 1 part of alcohol, which is kept in readiness; one drop of the solution of yellow potassium chromate is added, and the liquid is heated to incipient ebullition. If strontium is present it separates out at once (or after standing in heat for a short time) as a finely pulverulent yellow precipitate of strontium chromate.

For the quantitative separation of barium, strontium, and calcium, the following considerations are decisive:—

1. For the accurate separation of barium, strontium, and calcium, only two methods have been found quite suitable,—*i.e.*, the separation of the barium as chromate or as silico-fluoride.

2. The separation of strontium from calcium succeeds only by treating the nitrates with ether-alcohol. This

treatment is also suitable for separating barium from calcium.

3. A liquid in which hydrosilico-fluoric acid is present along with strontium and calcium is not well suited for determining the two alkaline earths, since they can then be thrown down only as sulphates, consequently in a state in which they are not directly separable.

To effect the purpose the following proceedings are essential:—

(a) Barium and strontium are separated from calcium by treating the nitrates with ether alcohol, and from the solution of the former the barium is separated as chromate.

(b) The barium is separated in the first place as chromate. The strontium and calcium are converted first into carbonates and then into nitrates which are separated by ether alcohol.

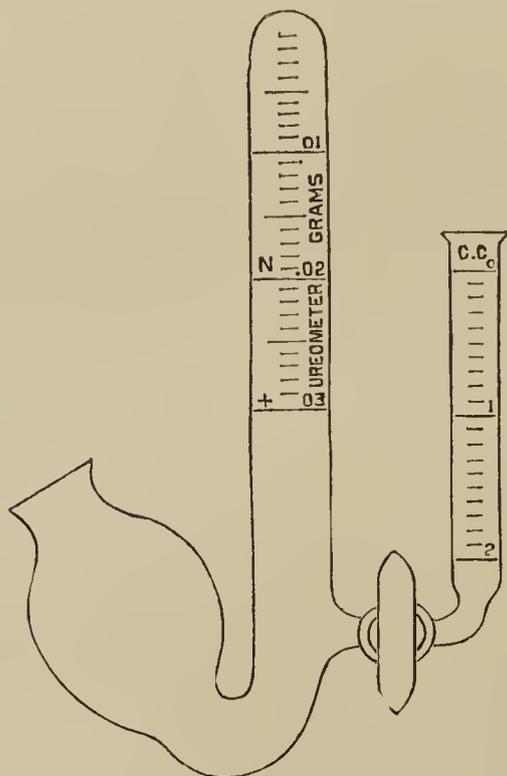
Both these methods yield satisfactory results, and the one or the other will be found preferable according to the circumstances.—*Zeit. fur Anal. Chemie*, xxxii., p. 312.

### IMPROVED UREOMETER.

By Prof. J. I. D. HINDS,  
Cumberland University, Lebanon, Tennessee, U.S.A.

In using the ureometer designed by Professor Doremus I have found two sources of considerable error. In the first place it is impossible to run in from the pipette exactly 1 c.c. of the urine. In the second place some bubbles of nitrogen almost invariably escape at the bulb.

To avoid these errors I have devised the apparatus shown in the accompanying figure. A tube graduated to



(Half natural size).

tenths of c.c. is attached on the side opposite the bulb, and the two tubes are connected by a stop-cock. The instrument is filled with the test-fluid in the usual way, and then the small tube is filled with the urine. Exactly 1 c.c. is allowed to run in through the stop-cock, and then the nitrogen evolved is measured in the larger tube. The instrument gives as great accuracy as can be attained with the small quantities dealt with.

The hole in the stop-cock should be filled with the urine. This can be done by running in a few drops of

the urine before filling with the test-fluid. The instrument is conveniently held with the left hand, while the stop-cock is being operated with the right.

### ON THE ACTION OF IODINE ON SOME PHENOLS AND ALLIED COMPOUNDS IN PRESENCE OF FREE ALKALI, AND A NEW CLASS OF DERIVATIVES RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 203).

#### NAPHTHOL $\beta$ ( $C_{10}H_8O$ ).

A SOLUTION was prepared containing 2 grms. naphthol and 3 grms. caustic soda in 300 c.c. of water. 20 c.c. of this solution was diluted to about 300 c.c., and the whole heated to 60° C., the iodine solution being then run in to large excess. The solution soon became opalescent, and after cooling a little the bulk of the product fell out as a precipitate. The mixture was then acidified in order to practically complete the precipitation. This process was repeated until a sufficient quantity was obtained.

The precipitate, when washed and dried, was of a dark greenish brown colour and of pulverulent character; when treated with cold alcohol, only a very small portion dissolved out. It was then treated with boiling alcohol, which dissolved out the greater portion of the remainder. The alcohol-soluble portion, when recovered, was of a shiny brittle character, and appeared black; but when powdered was of a dark brown colour. This was air-dried and then taken for analyses; it melted readily with decomposition.

Total iodine of the boiling alcohol-soluble portion:—

Quantity taken = 0.1297 gm.

Silver iodide found = 0.0696 ,, = 28.99 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1282 gm.

Water found = 0.0419 ,, = 3.63 p.c. hydrogen.

Carbon dioxide found = 0.2581 ,, = 54.80 ,, carbon.

By difference .. .. = 12.58 ,, oxygen.

The presence of water being suspected, the remainder was dried for fourteen days, and the iodine re-estimated.

Quantity taken = 0.1899 gm.

Silver iodide found = 0.1032 ,, = 29.36 p.c. iodine.

The remainder of the precipitate from the boiling alcohol treatment was dissolved out with chloroform and recovered. It was of a black-brown colour, and melted with decomposition.

Total iodine of the alcohol-insoluble portion:—

Quantity taken = 0.1089 gm.

Silver iodide found = 0.0312 ,, = 15.48 p.c. iodine.

Combustion of same:—

Quantity taken = 0.0978 gm.

Water found = 0.0387 ,, = 4.39 p.c. hydrogen.

Carbon dioxide found = 0.2145 ,, = 59.81 ,, carbon.

By difference .. .. = 20.32 ,, oxygen.

As no satisfactory formulæ could be derived from the above analyses, a new batch was prepared under like conditions. The precipitate obtained was of precisely the same appearance. The whole precipitate was heated in sealed tube with copper and water at a temperature of about 140° C. for twelve hours. The product was dried and treated with cold alcohol, which dissolved out a small quantity. The remainder was then treated with

ether and the soluble portion recovered. This was of a light brownish colour, and melted readily with decomposition. It gave the following results on analyses:—

Total iodine of the alcohol-insoluble portion, soluble in ether:—

Quantity taken = 0.1043 gm.  
Silver iodide found = 0.0103 „ = 5.33 p.c. iodine.

Combustion of same:—

Quantity taken = 0.0938 gm.  
Water found = 0.0350 „ = 4.14 p.c. hydrogen.  
Carbon dioxide found = 0.2562 „ = 74.49 „ carbon.  
By difference .. .. = 16.04 „ oxygen.

The remainder of precipitate was then treated with chloroform, the soluble portion recovered and submitted to analyses. Colour of a dark greenish brown.

Total iodine of the alcohol-ether-insoluble portion:—

Quantity taken = 0.1306 gm.  
Silver iodide found = 0.0506 „ = 20.93 p.c. iodine.

Combustion of same:—

Quantity taken = 0.0918 gm.  
Water found = 0.0292 „ = 3.53 p.c. hydrogen.  
Carbon dioxide found = 0.2436 „ = 72.37 „ carbon.  
By difference .. .. = 3.17 „ oxygen.

The naphthol, originally taken as the basis of those preparations, was again very slowly sublimed over a sulphuric acid bath, and the sublimate used for the preparation of another batch. The precipitate obtained was quite similar in appearance to those already examined.

This precipitate was treated with cold alcohol and the soluble portion recovered. This was re-dissolved in alcohol, and the alcoholic solution treated with successive portions of water until the dissolved substance was almost completely precipitated; the precipitate was then filtered out, washed, and dried. It was of a light yellowish brown colour and melted readily.

Total iodine of the alcohol-soluble portion (precipitated):—

Quantity taken = 0.1728 gm.  
Silver iodide found = 0.0311 „ = 9.73 p.c. iodine.

Combustion of same:—

Quantity taken = 0.1066 gm.  
Water found = 0.0421 „ = 4.38 p.c. hydrogen.  
Carbon dioxide found = 0.2801 „ = 71.65 „ carbon.  
By difference .. .. = 14.24 „ oxygen.

The remainder of the precipitate was treated with ether, to which it yielded the greatest part. The soluble portion was recovered, dried, powdered, and heated for about twelve hours in air oven at a temperature of about 100° C. The colour and physical properties were quite similar to those of the alcohol-soluble portion.

Total iodine of the alcohol-insoluble portion:—

Quantity taken = 0.1235 gm.  
Silver iodide found = 0.0239 „ = 10.46 p.c. iodine.

Combustion of same:—

Quantity taken = 0.0699 gm.  
Water found = 0.0235 „ = 3.73 p.c. hydrogen.  
Carbon dioxide found = 0.1866 „ = 72.79 „ carbon.  
By difference .. .. = 13.02 „ oxygen.

The remainder of precipitate was treated with cold chloroform, which dissolved out a small quantity. The remainder was then treated with boiling chloroform, which dissolved out a further portion. This was recovered, and when dry presented a dull, dark, greenish brown appearance. It was heated in the air-oven at

about 100° C. for two days, at the end of which time it had assumed a beautiful lustrous green colour, somewhat dichroic and almost crystalline. It was then submitted to analyses.

Total iodine of the alcohol-ether-chloroform-insoluble portion (soluble in boiling chloroform):—

Quantity taken = 0.0759 gm.  
Silver iodide found = 0.0144 „ = 10.25 p.c. iodine.

Combustion of same:—

Quantity taken = 0.0690 gm.  
Water found = 0.0222 „ = 3.57 p.c. hydrogen.  
Carbon dioxide found = 0.1737 „ = 68.65 „ carbon.  
By difference .. .. = 17.53 „ oxygen.

“Encluded” iodine being still further suspected, a weighed quantity of the same was heated to about 150° C., when a further small portion of iodine was given off, which may be stated roundly as 1 per cent.

The remainder of the precipitate from the boiling chloroform treatment was dried and heated on an acid bath at a temperature of about 150° C. until it had parted with all its “encluded” iodine. (Iodine lost by heating 1.76 per cent). It was then taken for analyses.

Total iodine:—

Quantity taken = 0.1358 gm.  
Silver iodide found = 0.0568 „ = 22.59 p.c. iodine.

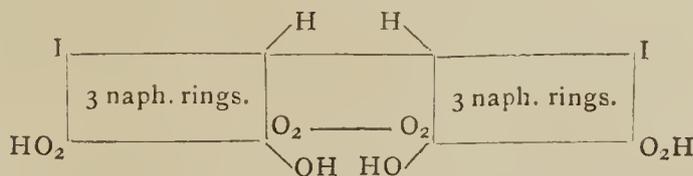
Combustion of same:—

Quantity taken = 0.0808 gm.  
Water found = 0.0214 „ = 2.94 p.c. hydrogen.  
Carbon dioxide found = 0.1646 „ = 55.55 „ carbon.  
Ash .. .. . = 5.40 „

Allowing for ash in above analyses we have—

Carbon .. .. . = 58.72  
Hydrogen .. .. . = 3.11  
Iodine .. .. . = 23.88  
Oxygen .. .. . = 14.29

This portion, therefore, may possibly be represented by the formula  $C_{26}H_{15}IO_5$ . Following up this result analogously one would be compelled to double this formula and assume a chain of rings made up of three naphthalene rings, with elimination of four carbon atoms, and then assume condensation of such molecules, thus—



To assume such without the most convincing confirmatory evidence would be altogether out of the question. At the same time, if one naphthol molecule substituted an atom of iodine for hydrogen, why not all? As an alternative the following structure might be assumed, which will explain itself:—



Admitting this it would appear that  $\beta$ -naphthol takes up no iodine under the conditions. This, and also the portions dissolved out by chloroform, is soluble in strong sulphuric acid, with beautiful violet colour, a brownish precipitate falling out on dilution with water. The portions dissolved out by alcohol and ether are not affected.

Messinger and Vortman in their paper remark that the analyses did not give good results. The iodine percentage

reported by them for the total precipitate obtained from  $\beta$ -naphthol was 40.7, whilst they point out that naphthol iodide requires 47 per cent. They give the colour of the precipitate as yellowish green, but this is only the case when a meagre excess of iodine is added. It is worthy of remark that the highest iodine percentage obtained by me was from a precipitate prepared from the more impure sample. However, conditions might possibly be set up which would yield compounds containing an equivalent of iodine to each original molecule, as would appear to have been obtained by Messinger and Vortman.

(To be continued.)

ON THE  
ESTIMATION OF CHLORATES AND NITRATES,  
AND OF NITRITES AND NITRATES  
IN ONE OPERATION.\*

By CHARLOTTE F. ROBERTS.

A RECENT paper by Gooch and Gruener (*Am. Journ. Sci.*, xlv., 117) has shown that nitrates may be estimated most accurately by treatment with manganese chloride, the chlorine thus liberated being collected in potassium iodide, and the amount of iodine set free determined by titration with sodium thiosulphate. In a late number of the *American Journal of Science* (xlv., 126, August, 1893), I have shown that good results are also obtained by treatment of the nitrate with ferrous chloride, and collecting and measuring the nitric oxide evolved over sodium hydroxide with the apparatus described and pictured in that article.

This apparatus consists essentially of a small retort fitted with a hollow ground-glass stopper prolonged beneath in a tube, and joined above with two branching tubes through one of which carbon dioxide may enter, and the other of which is attached to a funnel-tube with stopcock, through which liquids may be introduced without admitting air. The retort is connected with a small condenser, which in turn is attached to a Will and Varrentrapp tube containing potassium iodide, and this with a Hempel's burette containing a strong solution of sodium hydroxide. In the experiments described, the potassium nitrate was introduced into the retort, carbon dioxide passed through until the air was completely driven out, and then ferrous chloride added through the funnel-tube. After heating, and passing a current of carbon dioxide through the apparatus, the volume of gas unabsorbed by sodium hydroxide was measured at the observed temperature and pressure, and from this the weight of potassium nitrate was calculated. This is merely a special form of a very common method of estimating nitrates, but the apparatus is in a form which can be conveniently handled and which readily adapts itself to other uses beside the simple determination of nitrates. In a mixture of chloric and nitric acids, for example, it becomes possible by a combination of the two above-named methods for estimating nitrates, and the use of the apparatus described, to determine in one operation the amounts of each present. A method for the determination of chlorates which has long been in common use consists in treatment with hydrochloric acid, the liberated chlorine being conducted into potassium iodide, and the iodine set free determined by titration by sodium thiosulphate. This method is entirely analogous to the first-mentioned method of determining nitrates, the only difference being that in the latter case a solution of manganous chloride in hydrochloric acid is used instead of the acid alone. In case of the nitrate, however, there is a second product, nitric oxide, which may be collected and measured. It would then seem possible, with the use of the apparatus hereto-

fore described, to treat a mixture of a chlorate and nitrate with manganous chloride, pass the resulting gases through potassium iodide, and then into the Hempel's burette. The amount of nitric oxide will give at once the amount of nitrate present. The iodine liberated will give the total chlorine set free by the reduction of the nitrate and chlorate. After that which is due to the nitrate determined has been deducted, we have an exact measure of the chlorate present.

To verify these presumptions, a few preliminary experiments were first made with potassium chlorate alone. In these, and all of the following experiments, great care was taken that the escaping gases should only come in contact with glass. Between the condenser and Hempel's burette were two Will and Varrentrapp tubes sealed together and containing potassium iodide, and generally a Geissler bulb containing potassium iodide was also added to make sure that no chlorine escaped absorption. The potassium chlorate was weighed out and introduced into the retort, air driven out by carbon dioxide, and then manganous chloride added through the funnel-tube. The liquid became dark at once, and a short heating sufficed to restore it to its original clear light green colour. When this was accomplished, a current of carbon dioxide was passed through the apparatus, the bulbed tubes were disconnected, and their contents titrated with sodium thiosulphate. The following results were obtained from five trials:—

	Wt. $\text{KClO}_3$ taken.	Wt. $\text{KClO}_3$ found.	Difference.
1.	0.1000	0.0990	0.0010
2.	0.1000	0.0995	0.0005
3.	0.0500	0.0484	0.0016
4.	0.0500	0.0498	0.0002
5.	0.0500	0.0496	0.0004

Working in the same way with a mixture of potassium chlorate and potassium nitrate, and estimating the amount of nitrate first from the nitric oxide produced, the following results were obtained:—

	Weights taken.	Weights found.	Difference.
1.	Potassium chlorate.. 0.0500	0.0515	0.0015
	Potassium nitrate .. 0.0500	0.0494	0.0006
2.	Potassium chlorate.. 0.0500	0.0508	0.0008
	Potassium nitrate .. 0.0500	0.0493	0.0007
3.	Potassium chlorate.. 0.1000	0.0987	0.0013
	Potassium nitrate .. 0.1000	0.0995	0.0005
4.	Potassium chlorate.. 0.1000	0.1007	0.0007
	Potassium nitrate .. 0.1000	0.0980	0.0020
5.	Potassium chlorate.. 0.0300	0.0305	0.0005
	Potassium nitrate .. 0.1000	0.0990	0.0010
6.	Potassium chlorate.. 0.1000	0.1006	0.0006
	Potassium nitrate .. 0.0300	0.0293	0.0007

The method is simple, rapid, and easy, and sufficiently accurate for most analytical work. One objection that may be urged against it is that any error in the determination of the nitric acid involves a corresponding error in the amount of chloric acid, but the above results show that such errors will be quite small if the experiment is conducted with proper precautions.

It also appeared probable that a nitrate and nitrite could be estimated at one operation in a somewhat similar manner. By the action of manganous chloride on a mixture of nitric and nitrous acids, nitric oxide and iodine would be set free from each. Representing the weight of nitric oxide found by  $a$ , and the weight of iodine found by  $b$ , and letting  $x$  equal the amount of nitric acid operated upon, and  $y$  the amount of nitrous acid,—

$$\frac{30}{63} x + \frac{30}{47} y = a, \text{ and}$$

$$\frac{379.5}{63} x + \frac{126.5}{47} y = b;$$

whence,—

$$x = 0.249 b - 1.049 a$$

$$y = 2.35 a - 0.186 b$$

\* *American Journal of Science*, xlv., Sept., 1893.—Contributions from the Kent Chemical Laboratory of Yale College.

In the attempt to verify these formulæ by experiment, a little difficulty was found in getting a pure and stable nitrite upon which to operate. Some silver nitrite was prepared by precipitation from potassium nitrite and silver nitrate. This was washed well and dried as thoroughly as possible over sulphuric acid in the dark. Weighed portions were put in the retort, and after the air was expelled, manganous chloride was added. The amount of silver nitrate was then estimated from the iodine set free in the bulb tubes, and also from the nitric oxide left in the Hempel burette. The results varied from one another by 4 or 5 per cent on different portions, but a few trials were sufficient to indicate that the trouble lay in the silver nitrite, and not in the process itself. The percentage of purity as obtained from several trials by ignition was 98.4 per cent. The average of ten trials estimating from nitric oxide gave 98.1 per cent, and from the liberated iodine 98.7 per cent. This was uniformity enough to indicate that the method of work was trustworthy, although there was apparent such a lack of homogeneity in the silver nitrite as to make it impossible to use it in testing the value of the formula given above.

To obviate this difficulty more silver nitrate was precipitated, well washed, dissolved in warm water, and a solution of sodium chloride added. The silver chloride was then filtered off, and the resulting solution of sodium nitrite was used in the following experiments. To determine the strength of this solution 10 or 15 c.c. were drawn off from a burette, and the nitrite estimated with potassium permanganate according to the method of Kinnicutt and Nef (*Ann. Chem. Journ.*, v., 388). At the same time similar amounts were introduced into the retort with manganous chloride, and the nitrite estimated both from the liberated iodine and the nitric oxide formed. It was found that the air must be thoroughly driven out of the apparatus before the nitrite was introduced, as the carbon dioxide, passing over the solution, decomposed it with liberation of nitric oxide, which, in presence of air, gave an excess of free iodine, and at the same time a little gas was lost. Accordingly carbon dioxide was first passed through the apparatus for some time, then the nitrite was introduced through the funnel-tube and rinsed in with a little water, followed by the manganous chloride solution, care being taken that the water should not exceed one-third of the total volume of the liquid, according to the precaution to be shown necessary by Gooch and Gruener. Working in this way with the solution of sodium nitrite, the following results were obtained:—

	Vol. taken C.m.	Weight reckoned from KMnO <sub>4</sub> . Grm.	Wt. reckoned from NO. Grm.	Wt. reckoned from Iodine. Grm.
1.	10	0.0463	0.0456	0.0450
2.	10	0.0460	0.0460	0.0470
3.	15	0.0704	0.0708	0.0722
4.	15	0.0690	0.0712	0.0750
5.	15	0.0701	0.0704	0.0722
6.	15	0.0688	0.0696	0.0695
7.	15	0.0706		
8.	15	0.0712		

It will be seen that the results reckoned from the iodine are in general larger than those obtained by either of the other methods. This is what might be expected on account of the difficulty of completely removing air from the apparatus and solutions employed, and such air would naturally cause an excess of iodine. In No. 4 especially it will be noticed that we have an abnormally large amount of iodine set free, and this may undoubtedly be attributed to air, since it was observed that the current of carbon dioxide was rather sluggish at the time of that experiment.

The average of the above-recorded experiments would give as the value of 15 c.c., from the method of Kinnicutt and Nef, 0.0697 grm., from the nitric oxide 0.0699 grm., and from the iodine 0.0711 grm. If we assume that the

mean weight per 15 c.c. is represented by the average of these three modes of determination, we obtain 0.0702 grm., and that is the number which is used in the following determinations to represent the weight of sodium nitrite in 15 c.c. of the solution. The following experiments were made in the same way as the preceding, except that potassium nitrate was introduced in the dry state before the air was driven out of the apparatus, and the results were calculated from the formula given above:—

		Weights taken.	Weights found.	Difference.
1.	Sodium nitrite .. ..	0.0702	0.0718	0.0016
	Potassium nitrate .. ..	0.1000	0.1000	0.0000
2.	Sodium nitrite .. ..	0.0702	0.0712	0.0012
	Potassium nitrate .. ..	0.1000	0.0999	0.0001
3.	Sodium nitrite .. ..	0.0702	0.0710	0.0008
	Potassium nitrate .. ..	0.1000	0.1004	0.0004
4.	Sodium nitrite .. ..	0.0702	0.0698	0.0004
	Potassium nitrate .. ..	0.1000	0.1012	0.0012
5.	Sodium nitrite .. ..	0.0468	0.0453	0.0013
	Potassium nitrate .. ..	0.1000	0.0994	0.0006
6.	Sodium nitrite .. ..	0.0468	0.0444	0.0024
	Potassium nitrate .. ..	0.0500	0.0519	0.0013

Though the process is one in which the most perfect accuracy cannot be assured in all cases, the above results show that it is capable of giving fairly accurate results, sufficient for many analytical purposes. It seems to be especially well adapted to the estimation of the commercial alkali nitrites, the whole determination being made on one portion and by one operation, instead of on two different portions.

ON ERBIA.\*

By GERHARD KRÜSS.

(Concluded from p. 202).

WE must further report on the elaboration of the third portion of the erbium earths received from L. F. Nilson. This earth may be called

<sup>II</sup>  
Erbium Material No. 10 (R = 166.9),

This material was in the alcoholic solution of its chloride submitted to fractionated precipitation with an alcoholic solution of aniline.

Series 20.

Weak bases ←—  
"Aniline precipitates."

I	2	3	4	5	6	7	8
167.7	168.0	—	167.2	—	168.5	—	165.6
α			β			γ	

—→ Strong bases.  
"Aniline precipitates."

9	10	11	12	13 (Residue).
167.3	168.7	167.3	—	166.5
δ				ε

Mutually adjacent fractions of this series were systematically united as the materials α, β, γ, δ, ε, as shown by the brackets placed underneath Series 20, and from α a solution with aniline hydrochlorate was added to β, and finally one from ε to the fraction 13. In an analogous manner the least basic portions of an earth were carried over into the fraction to the left in Series 20. Lastly, the material α was resolved into two portions, as—

\* *Zeitschrift für Anorganische Chemie.*

Series 21.

Weak bases ←←.

α	β
1 Not dissolved 168·8	2 Dissolved 167·7
γ 164·3	δ 167·0
	ε 164·7

→→ Strong bases.

Between δ and ε there was an intermediate fraction δ/ε obtained in the manner indicated in Series 19, fraction 6/7 and 7/8 in the same manner subsequently between γ and δ and between β and γ. At the same time the series of fractions No. 21 was worked up from side to side, and then inversely by aniline solutions and precipitations, and the α material obtained was resolved into several sub-fractions by treatment with aniline hydrochlorate.

Series 22.

Weak bases ←←.

α						
1	2	3	4			
172·4	168·5	—	167·4			
→→ Strong bases.						
β	β/γ	γ	γ/δ	δ	δ/ε	ε
168·4	168·7	166·9	—	166·8	165·4	166·6

The erbium material No. 10 ( $R = 166·9$ ), which possessed in the most distinguished manner the attributes ascribed to erbium, was resolved according to Series 22 into portions the analyses of which showed from fraction to fraction

undulations in the value of  $R$  and behaved like the larger erbium material (Nilson's) No. 9 corresponding to Series 19.

The above results may be associated as follows:—

If we resolve erbiferous yttria earths by fractionated, partial decompositions of the nitrates in heat, and further by the action of aniline or aniline hydrochlorate, and always consider as erbium materials those fractions which, according to gravimetric and spectroscopic analysis,

should contain an erbium with  $Er = 166-168$ , and display absorption spectrum lines at  $\lambda = 654·7$  and  $\lambda = 523·1$ , we arrive in fact at an apparently unitary oxide, with about the equivalent which P. T. Cleve found for erbium. We arrive at the same confirmation of Cleve's researches if we resolve erbiferous yttria earths into a great number of fractions by the decomposition of the nitrates by heat alone. The erbium earths prepared in this manner by L. F. Nilson were excellent types of erbium earth.

But if by the above methods all the ytterbium, holmium, terbium, and yttria are eliminated from the erbium earth, and

the value found for  $R$  in determining the equivalents of the fractions has become almost constant (absolute con-

stancy of the  $R$  values was never found attainable in a large number of successive fractions), erbium is now found—perhaps by the very removal of the kindred earths—to have lost its relatively great stability and proves to be complex. Erbium can be resolved by treatment with aniline hydrochlorate into earths with different equivalents, so that we are not justified in regarding erbium as a peculiar oxide,  $Er_2O_3$ .

I shall endeavour to discuss the question of what erbium consists after the publication in early parts of this journal of two researches simultaneously conducted on holmium and terbium.

I must here express my thanks to my former assistant, Dr. Karl Hofmann, for his most valuable aid in conducting the above investigation.

## PROCEEDINGS OF SOCIETIES.

## PHYSICAL SOCIETY.

Ordinary Meeting, October 27th, 1893.

Prof. J. PERRY, F.R.S., Vice-President, in the Chair.

MR. E. C. RIMINGTON read a paper "On the Behaviour of an Air-core Transformer when the Frequency is below a certain Critical Value."

Taking the ordinary differential equations for two circuits having self and mutual induction, and assuming sinusoidal E.M.F.'s and constant coefficients, the author shows that although the difference of phase between the primary P.D. and primary current is always diminished on closing the secondary circuit, yet, under certain circumstances, this closing increases the impedance of the primary. With constant P.D., this means that closing the secondary decreases the primary current—a phenomenon not usually observed. The critical conditions necessary for increased impedance are fully worked out in the paper, as well as those under which this increase becomes a maximum. In the case of two identical coils

with no magnetic leakage, the critical value of  $a$  ( $a = \frac{\rho L}{r}$ )

where  $\rho = 2\pi$  times the frequency,  $L$  the inductance of the primary, and  $r$  its resistance) is  $\sqrt{2}$ , whilst that to give maximum impedance is  $\frac{1}{\sqrt{2}}$ . The maximum increase

possible is  $15\frac{1}{2}$  per cent. The corresponding values are given for various amounts of magnetic leakage in tabular form, and curves were exhibited at the meeting showing how the impedance, current, power, and magnetising effect vary for different values of  $a$ .

To test his conclusions, the author made experiments on two coils close together; the observed increase in impedance amounted to 3·2 per cent.

In addition to analytical investigation, the subject is treated geometrically at considerable length.

Prof. MINCHIN showed that the impedances might be represented by two hyperbolas, having  $\rho$  as abscissæ and the squares of the impedance as ordinates. These could be readily constructed from the data given. A line representing the primary inductance, drawn on the same diagram, intersects one hyperbola, showing that the impedance has always a maximum value. By a simple construction the phase angle between the primary and secondary currents could be determined for any given conditions.

Dr. SUMPNER observed that increased impedance on closing the secondary necessarily meant a decrease in the lag of the primary current behind the primary P.D.

Mr. BLAKESLEY was pleased to see the geometrical method of such service, and thought it much simpler than the analytical one. The reason why increased impedance on closing the secondary of ordinary transformers had not been noticed, was because their lag angles were very large. In a figure published some years ago to represent the actions of transformers, the angles he had chosen were such as would make the primary impedance increase on closing the secondary. Giving an expression connecting the primary currents on open and closed secondary respectively, he now showed that to get increased impedance the sum of the lag-angles in primary and secondary must exceed  $90^\circ$ . To get large power in the secondary, the primary lag should be nearly  $90^\circ$  and the secondary about  $45^\circ$ . He also pointed out that some of the figures in the paper might be simplified considerably.

Prof. PERRY said he had long had the impression that if a sufficiently small current were taken from the secondary, increased impedance would be observable in all cases, and he quoted some numbers he had given in the *Phil. Mag.* for 1891, showing a decided increase.

Mr. RIMINGTON, in reply, said he was not aware that the effect he had now brought forward had been observed previously. The result was completely worked out analytically before using geometrical methods.

Mr. W. B. CROFT, M.A., showed two Lecture-room Experiments. One, on "*The Rings and Brushes in Crystals*," was performed by very simple apparatus in two ways. In the first a bundle of glass plates was used as polariser, and a Nicol prism as analyser. When a Nicol could not be conveniently obtained, a glass plate could be used as a reflecting analyser. For a convergent system two glass card-counters were used, the crystal being placed between them. Very good results were produced by this simple apparatus.

In the second arrangement the crystal was placed on the eye-piece of a microscope (whose objective was removed), and covered by a tourmaline. On reflecting light up the tube by means of a piece of glass held at the proper angle, excellent results were obtained.

Another experiment, on "*Electric Radiation in Copper Filings*," was similar to those described by Dr. Dawson Turner at the Edinburgh Meeting of the British Association. A battery, galvanometer, and glass tube containing copper filings were joined in series. Under ordinary circumstances no current passed, but immediately an electric spark was produced by an electric machine many feet away, the galvanometer was violently deflected, and remained so until the tube was tapped. On trying different materials, aluminium and copper seemed about equal, but iron not so good. Carbon allowed the current to pass always.

Prof. MINCHIN said the phenomena were strikingly like those exhibited by his "impulsion cells," for the moment a spark passed, even at a distance of 130 feet, they became sensitive to light. Very minute sparks were capable of producing the change, but by adding capacity to the sparking circuit the effect could be greatly modified. Replying to a question from Mr. Rimington, he said the change was due to electro-magnetic vibrations, and not to light emitted by the sparks.

Mr. BLAKESLEY enquired if lengthening the sparks produced greater effect on the copper filings.

Mr. LUCAS asked if the resistance of a tube ever became infinite again if left for a long time.

In reply, Mr. CROFT said the current sometimes passed before the spark actually occurred between the knobs. He had not left tubes for very long, and had not found the resistance re-appear without tapping.

#### CONGRESS OF THE GERMAN SOCIETY FOR THE PROMOTION OF RATIONAL PROCESSES OF PAINTING.

ACCORDING to the *Chemiker Zeitung* the Congress of this Society was held at Munich on September 28th, 29th, and 30th, and was attended by upwards of 150 chemists and artists. The Honorary President was Prof. von Pettenkofer.

Prof. Petruscheffsky, of the University of Petersburg, sent in a paper on the permanence of oil-paintings, which, in the absence of the author, was read by Prof. A. W. Keim, the founder of the Grünwald Experimental Station for Painting.

Theodor Niederländer, Chemist to the Experimental Station, read an interesting paper on the preparation and properties of cadmium yellow.

L. Lethenmayer read a paper on the ethereal oils, their applicability in painting, and their comparison with mineral oils. He recommends, as rapidly drying materials, rectified oil of turpentine, light camphor oil, and rosemary oil. Oils of lavender and spike delay drying. He insisted on the use of pure, genuine products.

The same author communicated the results of an in-

vestigation on the absorption of oxygen by certain drying oils and their acid and iodine numbers. He condemns all "dryers" which contain lead, as it forms with the oil a compound which darkens strongly in course of time. He finds that the oil of *Lallimentia iberica*, a labiate plant cultivated near Kiev, surpasses all other oils in its drying power.

Further papers were read on asphaltum, the use of which in art should be restricted as far as possible, and on strontium uranate.

There followed a discussion of a normal scale of colours, including such only as are genuine and permanent.

#### NOTICES OF BOOKS.

*The Essentials of Chemical Physiology for the Use of Students.* By W. D. HALLIBURTON, MD., F.R.S. London: Longmans, Green, and Co.

THE author of this work, who is the Professor of Physiology in King's College, London, writes to supply students with instructions for the practical investigation of the most important subjects included under the head of Physiological Chemistry, and at the same time to furnish an elementary text-book of the subject. In both these respects he has executed his task in a most able and satisfactory manner. It has been regretfully pointed out in several quarters that, in physiology, Britain now occupies a position less creditable than she has secured in the other departments of biology, and we are by no means secure that the work before us will escape the hostile scrutiny of Victoria Street.

The author's general views, laid down in the Introduction, are judicious. He does not admit that the chemical structure of protoplasm can be studied until it has been killed. He does not deny to animals *in toto* the power of building up complex structures from simple materials. Consequently he rejects an erroneous distinction which some writers have attempted to draw between animals and plants. He does not, however, admit iodine and bromine as occasional constituents of the animal body.

In speaking of food-stuffs the author shows that the percentage of nitrogen, or even of the proteids, does not at once furnish decisive evidence as to the dietetic value. Peas and lentils doubtless contain more proteid than animal matter; but vegetable matter is less nutritious, as much of its nitrogenous matter is sparingly assimilable. Here is the refutation of one of the vegetarian dogmas.

We are glad to notice that attention is drawn to the value of the spectroscope in chemico-physiological research. In some instances where blood is required for an observation, the student is directed to obtain it by pricking his own finger—a "painful experiment upon an animal" which may be performed without any red-tape formalities.

A somewhat questionable statement is met with in the section in flour. The author writes that brown flour "is useful as a mild laxative, the insoluble cellulose mechanically irritating the intestinal canal as it passes along." We know of cases where this mechanical irritation has given rise to obstinate diarrhoea.

The crystals of oxyhæmoglobin are mentioned and figured. Here we are reminded of the perplexing fact that the form of these crystals in animals of the same order—*i. e.*, the guinea-pig, the squirrel, and the hamster—are very dissimilar. This is an argument against organic evolution which has not yet found a satisfactory explanation.

A remarkable difficulty is here mentioned referring to the poisons produced by bacteria in the animal body. They may be either alkaloidal (ptomaines) or proteids. The existence of deadly proteids is as yet a mystery;

since no chemical difference has been found between them and the proteids, which are harmless and serve as foods.

The illustrations to this work are numerous, well selected, and well drawn. To students of the chemical phase of physiology this work may be safely recommended.

*A Select Bibliography of Chemistry, 1492—1892.* By HENRY CARRINGTON BOLTON. Washington: The Smithsonian Institution. 1893. 8vo., pp. 1212.

DR. H. C. BOLTON is recognised as, perhaps, the highest living authority on the bibliography of chemistry and the allied sciences, and those readers who expect to find here a very full and trustworthy book of reference will not be disappointed. The author has carefully studied the catalogues of the chief Royal and National libraries of civilised countries, and has, in the most important cases, had "access to the shelves." He has summarised the particulars of 12,031 works, not merely in the "cultursprachen," English, French, and German, but in Arabic, Finnish, Gujerathi, Hebrew, Hindi, Rumanian, and Welsh.

The work is divided into seven sections—bibliographies, dictionaries, histories, biographies, chemistry (pure and applied), alchemy, and periodicals.

The fifth section is more extensive than the remaining six taken jointly, but the author considers it the least satisfactory. It includes merely independent works, but not contributions to periodicals. The author has sought to include the applications of chemistry to the various arts, but not the arts themselves. Thus works on agricultural chemistry are admitted, but not those on agriculture. Here there is sometimes, admittedly, no small difficulty in drawing the line.

Omissions in a work of such compass must be considered unavoidable. Thus in the index we find only one work on sewage and its treatment. Two others, more widely known, but which it is not our duty to advertise, have been omitted.

The section on Alchemy may cause some amusement, though some of the works here mentioned may find earnest admirers in an age like the present, which seems inclining to the re-habilitations of views generally considered as superstitious. But we may feel surprise and regret on finding the illustrious naturalist De Lamarck combatting the Lavoisierian theory of combustion. Chenevix also condemned the "French Neologists." Towards the end of the last century, K. A. Kortum came forward in defence of alchemy. In 1889 Papus seriously undertook a proof of the existence of the philosopher's stone. In 1887 R. Mendes Teixeira attacked Wurtz and Berthelot, and attempted to show that Comte anticipated the theoretical views of Gerhardt.

No library of a university or learned society can be considered complete if it does not possess a copy of a book at once so useful and so curious.

*Catalogue of Chemical Apparatus, Balances, Drying Ovens, Furnaces, Laboratory Stands, &c.* In Two Volumes. Also Special and General Glass Apparatus, Hydrometers, Porcelain, and Clay Ware. (At end of this list is a Complete Index for the two Lists). A. Gallenkamp and Co., 2, 4, 6, Cross Street, Finsbury, London, E.C.

THIS catalogue of chemical apparatus is exceedingly complete. Here are mentioned many of the most recently devised appliances for analysis and research. Under the various prices of apparatus we find frequently a reference to the journal or text-book in which their structure and use are described *in extenso*.

As a very useful appliance here mentioned we may

notice the Gallenkamp-Heele colorimeter, which is said to give readings accurate up to 1-10th per cent.

It is to be regretted that hydrometers with the Baumé scale figure to such an extent. For this graduation no reason can be shown, especially as it exists in three different modifications, and the purchaser of an instrument cannot tell without actual experiment which type it represents. Thus in some standard works 76° B. = sp. gr. 2.000, whilst in this catalogue it appears = 2.118.

A peculiarity of this catalogue is that for a great number of articles, those especially of glass, the prices are given as in Germany and in London. The difference is surprising, if we remember that there is no import duty.

The catalogue is stated as having been printed in Antwerp. Certainly it is rich in errors. We should beg to suggest to Messrs. Gallenkamp that, if for unknown reasons they cannot have their printing done in Britain, they would at least do well to have the MS. or the proofs very carefully read by some one acquainted with the English language.

*The Pharmacopœia of the United States of America.* Seventh Decennial Revision (1890). By Authority of the National Convention for Revising the Pharmacopœia. Philadelphia: Lippincott Co.

IN this edition we find certain principles laid down which must be considered decidedly judicious. Thus the allowable percentage of impurity is to be prescribed as closely as practicable. Chemical formulæ are to be given only in the new notation. "No substance which cannot be produced otherwise than under a patented process, or which is protected by proprietary rights, shall be introduced into the Pharmacopœia." This proviso is good, but it is not so good as the German law, which refuses patents to medicines, &c., and a still more excellent way would be to refuse protection to all processes for preparing medicines, foods, &c.

We are glad to see that the semi-barbarous notion of "proof" is abandoned as regards alcohol and its mixtures. In its stead, the specific gravity is laid down. There are comparative tables of measures according to the metric system, the American customary system, and the British system. This is the more necessary, as the pints, gallons, &c., of the two latter are by no means equal. The American grain is, however, identical with the British grain.

We find no comparative tables of hydrometric scales, and hence we cannot say whether Baumé's scale has been abandoned or not.

*Practical Work in Heat.* For Use in Schools and Colleges. By W. G. WOLLCOMBE, M.A., B.Sc., Senior Science Master in King Edward's High School, Birmingham. Oxford: Clarendon Press, 1893. 8vo., pp. 61.

THE author very justly remarks in his Preface that "the chief value of a scientific education consists not so much in storing the mind with a large number of facts as in the training of the powers of accurate observation and reasoning." He might have usefully said "inductive reasoning." He considers that a course of experimentation in heat is one of the best means to this end.

The experiments to be performed are very judiciously selected for the purpose in view, and are remarkable for the simplicity of the apparatus required. Hence no objection can be raised by the heads of schools on the score of expense.

The operations are arranged under the heads of thermometry, expansions, calorimetry, evaporation, and radiation.

This excellent little book is a proof that in the High Schools the ice of mediæval pedantry is beginning to melt.

*Electric Light Installations.* Vol. I., *The Management of Accumulators.* A Practical Handbook. By SIR DAVID SALOMONS, Bart., M.A., V.-P. Inst. Elect. Engineers, Assoc. Inst. C.E., Memb. Amer. Inst. Elect. Engineers, Memb. de la Soc. Int. des Elect., Memb. Phys. Soc., &c. Seventh Edition, Revised and Enlarged. An Edition, mostly Re-written, of Electric Light Installation and the Management of Accumulators. London: Whittaker and Co., G. Bell and Son. 1893.

WHEN a technical work has reached its seventh edition we may feel confident that it must meet a widely-felt public want. The treatise before us has thus fairly "won its spurs." We find here a description of accumulator-cells and their mode of employment, instructions for setting up the cells and the accumulator-house for charging and discharging. A very important chapter is that on failures, with their causes and remedies. There are instructions for testing a section, but with the remark that there is no method at present known for testing a cell satisfactorily in a short time. In the final chapter, or summary, we are told that no rules "unmixed with brains" are of the least service.

## 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. cxvii., No. 16, October 16, 1893.

**Certain Properties of Lead Oxides.**—A. Bonnet.—If we mordant cotton in an alkaline plumbate and wash it in much water, there takes place dissociation in favour of the fibre, which becomes loaded with the puce lead oxide. The oxidising power of this substance occasions the destruction—more or less complete—of the fibre. The same phenomenon of dissociation occurs with the plumbites, without the inconvenience of oxidation. The white oxide thus deposited, in addition to the known properties of the lead compound, effects a series of other reactions. Cotton mordanted and steeped in baths of logwood, sumac, fustic, &c., forms immediately, especially in heat, a coloured lake, black with logwood, yellowish green with sumac, and bright yellow with fustic. The tannins and the catechus are strongly attracted. By means of this mordant we may also deposit upon cloth the majority of metallic oxides on using suitable baths. Gold, silver, mercury, vanadium, manganese, chrome, iron, cobalt, nickel, and zinc give very distinct reactions using neutral salts in hot solutions. These reactions are so sensitive that with a bath of potassium permanganate at 0.25 gm. per litre we can obtain at 80°–90° a good bronze deposit of manganese peroxide. Traces of vanadium in an ammonium chloride are rendered manifest, and give a yellowish deposit with the salts of aromatic amines. This displacement of the oxides of different salts is explained by the formation of lead salts soluble in heat. It is thus that the iron, cobalt, nickel, and chrome salts are decomposed in heat and give on the fibre a deposit of the corresponding oxide, whilst there is formed in the bath a lead chloride soluble in heat, but precipitable on cooling.

**Internal Temperature of Bread when Drawn from the Oven.**—M. Ballard.—We are led to infer from these experiments, made in different ovens, on loaves and cakes of different size and shape, with paste risen and not risen, that the temperature of the crumb reaches from 100°–102°. That of the crust is distinctly higher.

*Bulletin de la Société Chimique de Paris.*  
Series 3, Vols. ix. and x., Nos. 17 and 18.

**Sulphones of Benzylic Alcohol and of Benzoic Acid.**—P. Genvesse.—The author has obtained and ex-

amined the dibromhydrine of the sulphone of benzylic acid, the sulphone of benzylic alcohol, that of benzoic acid, and that of silver benzoate.

**Constitution of the Colouring-matters of the Rosaniline Group.**—M. Prudhomme and C. Rabaut.—Rosenstiehl has established that the colouring-matters of the rosaniline group may form acid salts (hydrochlorates or hydrobromates) containing an atom of Cl or of Br more than the molecule contains atoms of nitrogen. This result is possible only if one of the atoms of chlorine or of bromine is directly linked to the methanic carbon. The facts which the authors expound seem to support this view.

**On Benzoylcinchonine.**—E. Léger.—The author has obtained this compound in crystals, and has examined its basic hydrochlorate, neutral hydrochlorate, basic hydrobromate, chloroplatinate, monoiodomethylate, diiodomethylate, iodoethylate, and bromomethylate. In all these compounds it is easy to recognise the presence of the benzoyl radicle by means of the reaction of Ferreira da Sylva.

**Combination of Albumenoid Matters and of Hematines Extracted from the Blood of Various Animals.**—H. Bertin-Sans and J. Moitessier.—The authors have succeeded in obtaining solutions presenting the spectral reactions of hæmoglobine by combining the hæmatine of the ox with the albumenoid matter extracted from the blood of sheep.

**Method for Rapidly Demonstrating the Displacement of Carbon Monoxide of Carboxyhæmoglobine by means of Oxygen.**—H. Bertin-Sans and J. Moitessier.—Into 50 c.c. of distilled water the authors pour 10 to 12 drops of blood saturated with carbon monoxide. Into 10 c.c. of the solution of carboxyhæmoglobine thus obtained they pass a rapid current of air for four minutes. On taking 50 c.c. of the solution thus obtained and adding an equal volume of a solution of 20 per cent NaOH and 4 to 5 drops of ammonium sulphide, the liquid, if examined in a thickness of 2 c.m., quickly presents the spectrum of hæmochromogen, which detaches itself very distinctly from the very attenuated spectrum of the carboxyhæmoglobine not yet decomposed.

**Composition of the Honey-dew of the Lime Tree.**—L. Maquenne.—The product seems to be melezitose, an isomer of raffinose.

**Citric Fermentation.**—Charles Wehner.—Not suitable for insertion.

No. 19.

**A New Reaction of Eserine, and on a Green Colouring-matter Derived from that Alkaloid.**—A. J. Ferreira da Silva.—A small fragment of eserine, or of one of its salts, of the size of a small grain of sand, is placed in a small porcelain capsule, and dissolved in one or two drops of fuming nitric acid. The light yellow solution thus obtained, on evaporation on the water-bath, turns successively to deep yellow and then to orange; but if it is evaporated to dryness whilst being constantly stirred with a glass rod, the colour of the residue passes to a pure green. The green matter thus obtained is soluble in water, and more readily in strong alcohol. The solutions are perfectly green, non-fluorescent, and on evaporation leave the colouring-matter unchanged. The solution of the matter in hot dilute nitric acid is very distinctly fluorescent; it is blood-red by reflected and greenish yellow by transmitted light. The watery solution of the green matter, if examined with the spectro-scope, is characterised by two absorption-bands; the more distinct is placed in the red, between  $\lambda$  670 and  $\lambda$  688. The other, which is broader, but less distinctly defined, occupies a part of the indigo and the violet, especially by  $\lambda$  400 and  $\lambda$  418. There is also a very faint band in the orange. The author proposes the name chloreserine for this substance, and purposes continuing its study.

## MISCELLANEOUS.

**Book Catalogue.**—The firm of J. B. Baillièrè and Son, 19, Rue Hautefeuille, Paris, has just published a Bibliography of the Chemical Sciences, which contains a detailed description of more than three thousand works on modern and ancient chemistry, in French and other languages. This pamphlet of 80 pages 8vo., double columned, will be sent gratis and post-paid to all chemists who write to Baillièrè and Son for a copy.

**An Improvement in Gas Burners for the Laboratory.**—All chemists in active laboratory work must have been struck by the rapid deterioration undergone by the gas burners used for boiling and igniting. Oxidation, under the influence of the heat and acid vapours, proceeds at an enhanced rate, and, in spite of frequent scraping and painting with Brunswick black, the burner soon becomes shabby and dilapidated. Messrs. Fletcher, Russell, and Co., the well-known gas engineers of Warrington, have submitted for our inspection one of their laboratory burners in which it is anticipated this great defect has been overcome. We have had it in use for some time, and it shows no signs of rust or deterioration at present. The cast-iron burner is coated on the surface by what is called Chimatto enamel, which is unchanged by a red heat continued for any length of time, and does not chip off. All colours, either dead or bright, and both gold and silver, either dead or polished, are obtainable on the same casting, and all alike are unchangeable, either with exposure to air or to any heat up to a bright red.

**The Franklin Institute.**—We have received the programme of lectures of this Institution for the Sessions 1893—1894. Among the lectures announced there are two by Horace Pettit on the law of inventions, and one on a plea for the study of forestry in the lower schools—a very important subject. Prof. S. P. Sadtler will give a review of recent progress in chemical technology; Prof. S. P. Sharples, on the fat and soap industries; Rudolph Hering, on the purification of water; Dr. C. S. Dolley, on economic botany in relation to modern civilisation; and Prof. E. Hart, on the number of the forms of carbon. O. Chanute, C.E., will lecture on aërial navigation—a subject of intense interest to the criminal classes and to conspirators. The library of the Institute comprises above 38,000 volumes, 24,000 pamphlets, the same number of charts and maps, and over 1100 photographs, all classified and catalogued.

**Thermic Study of the Acid Functions of Camphoric Acid.**—G. Massol.—The second function of camphoric acid is thermically weaker than the acid function of the organic acids.—*Bull. de la Soc. Chim. de Paris.*

**Photography in the Service of Chemistry and of the Practical Chemist.**—E. Valenta.—Under this title the *Chemiker Zeitung* publishes an important paper, from which we make the following extracts:—The acquirement of photography will always be of eminent service to the chemist. If engaged in metallurgy he can, by means of photography, prepare exact representations of the fracture of different metals, which will much facilitate the study of the different steels and irons in connection with their proportions of manganese, silicon, carbon, &c. The chemist concerned with the investigation of foods will often have occasion to make use of photography. A correct photograph of a microscopic preparation recognised as decisive evidence of sophistication may serve in support of the opinion which can be submitted to a court. In bacteriology photographs are more decisive than the best drawings or descriptions. The chemist requires for his purposes chiefly an accurate knowledge of the negative process with silver-bromide gelatin dry plates, and the simplest positive process. He must especially beware of portrait photography. For purely technical purposes he may acquire all that is necessary in one or two months.

## MEETINGS FOR THE WEEK.

**MONDAY, 6th.**—Society of Chemical Industry, 8. "Spirit Assaying by Weight," by J. Scarisbrick. "Estimation of Alizarin and Allied Colouring Matters," by P. W. Dreaper.

**FRIDAY, 10th.**—Physical, 5. "On the Separation of Three Liquids by Fractional Distillation," by Prof. S. Young, F.R.S., Prof. Barrett, and Mr. Thomas. "On the Critical Constants of Various Ethers," by Prof. S. Young, F.R.S. "An Instrument for Drawing Conic Sections," by J. Gillett, B.A.

## LECTURE NOTES

ON

## THEORETICAL CHEMISTRY.

BY

FERDINAND G. WIECHMANN, Ph.D.,

Instructor in Chemical Physics and Chemical Philosophy,  
School of Mines, Columbia College.

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1772.

SALTS OF A NEW PLATINUM-SULPHUREA BASE.\*

By W. J. SELL and T. H. EASTERFIELD.

VARIOUS platinum thiocarbamide compounds have been prepared by Professor Emerson Reynolds and by Rathke, but no derivatives of the base  $\text{Pt}(\text{CSN}_2\text{H}_4)_4(\text{OH})_2$  have been hitherto described. The chloride of this base is readily prepared by adding platinic chloride solution to a boiling solution of sulphurea in dilute hydrochloric acid. The filtered solution deposits crystalline needles of the chloride when mixed with strong hydrochloric acid, in which the chloride is very sparingly soluble. Analysis agrees with the formula  $\text{Pt}(\text{CSN}_2\text{H}_4)_4\text{Cl}_2$ .

The sulphate,  $\text{Pt}(\text{CSN}_2\text{H}_4)_4\text{SO}_4$ , is precipitated in regular octahedra when dilute sulphuric acid is added to an aqueous solution of the chloride.

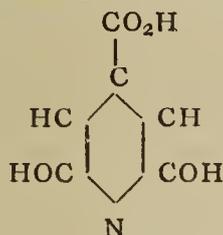
The picrate,  $\text{Pt}(\text{CSN}_2\text{H}_4)_4\text{Pk}_2$ , is very sparingly soluble in cold water; it crystallises from hot water in beautiful golden-yellow iridescent needles.

The free base,  $\text{Pt}(\text{CSN}_2\text{H}_4)_4(\text{OH})_2$ , has not been isolated in the pure state.

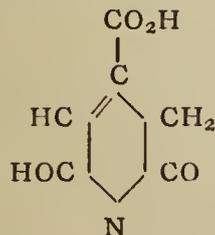
ON CITRAZINIC ACID.\*

By W. J. SELL, M.A., and T. H. EASTERFIELD, M.A.

CITRAZINIC acid was first prepared by Behrmann and Hoffmann, who obtained it by the action of sulphuric acid upon citramide; they assigned to it the formula—



A study of the reactions of the acid causes the authors of this paper to regard the formula—



tantomeric with that of Behrmann and Hoffmann, as more generally satisfactory. The following facts appear to support this formula.

1. Citrazinic acid is readily prepared from all anhydroaconitic derivatives, and is therefore most simply regarded as a condensation product of aconitamide.

2. Guthzeit and Dressel have shown that citrazinic acid is readily re-converted into aconitic acid.

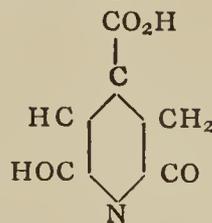
3. Only two classes of salts,  $\text{C}_6\text{H}_4\text{M}'\text{NO}_4$  and  $\text{C}_6\text{H}_3\text{M}'_2\text{NO}_4$ , can be prepared.

4. Chlorine produces trichlor-substitution derivatives, from which two of the chlorine atoms are much more

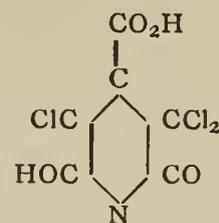
readily removed than the third chlorine atom. Similarly, bromine gives rise to tribrom-citrazinic acid.

5. Diazobenzene chloride reacts with citrazinic acid to produce phenyl-hydrizo (?) citrazinic acid.

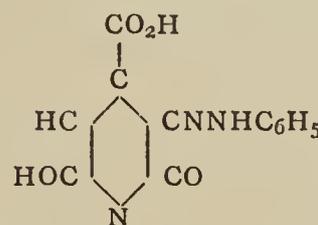
6. Nitrous acid converts citrazinic acid into an iso-nitroso compound, which when warmed with dilute sulphuric acid loses carbon dioxide and yields a quinhydro compound dissolving in alkalis with the production of an intense blue colour. Oxidation converts the quinhydrone into a quinone, resembling ordinary quinone in its appearance and behaviour. The following formulæ illustrate these relationships:—



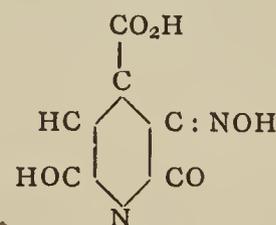
Citrazinic acid.



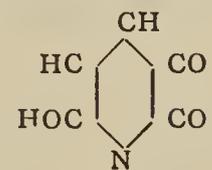
Trichlor-citrazinic acid.



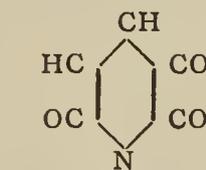
Phenyl-hydrizo-citrazinic acid.



Iso-nitroso-citrazinic acid.



Quinhydro-keto-pyridin.



Quino-keto-pyridin.

ON THE TEACHING OF INORGANIC CHEMISTRY.

By MARGARET D. DOUGAL.

ONE of the greatest difficulties connected with the teaching of Inorganic Chemistry in any systematic lecture-course arises from the great amount and diverse nature of the material which has to be dealt with, and this difficulty, so far from diminishing, will certainly increase as the science develops. Even now it is practically impossible in any lecture-course of the usual length to treat of matters such as the student of to-day may legitimately expect to have brought under his notice. The broad, general principles of the science are, on the whole, adequately considered in so far as they can be illustrated by the study of the non-metallic elements and the compounds which they form by their mutual union. So large a proportion of the course is, as a rule, occupied with these matters that but scant attention can be paid to the metals. Generally only the more technically important of these are considered, with special mention of their modes of extraction, their uses, and the commercially valuable salts which they yield, while whole groups of metals, and particularly the so-called rare metals, are seldom even mentioned, in spite of the fact that their chemistry is of considerable theoretical importance. These facts will be patent to every teacher. The problem is to find a remedy. There is no doubt that the teaching of modern Organic Chemistry, in any course at all commensurate with the importance of the subject, is more systematised and better arranged than the courses in Inorganic Chemistry, which are too frequently tram- melled by traditions and text-books.

\* Read before the British Association (Section B), Nottingham Meeting, 1893.

In a recent lecture to the Fellows of the Berlin Chemical Society\* Professor Lothar Meyer, one of the most eminent and experienced of German teachers, has sought to indicate a remedy for the present condition of things, which it is the object of this paper to explain. As the result of much thought and of personal practice he has elaborated a system which, in a course of about eighty lectures, enables him to take a fairly comprehensive survey of the present aspect of Inorganic Chemistry without prejudicing or in any way sacrificing the consideration of the fundamental principles of the science. The basis of his method rests upon the application of the Periodic or Natural System of classification of the elements, which he has done so much to elaborate and popularise. Similar attempts have, it is true, been made by other teachers, but their method has consisted only in the partial adoption of this principle. It must be confessed that the greater number of teachers at the present time content themselves with merely mentioning the existence of what is called the Periodic Law, and make little or no practical application of it in the arrangement of their lecture-courses. Professor Lothar Meyer seeks to show how this generalisation may be made use of from the beginning of a course of lectures adapted to beginners.

Taking the Natural System of the Elements in its usual form,

I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
Li	Be	B	C	N	O	F			
Na	Mg	Al	Si	P	S	Cl			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Cu	Zn	Ga	Ge	As	Se	Br			
Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd
Ag	Cd	In	Sn	Sb	Te	I			
Cs	Ba	La	Ce	—	—	—			
—	—	Yb	—	Ta	W	—	Os	Ir	Pt
Au	Hg	Tl	Pb	Bi	—	—			
—	—	—	Th	—	U	—			

there is in the outset some difficulty in determining where to begin. At first sight one of the groups of Family I. seems most naturally to constitute a starting-point, and, although it is contrary to the general custom of commencing with the non-metals, Prof. Lothar Meyer has tried this method and found it impracticable. To begin with the seventh Family and work backwards through the different families, whereby hydrogen, chlorine, oxygen, sulphur, nitrogen, and carbon are first treated, more nearly resembles the usual method; but it has disadvantages, for chloric and perchloric, sulphuric, nitric, and phosphoric acids, and generally the oxides of these families, do not belong to the simpler compounds, and therefore the systematic progression from simple to complex relations is reversed. We cannot lose sight of the fact that, among the non-metals which form compounds with oxygen, the hydrogen compounds are the simplest of all. In order to arrive at a feasible and just division of the material, Prof. Lothar Meyer found it necessary to adopt certain re-arrangements, whereby it was possible to follow the order in the Natural System, to take the student from the simple to the more complex compounds as in organic chemistry, to make clear to him analogies and differences, and to give him such a comprehensive survey of the great variety of substances that he can himself easily deduce the composition and also the behaviour of any compound so soon as the position of the element in question is noted in the system.

Dr. Lothar Meyer begins his course by defining the position of chemistry among, and its relations to, the other natural sciences. The relation of chemistry to physics is explained by a series of contrasted experiments, some showing purely physical, others chemical

phenomena: for example, platinum wire glows while magnesium wire burns in a flame; iron is magnetised and rusts; sulphur is electrified by rubbing, while phosphorus is inflamed; nitre dissolves in water and re-crystallises out unchanged, and zinc dissolves in sulphuric acid and re-crystallises as zinc sulphate; &c., &c.

After the various subdivisions of chemistry and its relations to other branches of knowledge have been spoken of, and the literature surveyed in some detail, Dr. Meyer then proceeds to give a brief account of the science. The chemistry of the Egyptians and Arabians, of the Alchemists and Iatrochemists, is rapidly dealt with; some little time is spent on Van Helmont's teaching; and the theory of phlogiston is gone into pretty fully, all that can be said in its favour being first stated, when its weaknesses are exposed, all of which naturally leads to the consideration of Lavoisier's doctrine.

We are thus brought to the question of the constitution of the air, and to the nature of oxygen, which, because it is the most widely distributed of all substances and occurs in largest quantities, is now fully treated of and in the usual way. Incidentally the student learns something of nitrogen, and to now distinguish it from some of the gaseous products of combustion, especially from those of carbon and sulphur. By the discussion of

Lavoisier's doctrine, his imperfect explanation of the cause of the heat of combustion is mentioned, together with Rumford's experimental proofs that heat is a form of motion. For the complete exhaustion of the subject of the phlogiston theory, the nature of the substances which were looked on, more or less, as pure phlogiston, must be examined, and, above all, the nature of hydrogen. With the discussion of it the usual experiments are given. Eudiometry affords an opportunity of speaking of the volume relations according to which gases combine, and also of the methods for the determination of density by which volume and weight are calculated, and electrolysis is demonstrated as a means of separating the constituent parts of a compound.

Water is now dealt with in detail, and special stress is laid on the constancy of the combination of hydrogen and oxygen, and a short account of stoichiometry and of the atomic theory is given incidentally. After, with water and air as examples, Lavoisier's thorough method of distinguishing elements and their compounds has been explained, the student can easily see that besides the three elements already spoken of—oxygen, hydrogen, and nitrogen—there must be many more. Dr. Meyer then, following the example of his own teacher, Bunsen, gives a general, but rapid, survey of all the known elements, which has the advantage of not disturbing the order; and if at any time in the course of the lectures a compound is mentioned whose elements have not yet been minutely described or experimented with, the student has only to recall this survey.

This survey is given in approximately three lectures in the following order. Next to the gases already described come first of all the gaseous, then the volatile and easily fusible non-metals:—Fluorine, Chlorine, Bromine, Iodine, Sulphur, Selenium, and Phosphorus. Of these only the

\* *Ber. d. Deut. Chem. Gesell.*, xxvi., 1230, 1893.

most important properties are explained, especially the capabilities of the salt-formers, of sulphur, and of oxygen to support combustion, and, on the other hand, the inflammability of sulphur and of phosphorus is demonstrated.

The difficultly or non-fusible non-metals follow:—Carbon, Silicon, and Boron.

Then come the semi-metals and easily fusible:—Tellurium, Germanium, Arsenic, Antimony, and Bismuth; and the difficultly fusible:—Chromium, Molybdenum, Tungsten, Uranium, Ruthenium, and Osmium.

With these Rhodium and Iridium together form, on the one side, and Manganese on the other, the connecting links with the true ductile metals of the platinum and iron groups:—Platinum, Palladium, Iron, Cobalt, and Nickel.

The less difficultly fusible—Copper, Silver, and Gold—follow, the best conductors of heat and electricity, then the eighth easily fused heavy metals—Zinc, Cadmium, Mercury, Gallium, Iridium, Thallium, Tin, and Lead.

The light metals conclude the survey,—first of all Aluminium, with its rare allies, then Magnesium and Beryllium, and finally the metals of the alkaline earths—Calcium, Strontium, and Barium—and of the alkalis—Lithium, Sodium, Potassium, Rubidium, and Cæsium.

Of each of these elements only so much is said as is requisite and sufficient to characterise them, and at the same time to bring out their association with the common things of daily life, and, as far as possible, matter of historical interest is introduced.

(To be continued).

## THE CHEMISTRY OF PLANT FIBRES: CELLULOSES, OXYCELLULOSES, AND LIGNO-CELLULOSES.\*

By C. F. CROSS, E. J. BEVAN, and C. BEADLE.

In a series of papers, 1880—93, we have dealt with special points in the chemistry of the constituents of the plant fibres. Our recent investigations have furnished data which enable us to consolidate this previous work into a more complete account of the lignocelluloses, and at the same time to exhibit a probable connection of the process of lignification with the general chemistry of the celluloses proper, through their oxidised derivatives, or oxycelluloses.

Without drawing any final conclusion as to the genetic relationships of the members of these several groups, we shall be able to show that in the jute fibre—the simplest type of lignification—the characteristic keto-R-hexene group is linked to the normal cellulose of the fibre through a series of oxidised and condensed derivatives, which are in constitutional features so related to the cellulose on the one hand and the R-hexene constituent on the other as to suggest a series of transitions from the one extreme member to the other.

As is well known, the non-cellulose constituents of jute are converted into soluble derivatives by a variety of treatments under which the cellulose remains more or less unaffected. Thus, by chlorine gas the keto-R-hexene groups are converted into quinone chlorides, soluble in sodium sulphite solution. The residue from this treatment is a lustrous white cellulose preserving the structural characteristics of the original fibre and amounting to 75—80 per cent of its weight.† Bromine (as bromine water) acts much less completely. After exposure to this reagent for some hours, and boiling the brominated fibre with dilute alkaline solution, much of the non-cellulose remains, and the treatment requires to be once or twice

repeated before arriving at a pure cellulose. When obtained, it is usually much more disintegrated than that from the single treatment with chlorine, and amounts to 72—75 per cent. The diminished yield is due to attendant oxidation and hydrolysis of a constituent which we shall subsequently describe as cellulose  $\beta$ . In addition to these actions of the halogens, there are processes by which the non-cellulose is attacked and dissolved in a single treatment. We cite two as typical, and of very opposite character:—(a) Digestion with dilute nitric acid at 70—80° (*Ber. Deut. Chem. Ges.*, xxiv., 1186, 1772), and by digestion with solutions of bisulphites at 130—150°C. The residue from these experiments is a cellulose, obtained as a disintegrated mass or pulp and amounting to 60—63 per cent of the weight of the fibre. This more resistant cellulose we may describe as cellulose  $\alpha$ . An important feature of distinction of these celluloses from one another is the presence in the cellulose  $\beta$  of the O.CH<sub>3</sub> group (*infra*). But for the present we are rather concerned with their common differentiation from the typical cotton cellulose. The jute cellulose, however obtained, has, in fact, the composition of an oxycellulose; that is, the carbon percentage is 43 or less, and the reactions are such as to indicate the presence of ketonic or aldehydic oxygen.

We are now able to give a more conclusive proof of its constitutional relationship to the oxycelluloses in the results of a new hydrolysis of their group of compounds; which consists in treating with a reagent prepared by saturating aqueous sulphuric acid of 1.5 sp. gr. with hydrochloric acid gas.\* In this acid the oxycelluloses dissolve completely, and on diluting and distilling furfural is obtained in quantity. We determined the yield of this aldehyd from such celluloses as we have previously noted to be differentiated from the normal type, viz.,—

	Furfural.
Straw cellulose yielded .. .. .	14.5 per cent
Wood .. .. .	6.5 ..
Jute .. (Cl method) yielded .. .. .	6.0 ..
Jute .. (HNO <sub>3</sub> method) yielded .. .. .	6.0 ..

These quantities are considerable, and sufficient to indicate differences of constitution.

We then examined typical celluloses of the normal and more resistant type—resistant, that is, to oxidation and hydrolysis. The following yields were determined:—

Fibres bleached by	Cellulose.	Per cent.
alkaline hydro- lysis and hypo- chlorite oxida- tion.	Cotton yielded .. .. .	0.2
	Flax .. .. .	0.7
	Rhea .. .. .	0.5

The fibres in the above cases were disintegrated by the reagent, but not dissolved. It appeared that the yield of furfural might be proportional to the degree of oxidation of the celluloses attending the process of bleaching or purification. In verification of this, we oxidised cotton in successive stages by a method admitting of more exact control than those which have been previously used, viz., by chromic acid in dilute solution and in presence of sulphuric acid, in quantity equivalent to the resulting Cr<sub>2</sub>O<sub>3</sub>. The products were treated with the reagent, and the solutions, after dilution, were distilled for furfural. The numbers obtained are appended:—

	Weight of cotton.	Weight of CrO <sub>3</sub> . Grms.	Volume of solution. C.c.	Oxy- cellulose. Per cent.	Yield of furfural.
(a)	4.7	1.5	70	93.0	4.1
(b)	4.7	3.0	90	87.0	6.3
(c)	4.7	4.5	110	82.3	8.2

\* From the *Ber. Deutsch. Chem. Gesell.*, November, 1893.

† We have analysed this cellulose on several occasions, and find it gives uniform numbers, viz, C, 42—43; H, 6.0. (*Chem. Soc. Journ.*, xli., 104).

\* The reagent is most conveniently made by mixing concentrated sulphuric and aqueous hydrochloric acids; at 1.56 sp. gr. the acid contains 57.3 per cent H<sub>2</sub>SO<sub>4</sub> and 5.5 per cent HCl.

The oxycellulose (c) was entirely dissolved by the reagent; (b) and (a) incompletely. The specimen (c) on ultimate analysis was found to contain 41.9 per cent carbon.

In further elucidation of these relationships, we have studied the oxidation of other typical carbohydrates, but of lower molecular weight. Starch, cane-sugar, and milk-sugar were treated with chromic acid in dilute solutions in the cold, and in presence of HCl in equivalent quantity. The quantities of chromic acid (weighed as  $K_2Cr_2O_7$ ) used represent approximately 1, 2, and 3 atoms O upon a formula weight  $C_6H_{12}O_6$  (=180). The oxidation completed, the products were distilled from hydrochloric acid and the furfural estimated in the distillate.

Carbohydrate.	Weight.	$K_2Cr_2O_7$ used to oxidise.	Yield of furfural per cent of original carbohydrate.	
			(1)	(2)
Milk-sugar .. ..	5.5	3.0	6.2	6.6
„ .. ..	5.5	6.0	10.5	
„ .. ..	5.5	9.0	10.0	
Cane-sugar .. ..	5.5	3.0	4.0	
„ .. ..	5.5	6.0	7.0	
Starch .. ..	5.5	9.0	11.0	
Starch (previously swollen with water)	5.5	9.0	10.3	

It appears, therefore, to hold generally that the hexoses, or carbohydrates immediately derived from them, are converted by regulated oxidation into products which yield furfural on hydrolysis. It is, of course, possible that the formation of a pentose may precede that of furfural; and, if so, that in that sense the pentoses are produced from the hexoses by oxidation. This question is being further investigated. In the meantime, it is important to remember that the formation of furfural from a carbohydrate by hydrolysis affords no conclusive evidence as between a hexose or pentose configuration of the parent substance.

By these results, therefore, the oxidation of the hexoses and their derivatives generally, and of normal cellulose in particular, is directly connected with the production of furfural-yielding carbohydrates, and the probability at once arises that these two groups of "natural" products may be similarly related in the plant. There is a good deal of collateral evidence of the existence of such a relationship, but as the purpose of this communication is limited, we shall not attempt to deal with physiological points.

We have already stated that jute cellulose isolated by the process of chlorination is a mixed product, and the evidence of the variation in yield, according to the methods generally employed, warrants the division, already indicated, into—

Cellulose  $\alpha$ , constituting from 60—63 p.c. of the fibre; and—

Cellulose  $\beta$ , „ „ 15—20 „ „

Having observed the formation of derivatives containing the methyl group in various decompositions of the lignified fibres and of purified celluloses, we were led to examine certain of these for the presence of methoxyl. We have made quantitative estimations of  $O.CH_3$  in jute celluloses by the well-known method, and find in the celluloses isolated by the chlorination process, *i.e.*, the mixture of the  $\alpha$  and  $\beta$  celluloses,—

1.2 per cent  $O.CH_3$ ;

whereas, in the celluloses from the treatments with dilute nitric acid and with bisulphites, *i.e.*, the  $\alpha$  cellulose, there is none present. Since, therefore, the cellulose  $\beta$  constitutes about one-fifth of the aggregate of cellulose in the former case, it may be calculated to contain—

$5 \times 1.2 = 6.0$  per cent  $O.CH_3$ .

Representing this cellulose  $\beta$  by the formula  $C_{18}H_{32}O_{16}$

( $C=42.8$  per cent), corresponding with the composition of the aggregate, we may express the result as follows:—

$O.CH_3$ found.	Calculated for $C_{17}H_{20}O_{15}.OCH_3$ .
6.0 per cent	6.0

We have here, therefore, a fibrous cellulose which may be described as fairly resistant to oxidation and hydrolysis—having survived the treatments of this nature—containing an ethereal alkyl group, and our views of the constitution of the celluloses as a group must receive a corresponding extension.

With regard to the composition and constitution of the jute fibre, it remains now to deal with the non-cellulose groups, and to apply the foregoing results to showing the connection of these groups with the cellulose.

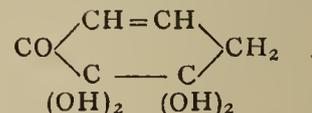
It will be convenient if we give a brief statement of the numerical data which have from time to time been determined, and from which we shall deduce the more simple and complete view of the constitution of this group of natural products.

(a) *Empirical Analysis* in normal specimens of the fibre is 46—47 per cent, and the empirical formula  $n(C_{12}H_{18}O_9)$  fairly expresses the mean composition of the organic constituents of the fibre.

(b) *Hydrolysis*.—The alkalis and more stable acids in dilute solution attack the fibre as a whole; the portions rendered soluble have the same empirical composition and reactions as the original fibre, and the fibrous residue, though it may have undergone structural changes, is similarly characterised. We have prepared a series of osazones from the soluble products, which are well defined compounds crystallising from toluene. We shall deal with these in a subsequent communication. For our present purpose it is sufficient to note that by simple hydrolysis all the constituent groups of the fibre are simultaneously attacked, and it is only when other conditions are added that these groups are more or less resolved. Such *complex hydrolyses* as are determined by nitric acid, sulphurous acid, and the bisulphites need only be mentioned in regard to their main action, which is to react synthetically with the non-cellulose constituents, forming soluble compounds, and at the same time to hydrolyse a constituent which by other treatment may be isolated as a cellulose ( $\beta$ ). The residue resisting their action we have termed cellulose  $\alpha$ .

(c) *Chlorination and Formation of Quinone Chlorides*.

—The fibre substance takes up 7—8 per cent of its weight of Cl, and the reaction appears to be simple, *i.e.*, unattended by oxidation. The chlorinated derivative isolated by solvents has the formula  $C_{19}H_{18}Cl_4O_9$ . It contains mairougallol or leucogallol in union with a group yielding furfural and acetic acid on hydrolysis (HCl). Expressing the derivative as  $3C_{19}H_{18}Cl_4O_9$ , and subtracting a molecule of a quinone chloride of corresponding formula, *i.e.*,  $C_{57}H_{54}Cl_{12}O_{27} - C_{18}H_6Cl_{12}O_9$ , we are left with the Cl-free complex  $C_{39}H_{48}O_{18} = 3C_{13}H_{16}O_6$ . The two remaining constituents of the fibre substance are therefore the keto-R-hexene derivative, which we assume to contain groups of the general form\*—



condensed by union of OH groups, and the empirical aggregate  $C_{13}H_{16}O_6$ , which remains to be further characterised.

(d) *Furfural Estimations*.—We have re-determined the yields of furfural from the fibre substance and its derivatives, using the improved method of Tollens. The celluloses isolated by the usual methods give only fractional yields when boiled with hydrochloric acid. The fibre

\* We make no attempt to assign definite relative positions to what may be regarded as the component groups of this molecule, *i.e.*,  $CO, CH_2=C$ , &c.;

itself (lignocellulose), on the other hand gives considerable yields.

The following numbers have been obtained\* :—

Raw fibre (pure specimens) ..	9.2 per cent
Fibre (previously chlorinated) ..	9.6 „

and they establish the following points:—The cellulose of the fibre under hydrolysis by HCl yields traces only of furfural, which is therefore produced mainly from the non-cellulose constituents. The hexene groups obviously contribute none, and the complex  $C_{13}H_{16}O_6$  is therefore the main source of this aldehyd, though it is possible that some quantity may be derived from the group which furnishes the cellulose  $\beta$ .

We note here that it has become customary to assume that the formation of furfural from vegetable products is evidence of the presence of a pentaglucose. But quite apart from the results communicated in the earlier part of this paper, the empirical formula we have deduced for the furfural yielding groups is altogether at variance with any such view in this case; and by the further evidence we have to adduce, is practically excluded.

We have frequently shown that acetic acid is produced in the simpler hydrolytic decomposition of lignified fibres, and we have been able to trace this to the presence of  $CO.CH_2$  residues in the non-cellulose groups. Another source of products of decomposition containing the  $CH_3$  group we now find in the presence of methoxyl groups.

(e) *Methoxyl Determinations.*—We made two estimations of  $O.CH_3$  in pure specimens of the fibre. The numbers obtained were—

	(1).	(2).
$O.CH_3$ per cent of fibre substance..	4.5	4.6

Of this, a portion is derived from the cellulose, as already stated. We found that the cellulose isolated by the Cl method, which gives the simplest resolution into cellulose and non-cellulose, yields 1.2 per cent  $O.CH_3$ . Calculating that the 80 per cent of cellulose in the fibre will yield 0.96  $O.CH_3$ , and deducting this quantity, the non-cellulose will contain the balance, *i.e.*, 3.6 per 100 parts of fibre substance.

Further, as the non-cellulose amounts to 20—25 per cent of the weight of the fibre, the proportion of  $O.CH_3$  in the non-cellulose cannot be less than four times this, *i.e.*, 14.4 per cent. Expressing this in molecules, the minimum is 2. $O.CH_3$  in the formula weight  $C_{19}H_{22}O_{10}$  (calc. 15.1 per cent  $O.CH_3$ ).

(f) *Oxidation by Chromic Acid.*—The fibre substance is only very slowly acted upon by chromic acid in presence of sulphuric acid at ordinary temperatures. The mean result of an extensive series of experiments under these conditions may be stated as follows:—

Oxidised with 50 per cent of the weight of  $CrO_3$ , the fibre loses 10 per cent of its weight.† The colour of the product is white, with a tinge of green due to residual  $Cr_2O_3$ . The carbon percentage in this fibrous product is 43—44 (extreme results of several analyses). The keto-R-hexene constituent is the first to undergo oxidation, the  $C=C$  union being resolved, and the product behaving as a saturated compound.

Distilled with HCl for furfural, the yield is 8—9 per cent. The configuration of the furfural-yielding groups appears, therefore, to be unaffected by the oxidation. They appear to be converted, together with cellulose  $\beta$ , into an oxycellulose, the product losing 30 per cent of its weight on treatment with dilute alkalis; the ultimate yield of the more resistant cellulose being, as in other oxidising treatment, 60 per cent of the weight of the fibre.

(To be continued.)

\* In these determinations of furfural the method of volumetric estimation (Gunther and Tollens) was employed. After the publication of the latest communication on this subject (Flint and Tollens, *Landw. Vers. Stat.*, 1893, xlii., 381—407), the determinations were repeated on the gravimetric plan, *i.e.*, of weighing the hydrazone. Identical results were obtained.

† Traces only of gaseous products are formed in these oxidations.

ON THE  
ACTION OF IODINE ON SOME  
PHENOLS AND ALLIED COMPOUNDS IN  
PRESENCE OF FREE ALKALI, AND  
A NEW CLASS OF DERIVATIVES  
RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Concluded from p. 216).

*On the General Structure and Positions of the  
Iodine Atoms.*

IN the constitutional formulæ used to express the supposed structure of the various molecules and individual positions of atoms several well-marked similarities have been assumed throughout. For instance, in all cases molecular condensation is represented as having taken place, and this even in cases where two contiguous carbon atoms of two benzene nuclei have become common. One consequence of this is the assumed existence of somewhat redundant-looking molecules.

Nevertheless, the great similarity displayed throughout the various series treated of, together with the number of oxygen atoms relative to the number of carbon atoms, and the almost certain positions taken up by those oxygen atoms in the molecules of lesser magnitude, enables one to treat as proofs what might otherwise be justly treated as analogies in dealing with those molecules of higher magnitude. For example, there is no doubt whatever but that two thymol molecules are condensed to a dithymol molecule as one result of the reaction, and from this we may assume the same to be true in those cases where actual coalescence, attended with elimination of carbon, of two contiguous molecules also takes place at one stage or another.

In representing the products from simple phenol, the iodine atoms have been placed vertically opposite without any proved reason for doing so. At least one of the iodine atoms must occupy the position in the benzene ring usually denoted by the cipher 4, whilst the second iodine atom might be supposed to be attached at positions 1 or 2.

There can be little doubt but that the positions actually taken up are the same as those occupied by the iodine atoms of the true di-iodophenol obtained at the same elevation of temperature under otherwise different conditions; and it may also be safely assumed that such true substituted phenol is, in general, primarily formed. However, the relative positions of the substituted iodine atoms of this particular di-iodophenol are not at present known, so that the information cannot be derived from this source.

In the ordinary, and what may perhaps be called the normal, product obtained from thymol, that is, the compounds which contain a dithymol molecule, the iodine atoms are represented as being attached to the carbon atoms of positions 6 in each ring. Those positions would almost naturally suggest themselves as being the most likely. Messinger and Voitman adjudicated those positions to the iodine atoms, because the red compounds could be prepared from Willgerodt's iodothymol, in which the iodine atoms are recognised as occupying such positions. This affords no proof whatever that the red compounds hold the iodine atoms in any particular position, except in such special cases where they are actually prepared from this particular iodothymol, because the formation of the red compounds is not a consequence of the true substituted iodine atoms occupying any particular positions; indeed, there is no reason why such red compounds should not be possible of formation without their containing any true substituted iodine whatever. True substitution by iodine must be looked upon as merely a consequence of the necessary method of manipulation and concurrent conditions existing, putting aside all con-

siderations as to accelerating physical influences induced as the result of substituting an atom of iodine in the molecule.

It will be observed that in those cases where coalescence of two benzene nuclei also takes place, the iodine atoms are represented in position 2 of the ring as a necessary consequence, without assuming attachment to oxidised carbon atoms or to oxygen atoms direct.

Messinger and Vortman represent the hypothetical third iodine atom of the condensed molecule as being directly attached to an oxygen atom, but I have shown that the compounds contain no such third iodine atom. This idea seems, however, to have taken possession of various authors, for we now find aristol represented as containing both iodine atoms attached directly to the oxygen of the hydroxyl groups without any apparent reason for doing so, and on that account called an iodide.

However, there would be nothing improbable in the compounds containing an oxy-iodine group in the ordinary places of substitution taken up by the simple iodine atoms, and, indeed, the number of oxygen atoms found in the compounds suggest distribution as such.

In order to prove or disprove this possibility a considerable quantity of the product from phenol and also one of the products from thymol were fused up with potash, but no such oxy-iodine radicle could be separated, and on that account the oxygen atoms throughout the foregoing paper have been represented as occupying the positions originally occupied by the hydroxyl groups. In doing so it has been assumed that if addition of oxygen took place it would most likely take place where oxygen already existed, the hydrogen of the hydroxyl being in general eliminated. The analytical data agree with this assumption; still it is not a little remarkable when we consider that other carbon atoms are simultaneously removed together. There is no reason why the iodine atom may not be united directly to the carbon atom also united to oxygen.

Too much stress should not be placed on the percentage of hydrogen shown by analysis, since this was generally regarded as a matter of secondary importance, and a slight difference in time of manipulation is capable of making a difference of 0.2 per cent, which indicates a considerable difference on calculating into atoms.

#### The "Encluded" Iodine.

The true substituted phenols are not capable of "including" iodine either at the moment of formation or by subsequent manipulation. It cannot be imagined that such a molecule oxidised would; indeed, I have shown in a special case that it does not (see *ante*). What, then, can be the cause of such "enclusion" if not molecular condensation?

On reviewing the constitutional representations of the molecules dealt with from this standpoint, one may be struck with the peculiar suitability for such "enclusion" by virtue of the relatively large vacant space which must exist around the points of condensation; and assuming the representations to be fundamentally true, this suitability may be considered largely increased by virtue of such vacant space being a closed one, and therefore admirably fitted to "enclude" matter presented in a sufficiently fine state of sub-division. Then, again, there is the mere mass attraction, consequent upon the individual masses of the opposite rings of the molecule. Moreover, the angles of attraction at the points of condensation may be regarded as abrupt. Abrupt angles and terminations are, generally speaking, abnormal natural products—at all events, in complex structures. May it not be that the iodine in this case arches the corners, so to speak? May not chemical spheroidicity play an important part in chemical constitution?

**Statue to the late M. Chevreul.**—A bronze statue of the late illustrious chemist Chevreul has been erected at his native town, Aggerz.

## RECENT ADVANCES IN AGRICULTURAL CHEMISTRY.

It has been repeatedly observed that if some one introduces into commerce a new toy, or a new game, or a new quackery, he will probably reap a golden harvest; but if he devises some great, decisive improvement in one of the most important arts, his reward will be neglect and opposition. Such has been the lot of M. Georges Ville. He has spent years and large sums of money in the improvement of agriculture. He has studied the action and the economy of manures, and has brought his conclusions to the test of experiment on a practical scale and with uniform success. The land-owners and farmers who have carried out the suggestions of M. Ville have had no reason to repent. The scientific and technical press has given him very generally its support. His works have had a wide circulation. Still the great mass of farmers hold aloof, and persist in following the routine which their forefathers used in the last century, which is no longer able to meet the conditions of the present day.

M. Ville seeks to convince the farmer that to keep cattle as producers of manure is a capital error. Such manure, if carefully valued, is found to cost more than its actual worth, and much more than the cost of an artificial manure of equal or superior value. Farm-yard manure is found to contain only 1.48 per cent of plant-food; it has the defect that its composition cannot be varied according to the requirements of any particular crop. Now, with farm-yard manure no such adaptation is possible. Further, if a pasture-land is poor in phosphates, the excreta of cattle fed upon it cannot be rich in phosphates, and will be very ill-adapted as a fertiliser for any crop which is in need of phosphoric acid.

In one of his works ("La Betterave et la Legislation des Sucres") M. Ville cautions his readers against the use of the Stassfurth potash salts. He contends that night-soil, at least if applied to the sugar-beet, yields very heavy crops, but at the expense of the quality of the roots, which are hollow and poor in sugar. He places the sources of nitrogen in the following ascending series as regards their efficacy:—Organic nitrogen, ammonium sulphate, sodium nitrate, and potassium nitrate. He insists, very justly, on the maintenance of a due equilibrium among the constituents of plant-food; if any one of these ingredients is in excess, the surplus contributes neither to the quantity nor to the quality of the crop, but remains in the soil without being taken up by the plants, and is consequently wasted as far as the farmer's returns are concerned.

M. Ville's conclusions agree in the main with those of the leading agricultural chemists in this country; but there is one important difference. He classes lime as one of the four constituents with which soils—without distinction of their character—are not provided by nature to an extent sufficient for the growth of plants. Hence it figures in all his formulæ in the state of calcium sulphate, gypsum. Now, in England, experience has shown that—except for certain special crops, such as clover—gypsum is of no appreciable value. Hence plants have been divided into calciphilous and calcifugous. The former grow by preference naturally in calcareous earth, and when growing in ordinary average soils are distinctly benefitted by dressings of lime or of manures containing lime. The calcifugous plants, on the contrary, may be exterminated by the application of lime. If we consider that the proportion of calcareous matter in soils capable of cultivation may exceed 30 per cent, we may be surprised when told that lime is universally necessary, as are nitrogenous matter, phosphoric acid, and potash. It may be said, in reply, that lime in the state of carbonate is insoluble in water, and thus is not available as plant-food. But it does dissolve in water charged with carbonic acid, and this is the condition generally occurring in the soil.

M. Ville has made a series of experiments by adding to a soil "complete manure," *i. e.*, nitrogenous matter, phosphate, potash, and gypsum, and has obtained a crop of 51,000 kilos. On omitting the lime the yield was only 47,000 kilos. If the potash is omitted it falls to 42,000 kilos.; without phosphate it is merely 37,000, without nitrogenous matter 36,000, and without manure at all 25,000. But we do not see that he has tried the effect of the soil with the addition of lime alone.

The cultivation of beetroot is recommended by the author as a key to the agricultural situation. As a nation we can look upon it with little sympathy. It was one of the weapons used against us by the first Napoleon, and it has wrought us a grave amount of injury.

Before passing on to examine in our next the author's social and economical views, we must notice his assertion that "in cold and misty regions the use of tea predominates over that of coffee, whilst in hot countries coffee has the upper hand." In contradiction to this rule we must point out that in Australia, which is hotter and drier than any European country, the consumption of tea is exceptionally large, whilst in cold Norway coffee is in almost exclusive use.

### ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 201).

THEY are certainly comparable among themselves, but not with the relations of sensitiveness of the photographic plate. They are this just as little as the behaviour of one kind of plate can be decisive for the behaviour of another kind. Between the ocular and the photographic method of determining the luminosity, in particular of the ultra-violet rays, there is certainly an internal connection, that of absorption; but how little decisive this is for the case in question is best proved by the fact that every substance has its own absorption spectrum. It must be also remarked, in passing, that ocular determinations of luminosity, even when they refer to light of the same quality, afford only a very imperfect guide to the objective luminosity.

It was therefore absolutely necessary to re-examine quartz and gelatin in this respect. In the same manner I was restricted to my own resources in determining the absorptive action of the air.

A medium has still to be considered which is much more important for my proofs than the substances just named—the sensitive constituent of the photographic plate, silver bromide. The success of the photograph depended in the first place on the behaviour of this substance. If it was in reality so feebly sensitive to the most refrangible rays as my proofs seemed to indicate there then came up the further problem to find a suitable substitute for silver bromide.

The determination of the sensitiveness of silver bromide turned likewise in the first place in an absorption experiment. For it could possess higher sensitiveness only if it absorbed the rays with sufficient energy, preferably in the modification used in photographic dry plates. On the manner of the extinction of the rays, whether photo-chemic or photo-thermic could be decided only by the photographic behaviour of a silver bromide free from any admixture of foreign constituents. It might appear as if a proof with pure silver bromide would alone suffice for this purpose, and as if a knowledge of the absorption might be dispensed with. But this view is contradicted

by certain facts of that part of my preliminary researches concerning the production of a new photographic plate,—of which below.

In this manner I might anticipate better results in the region of the smallest wave-lengths than heretofore, but always with the apprehension that the hoped for rays beyond the limit of activity already reached might indicate a quite different behaviour than those on which my previous experiments were founded. I commenced my preliminary researches with quartz, followed in succession by gelatin, silver bromide, and air.

(To be continued).

### THE ACTION OF AMMONIA GAS UPON MOLYBDENYL CHLORIDE.\*

By EDGAR F. SMITH and VICTOR LENHER.

IN 1857, Tuttle (*Annalen*, *ci.*, 285) studied the action of ammonia upon molybdenum trioxide and molybdenum chloride ( $\text{MoCl}_4$ ). In the case of the trioxide the temperature at which the reaction was made approached a red heat. The resulting product was in part black in colour and possessed metallic lustre. Its analysis revealed the presence of nitrogen, oxygen, hydrogen, and molybdenum. The quantity of the latter constituent equalled 92.9 per cent. Upon conducting the reaction at more elevated temperatures, the product was found to contain 77.9 per cent and 73 per cent of molybdenum, while the hydrogen content did not exceed 0.18 per cent. The results consequently were not constant.

On exposing molybdenum chloride to the action of ammonia gas at a temperature just sufficient to volatilise the ammonium chloride which arose in the reaction, Tuttle obtained a black metallic sintered mass. It was found to contain 82.83 per cent of molybdenum, and was assumed to have the composition expressed by the formula  $\text{Mo}_2\text{N}_2 + \text{Mo}(\text{NH}_2)_2$ , analogous to a compound of tungsten obtained in a similar manner by Wöhler (*Annalen*, *lxxiii.*, 190).

Several years after the publication of the preceding investigation, Uhrlaub presented an inaugural thesis entitled "Die Verbindungen einiger Metalle mit Stickstoff" (Göttingen, 1859), from which we collate the following interesting facts:—

In the action of ammonia gas in the cold upon molybdenum chloride much heat was evolved and a black coloured product resulted; its analysis showed the presence of 76.457 per cent of molybdenum, 23.134 per cent of nitrogen, and 0.677 per cent of hydrogen. In subsequent experiment Uhrlaub employed a more intense heat, thus hoping to eliminate the slightest hydrogen content, but this element continued to show itself in his various products, until on raising the tube in which the reaction took place to an intense red heat he obtained a compound that careful analysis gave a composition which may be expressed by the formula  $\text{Mo}_3\text{N}_2$ . In other words, a molybdenum nitride had been formed by acting upon the chloride of the metal with ammonia gas at a high temperature.

When Uhrlaub tried the action of ammonia upon molybdic acid at a gentle heat, he obtained "pseudomorphuen," as he designated them, bluish black in colour. Several were prepared; they varied much in composition. Uhrlaub attributes this variation to the different degrees of heat employed and to the length of time during which the heated molybdenum trioxide was exposed to the action of the gas.

The preceding facts indicate that the action of ammonia gas, either upon the trioxide or chloride, is not as simple as might be presumed. An amide that might well be ex-

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. *cii.*, Part II., April, 1893).

\* Read before the Chemical Section of the Franklin Institute, May 16th, 1893.

pected in either case appears not to have been obtained by either Tuttle or Uhrlaub.\*

We hope to reach this result by the action of ammonia gas upon molybdenyl chloride, in accordance with the equation—



It will be noticed that we apply the term molybdenyl chloride to the compound generally called molybdenum dioxchloride. Our assumption of molybdenyl is based upon the terms sulphuryl, chromyl, &c., applied to compounds possessing a constitution similar to that of the dioxchloride of molybdenum,  $\text{MoO}_2\text{Cl}_2$ ,  $\text{SO}_2\text{Cl}_2$ ,  $\text{CrO}_2\text{Cl}_2$ .

*Preparation of Molybdenyl Chloride.*—Of the various methods proposed for the formation of this derivative of molybdenum, we discovered that the action of dry chlorine upon the dioxide of the metal yielded by far the most satisfactory product, both as to purity and quantity.

At a very gentle heat the molybdenyl chloride forms rapidly and sublimes in feathery crystals. Schulze (*Journ. Prakt. Chemie*, xxix., N. F., p. 440), in discussing the action of molybdic acid upon metallic chlorides, proposes this procedure for the object we had in view, but we failed to meet with success in our applications of the method. The yield was not very abundant.

The crystalline molybdenyl chloride, prepared as described, was introduced into porcelain boats, and these placed in tubes of hard glass, through which we conducted a brisk current of well dried ammonia gas. The molydenyl chloride immediately assumed a deep black colour, much heat was evolved, and copious fumes of ammonium chloride vapour were carried out of the tube. Considerable moisture also collected upon the anterior portion of the combustion tube. At last heat sufficient to expel any ammonium chloride retained by the compound was applied; but it was not for a longer period than half an hour. The boat and contents were cooled in ammonia gas. The product of the reaction was placed over sulphuric acid to absorb any retained gas; a portion of it was also washed with water, and the aqueous solution examined for chlorine, but this was not found present. In general appearance the product was metallic and black in colour. Analyses were made of different preparations. The molybdenum content was determined by oxidising weighed portions of material with dilute nitric acid, evaporating carefully to dryness, finally applying a gentle heat for a period of fifteen minutes.

The hydrogen was estimated by burning the material in a current of oxygen, and collecting the water that was produced in a weighed calcium chloride tube.

The nitrogen estimations were three in number; one of them was carried out by the method of Dumas, while the other two were made by the soda-lime process.

The oxygen was obtained by difference.

Our analytical results may be tabulated as follows:—

#### Molybdenum Determination.

	MoO <sub>3</sub> found.	Mo.
	Grm.	Per cent.
1. 0.1047 grm. substance taken	0.1156	= 73.65
2. 0.1006 " " "	0.1108	= 73.42
3. 0.1004 " " "	0.1110	= 73.70
4. 0.1028 " " "	0.1113	= 73.47
5. 0.1017 " " "	0.1126	= 73.80

The mean molybdenum percentage of these five determinations is 73.61 per cent.

#### Hydrogen Determination.

	Water found.	H.
	Grm.	Per cent.
0.2088 grm. substance taken	0.0082	= 0.43

\* The primary object of these gentlemen seems to have been the preparation of molybdenum nitrides.

#### Nitrogen Determination.

	Pt found.	N.
	Grms.	Per cent.
1. 0.1510 grm. substance taken	0.0643	= 6.05
2. 0.1529 " " "	0.0642	= 5.96

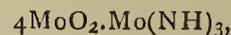
The nitrogen found by the Dumas method equalled 6.00 per cent, and the mean of the three nitrogen estimations was also 6.00 per cent.

Two-thirds of this nitrogen content were expelled when our compound was exposed to the action of hydrogen at the highest temperature attainable with a good combustion furnace.

Taking the mean of our analysis as a basis of calculation:—

	Per cent.
Mo.. .. .	73.60
N .. .. .	6.00
H .. .. .	0.43
O (by difference).. ..	19.96

we deduce  $\text{Mo}_5\text{O}_8\text{N}_3\text{H}_3$  as the most probable empirical formula, which may be variously written to express the enigmatical constitution of this compound. Thus it might be  $\text{MoO}(\text{NH})_2 \cdot \text{MoONH}_3 \cdot \text{MoO}_2$ , or—



which may be correctly termed tetramolybdenyl molybdenimide.

Our compound is stable in the air. Hydrochloric acid does not affect it. Nitric acid of sp. gr. 1.42 causes it to burn very energetically. Dilute alkalis attack it very sluggishly. It liberates ammonia when fused with caustic potash. When heated in a current of oxygen it is slowly oxidised. Heated in nitrogen gas, the black compound loses water and assumes a reddish colour. An analysis of this product indicates that it was probably molybdenum dioxide mixed with a very small amount of nitride; at least, traces of nitrogen were found upon examination. Another interesting observation was that when the black product was introduced into an aqueous solution of silver nitrate, crystals of metallic silver gradually appeared over the surface of the molybdenum compound.

We obtained our first product several times, but care must be exercised and the same conditions noted by us strictly observed if success in its formation is desired.

An examination of Uhrlaub's analytical results will show that one of his products approaches very closely the compound we have just described. He speaks of it as a black "pseudomorph" with the composition—

Mo .. .. .	73.55 per cent.
N .. .. .	5.58 "
H .. .. .	0.54 "
O .. .. .	20.30 "

The formula deduced from these figures differs from that presented by us, and what is more, if we understand Uhrlaub correctly, his compounds prepared from ammonia gas and molybdenum trioxide were all "blau-schwarz" in colour, and were not acted upon in the cold by nitric acid (see his "Dissertation," pp. 13, 14, 17).

However, it is evident that the product we obtained by the action of ammonia gas upon molybdenyl chloride is not the amide we had in view. Thinking that perhaps the heat we applied to drive out the final traces of occluded ammonium chloride may have been sufficient to alter the composition of the product formed at first, we allowed the ammonia to act upon the molybdenyl chloride at the ordinary temperature, and when there was no further evolution of ammonium chloride and the boat had become perfectly cold,\* we introduced carbon dioxide, applying a very gentle heat at the same time,

\* Portions of the product removed at this stage and shaken with cold water decomposed into a mixture of blue- and brown-coloured masses. The possibility of removing the ammonium chloride was, therefore, excluded.

but we failed to achieve our aim. Nitrogen, when substituted for carbon dioxide, gave us no better result. We next dissolved molybdenyl chloride in the purest ether we could get, and conducted ammonia gas into this solution. We obtained decomposition products. A closer examination of the behaviour of the molybdenyl chloride towards ether revealed the fact that the moment the two came in contact a slight hissing sound was perceptible, and the ether at once imparted a strong acid reaction to blue litmus. The same was observed when pure chloroform was employed as a solvent.

If molybdenyl chloride be gradually heated in an ammonia atmosphere until the tube of hard glass becomes bright red in colour, and the gas action be continued for an hour, the resulting product will be an amorphous metallic black mass. Subjected to analysis it gave results as appended.

*Molybdenum Determination.*

	MoO <sub>3</sub>	Mo
	found.	per cent.
(1) 0.1042 grm. substance taken ..	0.1061 grm.	= 67.87

*Nitrogen Determination.*

0.1025 grm. substance burned with soda-lime gave 7.00 per cent N.

*Hydrogen Determination.*

0.1012 substance ignited in a current of oxygen gave 0.0109 grm. of water equal to 1.19 per cent H.

Mo .. .. .	67.87	per cent.
N .. .. .	7.00	„
H .. .. .	1.19	„
O (by difference) ..	23.94	„

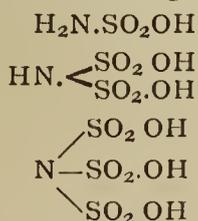
The empirical formula deduced from these figures is Mo<sub>7</sub>O<sub>14</sub>N<sub>5</sub>H<sub>10</sub>, which can also be written—



Dilute alkalies have no effect upon this compound; but it liberates ammonia when fused with caustic potash. It is converted into molybdenum trioxide very energetically—with evolution of sparks—when brought in contact with cold nitric acid.

Other products were obtained by us; their analyses lead us to the conclusion that with us, as with Uhrlaub, the composition of the derivative depended wholly upon the length of time during which the gas acted upon the molybdenyl chloride, and the degree of heat employed in the experiment. It seems highly improbable to us that the amide MoO<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub>—molybdenyl amide—can be prepared after the fashion pursued by us, for it is quite certain that the heat of the reaction evolved in the first contact of the ammonia with the molybdenyl chloride exercises a very potent influence upon the composition of the product.

When we recall the action of ammonia gas upon sulphur trioxide and sulphuryl hydroxy-chloride resulting in the compounds with the following constitution—

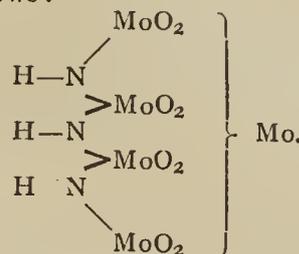


the question that obtrudes itself is: Are not these products and their methods of formation types of the processes and results that have occurred not only in our studies described in this paper, but also in the studies of Tuttle and Uhrlaub? Are not their products, as well as our own, only residues of amide, imido, and nitrito molybdc acids?

Above we have written for our first product the consti-

\* At least in so far as the action of ammonia gas upon molybdenum trioxide was concerned.

tutional formulæ MoO(NH)<sub>2</sub>.MoONH<sub>3</sub>.3MoO<sub>2</sub>, and 4MoO<sub>2</sub>.Mo(NH)<sub>3</sub>, but after considering the sulphur types we would express our empirical formula Mo<sub>5</sub>O<sub>8</sub>N<sub>3</sub>H<sub>3</sub> differently, as follows:—



We have here several broken-down molybdenyl amide nuclei in conjunction, not chemically combined, with metallic molybdenum. Reviewing the behaviour of the product which we thus graphically represent, we may be allowed to emphasize the fact that when it was brought in contact with an aqueous argentic nitrate solution, metallic silver was precipitated, and this we know from Smith's (*Zeit. für Anorg. Chemie*, i., 360) observation is a property of metallic molybdenum. Further, it will be recalled that when our product was heated in an atmosphere of nitrogen it left a reddish coloured compound, which upon analysis approximated the requirements of molybdenum dioxide, and that traces of nitrogen were also detected in it. All these experimental facts find expression in our graphic representation above.

The second product obtained by us was even more active when introduced into a silver nitrate solution, throwing out metal quite rapidly, proving in our opinion the presence in it of even a greater quantity of metallic molybdenum than is contained in the first body. Similar reduced molybdenyl amide nuclei mixed with metallic molybdenum, could also be constructed for our second compound, and be in harmony with the observed deportment of this body if it were necessary.

IMPROVED PROCESS FOR THE  
RAPID AND CERTAIN DETECTION OF  
CHOLERA BACILLI.

By R. KOCH.

THIS process, according to the author, if suitably applied, indicates even single cholera microbes in drinking-water and river water. The method requires that, whilst observing the well-known precautions, a little of the suspected water is added to a solution of peptone and allowed to stand at 37°. If there are in the material only very few cholera bacilli capable of development, they increase very remarkably at the above temperature in from six to twelve hours. In consequence of their avidity for oxygen, they collect upon the surface of the liquid, where, under certain circumstances, they form a fine film, distinctly visible. On the microscopic examination of a drop of the liquid from the surface, the characteristic "comma bacilli" are seen in prodigious numbers.

In order to be quite certain in the diagnosis, we take a drop from the surface of the liquid containing the bacilli and make up gelatin—or, preferably, agar—plates according to the old method. If the gelatin plates are allowed to remain at 22° (or the agar plates at 37°), in from ten to fifteen hours the cholera bacilli (if present) will have grown to characteristic colonies, so that in the most difficult case a demonstration can be secured within about from twenty-one to twenty-seven hours.—*Zeit. für Hygiene and Zeit. Anal. Chemie.*

Mr. F. G. Adair Roberts, partner in the well-known firm of Boake, Roberts, and Co., Stratford, London, has just been elected to a seat on the West Ham Town Council. We understand his election gives general satisfaction to his fellow townsmen.

COLOUR REACTIONS OF  
CERTAIN AROMATIC TRIOXIDE COMPOUNDS.

By J. STAHL.

THE reactions mentioned occur in the cases of pyrogallol, gallic acid, pyrogallic carbonic acid, and tannin. In all these substances alkalies, with the simultaneous action of the oxygen of the air, produce brown or brownish red colours, even if the trioxy-compounds are present only in very minute quantities.

1-1000th m.grm. of pyrogallol gives the reaction with ammonia, and soda-lye with 5-1000th m.grm.; 2-1000th m.grm. gallic acid and tannin and 1-1000th m.grm. pyrogallic carbonic acid yield the reactions.

In a series of other reactions given for the trioxy-compounds, *e.g.*, potassium cyanide, sodium nitroprusside, arseniates, &c., the author ascribes the result to the alkalinity of the reagents, the other components merely producing slight modifications in the colour.

Baryta- and lime-water give the above named trioxide compounds the same colour reactions as the true alkalies. Other phenols give with the alkaline earths yellow or reddish tones (resorcine, hydroquinone, phloroglucine) or no colourations ( $\alpha$ -naphthol, thymol, paracresol).  $\beta$ -naphthol turns bluish; pyrocatechine, first violet, afterwards greenish black.

As regards the reactions—none of them characteristic—produced by osmic acid, molybdic acid, and solutions of chloride of lime, as also by the oxides of nitrogen and the compounds of chromic acid, we must refer to the original.

The behaviour of the trioxy-compounds with the compounds of iron is characteristic. Pyrogallic carbonic acid yields with concentrated solution of ferric chloride a greenish brown colouration or, if much diluted, a violet.

The most sensitive reaction for pyrogallol (5-1000th m.grm.) is a mixture of ferric chloride and potassium ferricyanide, which in consequence of the reduction of the ferric chloride to the ferrous state gives a precipitate of Turnbull's blue. Gallic acid, in the absence of air, is not affected by ferrous sulphate.—*Zeit. Anal. Chemie* and *Pharm. Central Halle*.

## PROCEEDINGS OF SOCIETIES.

## ROYAL INSTITUTION OF GREAT BRITAIN.

*General Monthly Meeting, Monday, November 6, 1893.*

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 Society:—John Astley Bloxam, F.R.C.S., Matthew Wilks Geary, F.R.G.S., James Sidney Hargrove, Gordon Donaldson Peters, Jean Paul Richter, Ph.D., Sir Richard Henry Wyatt, D.L., J.P.

The Managers reported, that at their meeting held this day they had elected Charles Stuart, M.R.C.S., Fullerman Professor of Physiology for three years (the appointment dating from January 13, 1894).

The special thanks of the Members were returned to Lord Armstrong for his donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures.

## NOTICES OF BOOKS.

*Agricultural Analysis: a Manual of Quantitative Analysis for Students of Agriculture.* By FRANK T. ADDYMAN, B.Sc., F.I.C. London: Longmans, Green, and Co. 1893. Small 8vo., pp. 200.

THE first part of this useful Manual treats of the appliances and manipulations used in quantitative operations.

It is to be regretted that a somewhat pedantic feeling has led the makers of French weights to adopt and cling to the divisions 0.3, 0.2, 0.1. Any one who takes the trouble to compare will find that any given weight can be made up more conveniently with touching a smaller number of pieces on the English division 0.6, 0.3, 0.2, 0.1. In like manner the French flat plates are much less convenient than bent wires. If these two little points could be attended to the advantages of the metric system would be at once recognised.

Part II. gives directions for determinations, gravimetric and volumetric, the latter section including the preparation of standard solutions and the selection of indicators.

Part III. is devoted to the determination of nitrogen. Here we note a curious slip of the pen. The soda-lime process is mentioned as due to Dumas, instead of to Will and Varrentrap. The Kjeldahl process, or rather its modification as devised by Dunning, is admitted as preferable in a number of cases, especially where very many determinations have to be conducted.

For the expeditious determination of nitrogen in nitrates the Ulsch method is recommended. Lunge's nitrometer method is also described, and the apparatus is figured.

In Part IV. instructions are given for sampling, a subject too much neglected, and productive of unedifying disputes between seller, buyer, and analyst.

In Part V. we find directions for the analysis of feeding materials, whilst Parts VI. and VII. are devoted respectively to the analysis of manures and soils. In determining phosphoric acid the magnesia process is given, and, where iron and aluminium are present, the molybdic method. The treatment of fish manure, the excreta of bats, &c., are specially described, with the caution that in all fish guanos oil must not be present in quantities exceeding 3 per cent. Night-soils, sewage-manures, and blood-manures are not specially mentioned. Instructions are given for the analysis of gas-lime.

The directions for the analysis of milk, butter, and cheese are somewhat brief. A caution is, however, given as to the possible presence in cheese of margarine and of lead chromate.

For the analysis of drinking-waters the Wanklyn process is given, with the addition of Hehner's method of estimating hardness. The necessity, in certain possible cases, of a bacteriological examination of waters and milks is not taken into consideration, probably as the necessary information is to be found in several recent works.

Throughout the book the author has kept his eye on "South Kensington," but he has not appended any lists of questions set at any "exam." His instructions are so clear and judicious that students will find the work a trustworthy guide.

*Measurement of Light in Colour Sensations.* A New Method of Investigating the Phenomena of Light and Colour by means of the Selective Absorption in Coloured Glass, Graded into Scales of Equivalent Colour Value. By JOSEPH W. LOVIBOND, F.R.M.S., The Colour Laboratories, Salisbury. London: G. Gill and Sons.

THE main object of the present work is to describe the structure and the applications of a most useful instrument which has been devised by the author, and which is, we hope, coming more and more into use. Not a few arrangements have been proposed for estimating and recording the exact tones and intensities of colours. We may mention the colorimeters of Dubosq, Stanmer, Wolff, Fleische, &c. None of these, however, are fully satisfactory, and we may therefore congratulate Mr. Lovibond on the invention of his *tintometer*, which obviates most of the defects of the instruments previously in use. The peculiarities of the tintometer include the use of graded coloured glasses as standards of comparison

instead of solutions, of appliances for excluding side-light, and for giving a direct view without the use of lenses, prisms, or reflectors. In addition to the instrument itself, the tintometer, the author puts forth as novelties in his system the glass colour scales and the colour equivalence of their several units, his scheme of notation and colour nomenclature, his system of colour charts, and the determination of the smallest increment of colour appreciable to a trained normal vision. This limit he fixes at 0.006 of a standard colour unit.

On the subject of primary colours he gives an uncertain sound. In addition to the theory of Newton and Chevreul (red, yellow, and blue), and that of Young and Helmholtz (red, green, and violet), he mentions a 4-, a 5-, a 6-, and a 7-ray theory, but he accepts "as the three primaries, in the original sense of the word," orange, green, and violet. He limits the number of separate colour sensations to twelve, six of which are simple and six compound. Like all practical men, he advises that diffused day-light, preferably from the north, should be used for examining and comparing colours, and he insists in all cases upon an equality of light in both tubes of the instrument.

Mr. Lovibond's method of measuring colour in the spectrum of diffused daylight depends on progressive absorption. He intercepts the spectrum of the light with glasses of a neutral tint until the weakest colour-ray is absorbed, then adding the necessary glasses until the next weakest, and so on until all are absorbed.

A description of the tintometer without the accompaniment of diagrams would be of little value. But it is our very agreeable duty to call attention to some of the practical applications which the tintometer has already received. Thus, Prof. Munro has worked out the tintometer measurement of ammonia in water and distillates under different conditions, taking into account the age of the Nessler solution and the time in which it is left in contact with the liquid under examination. The influence of the temperature of the solution has subsequently been studied by Messrs. Hazen and Clark (CHEMICAL NEWS, vol. lxii., p., 125).

Mr. T. Jobson has applied the instrument for estimating lead in waters. The analytical method is the same which has been established by W. A. Miller and J. A. Wanklyn, but the tintometer comes in to measure the depth of colour produced.

H. Le Neve Foster has found Mr. Lovibond's instrument most useful in the analysis of steels by the Eggertz colour method, or by Stead's colour method.

The tintometer is useful also, according to Mr. Sanderson, the secretary of the Association of British and Irish Millers, for measuring or reproducing the colour of any given sample of flour.

Use has already been made of colour in judging of the presence and proportion of organic impurities in drinking-water, reservoirs, rivers, sewage, and effluents. But the tintometer enables such observations to be made with more ease and with numerical accuracy.

In a variety of other cases the tintometer must also prove valuable. It will in many cases relieve the dyer and colour manufacturer from the necessity of depending entirely on swatch-dyeing, as well in their materials as in their finished products. The paper-maker can by means of this instrument examine his water, his half-stuff, and his bleached pulps. The wine-grower and distiller will find this instrument advantageous.

Mr. Boverton Redwood, in conjunction with the author, has examined by this means petroleum, shale, and coconut oils. But, perhaps, the most widely reaching application of Mr. Lovibond's instrument is in the study and detection of colour-blindness. In this department the author has enjoyed the co-operation of Mr. Priestley Smith, of Birmingham, who has suggested some improvements in the instrument for this especial purpose. It is incidentally remarked that some of the standard wools of

Holmgren's system fade considerably, and should be periodically verified.

The tintometer can be applied, not merely for examining liquids, but also for solids and pigments, and there is little doubt but that its uses will meet with rapid extension. Those who give the instrument a careful trial, whether in pure research—chemical, physical, or biological—or in practical operations, will find occasion to be satisfied with the results.

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*The Chemistry of Fire.* By PATTISON MUIR, M.A., Fellow and Prælector in Chemistry of Gonville and Caius College, Cambridge. Methuen and Co. 1893. Crown 8vo., pp. 163.

THIS little work, which belongs to the University Extension Series, is edited by J. E. Symes, Principal of University College, Nottingham. The author is already favourably known to most of our readers from his writings on questions in the philosophy of chemistry. In the present work Mr. Muir expounds the elementary principles of chemistry from the well-known facts of combustion, taking the case of a candle. He remarks that "to understand the occurrences included in the every-day process of burning a candle is to understand the whole of chemistry and no small part of physics." To the thoughtful reader, who is seeking to *know* and not to "pass," this book will prove a suggestive guide.

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*A Guide to the Examination of the Urine.* By J. WICKHAM LEGG, Fellow of the Royal College of Physicians of London, formerly Assistant Physician to St. Bartholomew's Hospital, and Lecturer on Pathological Anatomy in the Medical School. Seventh Edition. Edited by H. LEWIS JONES, M.A., M.D. London: H. K. Lewis. 1893. Fcap. 8vo., pp. 139.

THE examination of urine as a clue to the condition of health has been in use for centuries by herbalists, astrologers, wise women, village sages, and all manner of quacks. These worthies, if we may believe Shakspeare, knew how to give responses as ambiguous as those of the Delphian oracle. Said the doctor whom Falstaff consulted: "The water itself was a good healthy water, but for the party that owned it he might have more diseases than he knew for." But now urinoscopy has passed into the hands of qualified physicians who have at command the resources of chemical and physical science, the results obtained are of the utmost value.

The author of the work before us gives a table of the average composition of the urine, with its daily quantity. There follows a general preliminary scheme for the examination of urine, first physically and then chemically. In searching for albumen, the coagulation by means of picric acid is duly recognised as a valuable test. For the detection of sugar, the methods of Moore, Trommer, and Fehling are described, as also the fermentation process, the indigo-extract test, the picric acid and the phenylhydrazin tests. The question whether normal urine contains sugar is considered still undecided. For the recognition of blood, the spectroscopic detection of the absorption bands of hæmoglobine is recommended. The indications of the guaiacum test are regarded as indecisive, unless confirmed by other reactions. For the recognition of some of the urinary pigments, such as urobiline, uroerythrine, and hæmatoporphyrine, the spectroscope useful.

Throughout the book cautions are given concerning errors which may possibly arise from the presence of unusual and unsuspected substances. The illustrations are excellent, especially the photographic reproductions of specimens of urinary crystals. But there is little need to express further approval of a work which has reached its seventh edition.

*Inorganic Chemistry for Beginners.* By Sir HENRY ROSCOE, F.R.S., D.C.L., LL.D., assisted by JOSEPH LUNT, B.Sc., F.C.S. London: Macmillan and Co. 1893. Small 8vo., pp. 245, with 108 Illustrations in the Text.

THE publishers, says the author, have called his attention "to the want of a work for those beginning the study of the science in which the elementary principles of chemistry are more fully treated than is the case" in his "Elementary Lessons in Chemistry." We cannot for a moment question the judgment of Messrs. Macmillan in their own business, though we have certainly been for years of opinion that every type of book which beginners in chemistry might require has been produced in superabundance.

The author describes merely the non-metallic elements, and among those only oxygen, hydrogen, nitrogen, chlorine, sulphur, and carbon, with their more important compounds. The lessons which may be drawn from the study of these substances are very clearly developed.

The book will be excellent for the beginner, though we cannot commit ourselves to the assertion that it has any well-marked advantages over the elementary treatises which are already known.

## CORRESPONDENCE.

### EASY RULE FOR CONVERTING THERMOMETRICAL DEGREES.

*To the Editor of the Chemical News.*

SIR,—I think many of your readers will be interested in the appended rule for the mutual conversion of degrees Centigrade and Fahrenheit, which I devised many years ago for simplifying the usual method of calculation as given in various technical manuals, the latter being cumbrous and not quickly performed, except by an expert reckoner. Almost anyone can readily make the conversion by the new rule without even needing paper and pencil. Such a method might be expected to have been published before, but I have not seen it, nor has anyone to whom I have imparted it.

To reduce a given number of degrees Centigrade to Fahrenheit—

*Rule.*—Double the number and subtract one-tenth of the result.

Fahrenheit to Centigrade—

*Rule.*—Increase the number by its ninth part and halve the result.

The necessary subtraction or addition of 32 at the proper stage is performed in the usual manner.—I am, &c.,

G. WATMOUGH WEBSTER.

Chester, November 1, 1893.

### BARIUM SULPHATE IN SANDSTONE.

*To the Editor of the Chemical News.*

SIR,—In reply to Prof. Clowes's enquiry, I may just say that the barium sulphate occurs to a small extent in the cementing material of the grit as well as in the crevices or joints. I need not further trespass on your space, but will forward a portion of a sample I have to Prof. Clowes with more particulars.—I am, &c.,

H. T. MANNINGTON.

Flint, November 1, 1893.

## 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. cxvii., No. 17, October 23, 1893.

**Analysis of a Vanadiferous Coal.**—A. Mourlot.—The author, referring to a paper by J. J. Kyle which appeared in the CHEMICAL NEWS of October 28, 1892, on the "Composition of a Vanadiferous Coal from San Raphael, in the Province of Mendoza, La Plata," gives an account of a similar coal which he has received from M. Haeren, but for which he gives no locality. The sample is especially interesting as containing in its ash a large proportion of vanadic acid in the state of alkaline and metallic vanadates. The ash forms 0.63 per cent of the coal, and contains 38.5 per cent of vanadium, or 0.24 per cent as calculated upon the entire coal.

**Perfume of the Violet.**—F. Tiemann and P. Krüger.—The perfume of the violet is obtained either from the fresh flowers of the plant or from the dried root of the iris. The odoriferous principle is a ketone, which the author names irone, and which has the composition  $C_{13}H_{26}O$ . On submitting to distillation in a strong current of steam the extract obtained by exhausting iris root with ether, we obtain a mixture composed principally of—(1) myristic acid, oleic acid, and other fatty acids; (2) the methylic ethers of these acids; (3) traces of oleic aldehyd; (4) certain neutral substances in minute traces; (5) irone. Irone is an oil readily soluble in alcohol, ether, chloroform, &c. It boils at  $144^{\circ}$ , its specific gravity is 0.939, and its index of refraction = 1.50113.

**New Synthesis of Erythrite, and Synthesis of an Isomeric Erythrite.**—The author's results show that he has effected the synthesis of a new erythrite, presenting the same structure of atoms of carbon as ordinary erythrite.

**Influence of Organic Solvents upon Rotatory Power.**—P. Freundler.—The totality of these observations seem to demonstrate better than it has been done previously the considerable influence exerted by solvents. Many of the anomalies of the rotatory power of dissolved substances depend on two causes: (1) the polymerisation of the native molecule in solution; (2) the combination of the active substance with the solvent.

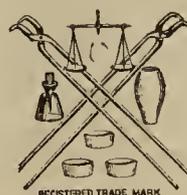
**Certain Chemical Conditions of the Action of Beer Yeast.**—J. Effront.—The author studies the action of fluorides upon yeast.

## MEETINGS FOR THE WEEK.

WEDNESDAY, 15th.—Society of Arts, 8. Opening Address, by Sir Richard Webster, Q.C.

THURSDAY, 16th.—Chemical, 8. "The Normal Butyl, Heptyl, and Octyl Esters of Active Glyceric Acid," by Prof. P. Frankland, F.R.S., and John Macgregor, M.A. "The Ethereal Salts of Diacetyl-glyceric Acid in their relation to Optical Activity," by the same. And other papers.

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THE CHEMICAL NEWS.

VOL. LXVIII., No. 1772.

THE CHEMISTRY OF PLANT FIBRES:  
CELLULOSES, OXYCELLULOSES, AND LIGNO-CELLULOSES.\*

By C. F. CROSS, E. J. BEVAN, and C. BEADLE.

(Concluded from p. 227).

HAVING now discussed the four constituent groups of the fibre substance, we give the approximate proportions per cent in the annexed diagram:—

Cellulose $\alpha$		Keto-R-hexene deriv.
60—65		7—9
Cellulose $\beta$ .	Complex, $C_{13}H_{16}O_6$	
20—15	18—22	
Cellulose, $3.C_6H_{10}O_5.H_2O.$	Non-cellulose, or lignone, $C_{19}H_{22}O_{10}.$	

These quantities have been deduced from the foregoing analytical results, and we shall now show that the various determinations taken together are mutually confirmatory, and therefore constitute a satisfactory account in general terms of the jute fibre substance.

**Keto-R-Hexene Constituent.**—The proportion is calculated from the weight of Cl combining with the fibre substance, viz., 7—8 per cent (*Chem. Soc. Journ.*, 1889), and from a study of the attendant results of the reaction (*loc. cit.*). Mairogallol,  $C_{18}H_7Cl_{11}O_{10}$ , may be considered as derived from a Cl-free molecule  $C_{18}H_{18}O_{10}$  [394], which is approximately  $3.C_6H_6O_3$ , and combines with 11 atoms Cl, i.e., 90 per cent of its weight. Taking the percentage of Cl combining at 7.5 and multiplying by 1.11, we obtain 8 as the approximate percentage of the keto-R-hexene derivative.

**Lignone,  $C_{19}H_{22}O_{10}$ .**—The formula of this complex, which is also described as *non-cellulose*, is deduced from that of the chlorinated derivative,  $C_{19}H_{18}Cl_4O_9$ , by substitution of  $H_4$  for  $Cl_4$ , and may be resolved into the keto-R-hexene group expressed in its simplest terms,  $C_6H_6O_3$ , and the empirical residue  $C_{13}H_{16}O_6$ .

The proportion of the formula weight of these groups is 1:2.6. If, therefore, the former constitutes 7—9 per cent of the fibre substance, the latter is by calculation 18—23 per cent. Taken together, we may regard the percentage of non-cellulose as 25 by this calculation.

Considering the lignone as an aggregate,  $C_{19}H_{22}O_{10}$ , we may verify this calculation in the following way:—The carbon contents of  $C_{19}H_{22}O_{10}$  is  $C=55.5$ . Taking the fibre as an aggregate of 75 per cent cellulose (with 44 per cent carbon), and 25 per cent non-cellulose (with 55.5 per cent C), the carbon percentage of the fibre substance is by calculation—

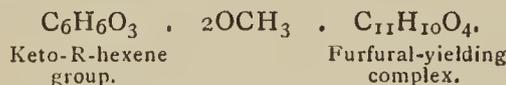
$$\frac{75 \times 44.0 + 25 \times 55.5}{100} = 46.9.$$

This is entirely in concordance with the results of ultimate analysis, and is further confirmed by the study of the chromic acid oxidation (*supra*). The most noteworthy result of this treatment is the disappearance of the constituent which reacts with chlorine, which appears to be selectively oxidised into soluble products. The loss of weight being 10 per cent, is a further confirmation of the previous estimate of the proportion of this constituent, and the residual fibre, behaving as a mixture of oxidised celluloses, may be regarded as composed of the celluloses

$\alpha$  and  $\beta$ , and the problematical residue,  $C_{13}H_{16}O_6$ , converted by oxidation (and hydration) into an oxycellulose and yielding furfural with the same facility and approximately in the same quantity as before oxidation.

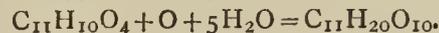
It must be admitted at this point in the discussion of our results that the deductions therefrom, being in a large measure indirect, are only approximations in regard to the relative proportions of the constituent groups with which we are dealing. Even if the fibre substance were constant in composition, we are limited to the investigation of derivative products, and are still in comparative ignorance as to the mode of union of the parent molecules in the original fibre substance. The fibre substance is, moreover, variable, though within certain limits, which do not appear to be very wide for the fibre produced under normal conditions; but a recent investigation of a specimen produced under "artificial" conditions of growth, has shown that the process of lignification may be made to vary very considerably (A. Pears, *Journal Chemical Soc.*, 1893). Mindful of these considerations, we have drawn our evidence as to composition and constitution from the study of several of the reactions and properties of the fibre substance, i.e., of its constituent groups, each presenting some independent feature of differentiation; and it is in view of the general concordance of the numbers so obtained that the degree of approximation to the truth is to be estimated.

We now have to deal more particularly with the complex represented by the empirical formula  $C_{13}H_{16}O_6$ . We have explained that this group must be regarded as in union with the keto-R-hexene constituent, and that the union survives the conversion of the latter into the corresponding chloride. The mixed chloride having the formula  $C_{19}H_{18}Cl_4O_9$ , we regard this as derived from a Cl-free complex,  $C_{19}H_{22}O_9$ , which we have shown to be decomposable into—



Respecting the group  $C_{11}H_{10}O_4$  we have established the following points:—

It yields, on hydrolysis, 50 per cent of its weight of furfural; it does not combine with the halogens to give substitution products; it is converted by oxidation and hydration (attending liberation from combination) into an oxycellulose, which change to a saturated hydroxy compound may be approximately formulated as under:—



This evidence leaves us no choice but to regard the methoxyl groups as attached to the complex  $C_{11}H_{10}O_4$ , and even then we cannot be dealing with any configuration of the carbons normal to the "carbohydrate" group. On the other hand, we are confronted with a yield of furfural on hydrolysis such as has so far been exclusively established for certain of the carbohydrates, viz., the pentaglucofuranoses, and for glycuronic acid (Tollens, *Agr. Vers. Stat.*, xxxix., 450). In further investigation of this problem, we have carried out a very large number of experiments upon the hydrolysis of the group, with subsequent oxidations by the well-known methods, in order to obtain the well-characterised dibasic acid derivatives of the  $C_6$  or  $C_5$  carbohydrates.\*

Nitric acid oxidations have failed to yield definite products. We have studied this reaction exhaustively in all its stages. We find that the lignocelluloses (jute, wood, &c.) may be completely resolved by digestion at 70° C. with three times its weight of 10 per cent  $HNO_3$ . This decomposition of the fibre takes place with very slight action upon the furfural-yielding constituent. Distilled with hydrochloric acid in presence of urea the dissolved

\* The pronounced tendency of the hexoses to condense to furfural as a secondary result of oxidations, throws a great deal of light upon the oxidations of the carbohydrates, especially by nitric acid—more particularly the difficulty of obtaining satisfactory yields of the dibasic  $C_6$  acids, excepting under carefully regulated conditions.

\* From the *Ber. Deutsch. Chem. Gesell.*, November, 1893.

products yield from 30—40 per cent of their weight of the aldehyd. These soluble derivatives have been further treated by the well-known methods, viz. :—(1) Prolonged digestion with lime; (2) nitric acid of 1·15 sp. gr.; and (3) bromine and silver oxide: none of which have yielded any products of definite relationship to the "carbohydrate" group.

We would note here that Lindsey and Tollens (*Liebig's Annalen*, cclxvii., 341) were equally unsuccessful in dealing with a similar complex, viz., the soluble by-products of the bisulphite (Mitscherlich) process of preparing "cellulose" pulp from pine wood. To this complex they assign the formula  $C_{24}H_{24}O_{10} \cdot 2(OCH_3)$ , containing the unsaturated or hexene group, *i.e.*, representing the entire non-cellulose constituent of the wool. This is therefore to be compared with our jute lignone formula  $C_{19}H_{22}O_9$ , or  $C_{17}H_{16}O_{7.2}(OCH_3)$ . This product, obtained as a sulphonated derivative, was investigated by the methods which have been exhaustively studied and generalised by Tollens.

They obtained traces of levulinic acid, no saccharic acid, traces of mucic acid, and a small proportion of mannose and small quantities of pentaglucose, such as could be identified by the well-known colour reactions.

On the other hand, the main constituent was an amorphous gummy body, behaving as a homogeneous compound, and giving a series of synthetical products, all indicating derivation from a molecule with the empirical formula  $C_{24}H_{24}O_{10} \cdot 2(OCH_3)$ .

A tetrabromo derivative of this compound is easily formed, and we may assume that in the above formula one keto-R-hexene group is represented. Deducting for this group the approximate expression  $C_6H_5O_3$ , we are left with the residue  $C_{18}H_{18}O_{7.2}(OCH_3)$ . This residue, as explained, failed to give any "saturated" products of oxidation or hydrolysis; but, as in the case of the jute lignone, gives a large yield of furfural when distilled with hydrochloric acid.

In regard, therefore, to this important constituent of the non-cellulose of typical ligno-celluloses, we are for the present thrown back upon such further evidences as to constitution as are afforded by the empirical formulæ. Taking the C atoms in either formula, it will be found impossible to "saturate" them unless we assume that the whole of the O atoms are united to carbon only, and even then there proves to be an excess of carbon "affinities," to dispose of which a cyclic disposition must be assumed. We are not without some experimental verification of these conclusions.

On dissolving the "lignone" by the limited action of nitric acid (at 70° C.) as described, and subjecting the dissolved derivative to limited oxidation with chromic acid; on then adding acetate of sodium in excess, and boiling, furfural continuously distils. Even if therefore OH groups are fixed by the process of hydrolysis, the reverse condensation takes place under unusual conditions, implying an exceptional configuration of the C-nuclei.

The "lignone" group is further characterised by considerable avidity for acids generally, and "fixes" certain of these in an exceptional way, *e.g.*, chromic and nitric acid. It must also be remembered that the woods can be perfectly resolved by digestion with sulphurous acid (7 per cent aqueous solution) at 100° (Raoul Piçet), a reaction which could hardly be accounted for otherwise than by the basicity of the constituents dissolved, *i.e.*, the predominance of a  $H_2C.O.CH_2$  configuration. We shall not pursue the discussion of these problematical groups into speculative directions. We have shown that all attempts to connect them with "carbohydrates" of known constitution have failed. We have indicated the lines of further investigation suggested by these negative results. We hope before long to communicate a more definite account of these peculiarly "condensed" products of vegetable growth.

In conclusion we revert to the consideration of the

fibre substance as an integral compound, but admitting of resolution into the groups which we have now considered in detail. We have on several occasions criticised the view, which appears to be widely current, that the lignified tissues and films are mixtures of cellulose and the non-cellulose in "lignin" group of compounds. The relationships which we have shown to subsist between the constituent groups of the jute fibre are sufficient to disclose in them synthetical activity in various directions, and it can hardly be doubted, *à priori*, that these are exerted reciprocally between the groups.

It is also to be inferred from the relationships of the groups that the connection is a genetic one.

Thus the cellulose  $\alpha$  has been shown to be susceptible of condensation to furfural, and this property has been definitely connected with oxidation of the normal celluloses, of which it is a secondary result.

Cellulose  $\beta$  is further differentiated by the presence of the  $O.CH_3$  group. In the non-cellulose or lignone complex we have a third group with these characteristics developed in such a way that furfural is obtained from it by the simplest of hydrolytic treatments; this group is, however, still "saturated" in the sense that it is free from  $C=C$  groups, although, on the other hand, condensation to this form takes place with the greatest facility. In the last group we find the  $C=C$  grouping associated with CO in a closed ring.

Regarded therefore in series, each group contains a prominent suggestion of the next-succeeding, and according to later developments of chemical theory it is not a very bold hypothesis that they constitute a genetic series. We make no assertion that the physiology of lignification is to be so explained, but the suggestion, we think, deserves serious consideration.

We wish to express our obligation to Mr. J. C. Chorley for valuable assistance in connection with this work.

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#### NOTE ON THE INDICATORS USED IN TITRATING WITH STANDARD SULPHIDE SOLUTIONS.

By P. WILLIAMS.

THE indicator commonly used is a solution of lead acetate with caustic soda. The solution is best made by adding to a solution of sodium tartrate a small quantity of caustic soda and lead acetate, then heating till the liquid is clear. Another substance which may also be used as an indicator is the compound sodium nitroprusside, which gives an intense violet colouration with a trace of sulphide, but it is inferior to the lead solution in delicacy, though in some circumstances it may be found more convenient than the lead. Sodium nitroprusside may be prepared by heating powdered potassium ferrocyanide with two parts of concentrated nitric acid diluted with an equal volume of water, until ferric chloride ceases to give a blue precipitate. The cooled solution is filtered off from the potassium nitrate, saturated with soda, and evaporated nearly to crystallisation; four parts of alcohol are then added and the compound filtered off. It is very soluble in water, but only a light coloured solution is needed in testing for sulphides. Drops of it are spread over a white tile, and the solution to be tested added in drops.

The delicacy of both these indicators was determined by gradually diluting with water a sulphide of known strength until the colour was visible when a drop was added to a drop of the indicator. 0·0000982 grm. of  $Na_2S$  in 1 c.c. of water may be recognised by means of the sodium nitroprusside, and 0·0000245 grm. of  $Na_2S$  in 1 c.c. by means of the lead test solution.

Chemical Laboratory,  
University College, London.

ON THE  
TEACHING OF INORGANIC CHEMISTRY.

By MARGARET D. DOUGAL.

(Continued from p. 225.)

AFTER this survey of the elements the question is naturally asked whether they form the sole constituents of the earth and of the cosmic system? In answering it Prof. Lothar Meyer again follows Bunsen's method, who was wont to point out that although the amount of the earth immediately accessible is small, it might be inferred from the composition of substances formed on it, as well as from that of the primæval crystalline rocks, that the same elements occur in the interior as are found on the crust; moreover, it might likewise be concluded from the analyses of numerous meteoric stones that the entire planetary system is composed of the same elements.

By means of spectrum analysis we have extended this inference to almost the whole visible universe. Whilst considering the chemical nature of the earth's surface, it is convenient to refer to the calculation of F. W. Clarke, according to whom 99 per cent of such parts of the earth as we can examine is made up of the nine elements O, Si, Al, Fe, Ca, Mg, Na, K, and H, and the remaining 1 per cent of all the other elements put together.

The student having now acquired a general idea of the nature of the distribution of the chemical elements, Dr. Meyer proceeds to discuss the rules according to which they enter into combination. The establishment and development of stoichiometry and of the atomic theory are described historically and briefly; likewise the electro-chemical theory, at least so much of it as is to-day applicable. The contrast between positive and negative is especially explained, and the influence of contact in chemical reactions experimentally shown. Opportunity is here taken to recall to the memory of the student the laws of the galvanic current so far as they find application later, and especially is Faraday's Law of Electrolysis elucidated in general terms.

The determination of electrolytic equivalents is then mentioned, together with the thermo-chemical equivalents deduced according to the Law of Dulong and Petit. The relations of both to chemical equivalents are exhibited by the aid of specific substances. Isomorphism is at the same time briefly spoken of, and reference is again made to the Law of Avogadro, already made mention of in connection with the synthesis of water.

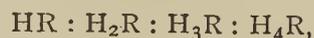
During the Course all these doctrines are again spoken of on their later application; but a preliminary knowledge of them is needed at this stage, since the atomic weights and their relations to one another as the basis of the systematic arrangement are discussed, according to which both elements and compounds are to be described in the special part of the Course.

The student has now acquired some idea of atomic weights and the rules by which they are determined. The natural system of the elements is then explained from a chart on the wall of the lecture theatre. Professor Lothar Meyer supplements his description by the aid of one or other of the models which have been devised for the purpose.

After these preliminaries it might now appear the simplest to begin with the consideration of Family I.—the Alkali Metals. This Professor Meyer has tried, and, although possible, found inconvenient owing to the necessity of having to mention so many substances hitherto not spoken of. The usual way of starting with the non-metals offers so many advantages that no teacher would willingly abandon it. That, however, is not necessary, for the Course can be adhered to quite strictly, according to the periodic system, without breaking down old traditions.

As hydrogen has served for long as the unit of atomic weight on whose numerical value the natural system of

the elements rests, it appears right to begin the consideration with the compounds of this element. How this can and must be done in a concise, comprehensive, and instructive way has been shown, as is known, by von Hofmann in his masterly "Introduction to Modern Chemistry." Following this method pretty generally, but with some alterations in details, Professor Lothar Meyer presents to his students the four chief types of hydrogen compounds—



and, as is self-evident, he begins with the simplest type, with the hydrogen compounds of Family VII.—the Salt-formers. The place of these elements in the system is at first not specially emphasised; it is merely said that they all belong to one family, and at the same time the reason given for their being first mentioned is that their hydrogen compounds are the simplest of all. The experimental treatment of these hydrogen compounds is easily accomplished without the necessity of speaking of things hitherto unmentioned. A certain knowledge of the elements has been acquired in the introduction. Salt and its analogues are generally known or are readily learnt. The useful sulphuric acid is likewise known as oil of vitriol; its composition is simply given, and the usual proofs of it are referred to later on. Instead of beginning with hydrofluoric acid, Dr. Meyer prefers to take hydrochloric acid, which is prepared before the class, reduced, oxidised, synthesised, and electrolysed in the general way. Its volume relations are particularly noted and compared with those of water and of its constituents. From hydrochloric acid it is convenient to pass on to hydrofluoric acid, which is prepared by analogous methods, and then to hydrobromic and hydriodic acids.

Of the next type,  $H_2R$ , water has already been so thoroughly considered that it is now only mentioned. Hydrogen peroxide, which could be discussed in connection with it, is briefly referred to, and its fuller consideration is postponed until barium peroxide is treated. Hydrogen sulphide, the preparation of which has some analogies to that of hydrochloric acid, is now dealt with. The hydrides of selenium and tellurium are only mentioned; on the other hand, hydrogen persulphide is shown, as also how liquid hydrogen sulphide is obtained by means of it.

Of the third type all the known members,  $NH_3$ ,  $PH_3$ ,  $AsH_3$ , and  $SbH_3$ , are experimentally prepared. The compounds of the same elements poorer in hydrogen,  $N_2H_4$ ,  $N_3H$ ,  $P_2H_4$ ,  $P_4H_2$ , are now described and their composition explained.

Of the fourth type, together with marsh gas and silicon hydride,—the only representatives of the type,—the higher hydrocarbons are briefly mentioned and shown, but their fuller consideration is referred to organic chemistry.

The hydrogen compounds of the metals are not spoken of here, but are deferred until the metals come up for consideration.

After the four types have been discussed the table of atomic weights is again referred to and the following survey given:—

HF	=	1	+	19.06	=	20.6
HCl	=	1	+	35.37	=	36.37
HBr	=	1	+	79.76	=	80.76
HI	=	1	+	126.54	=	127.54
$H_2O$	=	2	+	15.96	=	17.96
$H_2S$	=	2	+	31.98	=	33.98
$H_2Se$	=	2	+	78.87	=	80.87
$H_2Te$	=	2	+	125	=	127
$H_3N$	=	3	+	14.01	=	17.01
$H_3P$	=	3	+	30.96	=	33.96
$H_3As$	=	3	+	74.9	=	77.9
$H_3Sb$	=	3	+	119.6	=	122.6
$H_4C$	=	4	+	11.97	=	15.97
$H_4Si$	=	4	+	28.3	=	32.3

from which the dependence of chemical value, and accordingly also of chemical behaviour, on atomic weight is made evident. At the same time it is obvious that the generalisation follows, that quite analogous relations prevail throughout the natural system if we consider in compounds the monovalent salt-formers instead of the practically unknown hydrides.

This part of the Course, which has already been sketched out, is so arranged that it can be overtaken before the Christmas vacation. With the New Year the description of all the families according to the natural system and in the order of their atomic weights is systematically begun. It is, however, well to note that it is not generally advisable to treat the allied sub-groups along with the main groups, especially when they are connected with these by a few properties only, *e.g.*, the valency and isomorphism of their compounds. Their consideration is best left till later.

(To be continued).

## THE ACTION OF IZAL ON THE PTOMAINES.

By A. B. GRIFFITHS, Ph.D., F.R.S. (Edin.), &c.

THE new non-poisonous disinfectant known as "Izal" was extracted by Mr. J. H. Worrall, F.C.S., from an unknown oil obtained from certain coke ovens.

As Dr. W. B. Clarke has described in the columns of *The Lancet* (July 1, 1893) the treatment of wounds with "Izal," and as Dr. E. Klein, F.R.S., has investigated its action on pathogenic microbes, proving it to possess remarkable germicidal properties, I determined to test its action on the poisonous ptomaines which are produced in the system during the course of infectious diseases.

Until recently the vegetable kingdom was regarded as the only source from which alkaloids could be obtained, but it is now known that bodies which are very similar to the vegetable alkaloids are elaborated in the animal tissues, excretions, secretions, &c.,\* and can be obtained therefrom by suitable methods of extraction.

The animal alkaloids, ptomaines, or toxines, are produced during the putrefaction of animal matter, and they are abundantly found in the animal tissues and fluids in pathological states. The urines of persons suffering from scarlet fever, diphtheria, pneumonia, erysipelas, puerperal fever, measles, parotitis, eczema, &c., have all yielded in greater or lesser quantities alkaloidal substances or ptomaines which are extremely poisonous in the isolated state. As a rule the ptomaines are the specific products or chemical principles elaborated in the body as the result of the existence of microbes.

At the outset it may be stated that I have extracted and described eleven ptomaines which occur in the urine during certain infectious diseases (see Griffiths's papers in the *Comptes Rendus*, tomes cxiii.—cxvi.); and among these ptomaines are those described in this paper.

The experiments recorded in this paper were undertaken in order to ascertain the action of "Izal" on the ptomaines which occur in the system during certain infectious diseases. It is essential in the treatment of infectious diseases that not only pathogenic microbes should be destroyed, but also the poisonous substances, or ptomaines, which they indirectly produce.

The "Izal" used in the experiments was diluted with distilled water in definite proportions, and the action of the various aqueous mixtures was tried directly upon the poisonous ptomaines.

**Scarlatinine** ( $C_5H_{12}NO_4$ ) is the poisonous ptomaine of scarlet fever, and produces the disease when injected into the system of susceptible animals. To try the action of

"Izal" on this ptomaine the following mixtures of "Izal" and water were prepared:—

I part of "Izal" in	100 parts of water.
I " " "	200 " "
I " " "	500 " "
I " " "	1000 " "
I " " "	1500 " "

3 c.c. of the aqueous mixtures were mixed with 0.5 gm. of scarlatinine in each case. In the first four cases, the poisonous properties of the ptomaine were destroyed; but when the "Izal" was diluted to the extent of 1 in 1500 it failed to destroy the poisonous properties of the ptomaine in question. In the experiments with the weaker mixtures (1 in 500 and 1 in 1000), the mixtures of the ptomaine, "Izal," and water had to be warmed before the toxic properties were completely destroyed. The products of the action of "Izal" on scarlatinine, being non-poisonous, may readily be taken into the system, or administered to animals with impunity.

**Puerperaline** ( $C_{22}H_{19}NO_2$ ) is the ptomaine of puerperal fever. It is highly poisonous, and when administered to a dog it produced death within twelve hours. To try the action of "Izal" on puerperaline the following mixtures of "Izal" and water were prepared:—

I part of "Izal" in	150 parts of water.
I " " "	300 " "
I " " "	500 " "
I " " "	1000 " "
I " " "	1500 " "

3 c.c. of the aqueous mixtures were mixed with 0.5 gm. of puerperaline in each case, and with the complete destruction of the poisonous ptomaine. It may be suggested that a mixture of 1 part of "Izal" in 1000 or 1500 parts of water would form a suitable lotion for preventing puerperal fever declaring itself.

**Diphtherine** ( $C_{14}H_{17}N_2O_6$ ) is the poisonous ptomaine of diphtheria, and is produced in pure cultivations of *Bacillus diphtheriæ*. To try the action of "Izal" on diphtherine, the following mixtures of "Izal" and water were prepared:—

I part of "Izal" in	500 parts of water.
I " " "	1000 " "
I " " "	1500 " "

3 c.c. of the aqueous mixtures were mixed with 0.5 gm. of diphtherine in each case; and each mixture rendered the ptomaine inert.

**Erysipeline** ( $C_{11}H_{13}NO_3$ ) is the poisonous ptomaine of erysipelas. It produces high fever and death within eighteen hours. The strengths of the "Izal" mixtures used in the experiments were as follows:—

I part of "Izal" in	750 parts of water.
I " " "	1500 " "
I " " "	2000 " "

3 c.c. of the aqueous mixtures were mixed with 0.5 gm. of erysipeline in each case, and each mixture rendered the ptomaine inert.

**Glycoeyamidine** ( $C_3H_5N_3O$ ) is the poisonous ptomaine of measles. The same mixtures of "Izal" as used in the experiments with erysipeline destroyed this ptomaine, or, in other words, the products formed by the action of "Izal" on the ptomaine were non-poisonous.

**Parotitis**.—The ptomaine ( $C_6H_{13}N_3O_2$ ) of parotitis (CHEMICAL NEWS, vol. lxi., p. 87) is highly poisonous, and when administered to a cat it produced nervous excitement, cessation of the salivary flow, convulsions, and death. 3 c.c. of "Izal" (1 part in 2000 parts of water) readily destroyed 0.5 gm. of the ptomaine of parotitis.

**Pneumonia**.—The poisonous ptomaine ( $C_{20}H_{26}N_2O_3$ ) of pneumonia was rendered inert by "Izal" (1 part in 1200 parts of water).

\* See Dr. A. B. Griffiths's "Manual of Bacteriology," pp. 303—324; and "Researches on Micro-Organisms," pp. 86—141.

*Glanders.*—The ptomaine ( $C_{15}H_{10}N_2O_6$ ) of glanders is highly poisonous. A solution of it injected under the skin of a rabbit produced an abscess at the point of the injection, nodules in the lungs, spleen, and other organs, and, finally, death. This ptomaine was rendered inert by "Izal" (1 part in 800 parts of water).

In each of the above cases, the innocuous nature of the products formed by the action of "Izal" on the ptomaines was proved by experiments on animals; and such experiments were performed for me by a scientific *confrère* in France. After the action of "Izal" on each ptomaine, the characteristic tests failed to prove the presence of the smallest trace of ptomaine among the products.

From these experiments there is no doubt that "Izal" is a powerful agent, which readily destroys the deadly poisons produced in the system during the course of infectious diseases. Hence the reason that "Izal" should have a wide application in the treatment of infectious diseases, as it has the power of eliminating the poisonous ptomaines from the system.

In conclusion, I wish to record my obligations to Professors Brown-Séguard, Gautier, and Miquel, and to the late Dr. Charcot, of Paris, for the interest which they have taken in my own researches on the ptomaines; and I thank Messrs. Newton, Chambers, and Co. for the samples of "Izal" used in this investigation.

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 229).

### *The Absorption of the Most Refrangible Rays of Aluminium, Nos. 30, 31, and 32.*

*A. In Quartz.*—The observation was effected exclusively by means of photography. The absorption spectra were taken by means of the above-named spectroscopic apparatus, with a focal distance of 150 m.m. on highly sensitive plates (Zettnow). The source of light was a Leyden jar spark of the above-mentioned inductorium, 25 c.m. in length, striking between aluminium wires. Some photographs were also taken of the light of a tungsten spark, which is particularly suitable for absorption experiments on account of the uniformity of the distribution and the efficiency of its rays. The quartz plates the absorption of which was to be determined had been cut at right angles to the principal crystallographic axis, and their thickness was 3.0, 3.6, 5.2, 20, and 50 m.m. Their absorption was ascertained as follows:—

I covered the aperture of the collimator slit with the plate in question and then took (increasing constantly the time of exposure) a series of photographs of the aluminium spectrum placed below each other. I then removed the plate from the slit and repeated the series either with the same time of exposure or with one proportionately abridged. The difference between the two series showed then the absorption of the rays in question in the quartz plate selected. For demonstrating very small differences of such parallel photographs, and also where the inevitable small fluctuations of the luminosity of the source of light have to be taken into account, both spectra were photographed simultaneously. For this purpose I covered the slit for half its length with the quartz plate, whilst the other half of the slit was freely traversed by the rays. I thus obtained on each exposure two spectra separated from each other by a very narrow stripe of light, derived from the lateral surface of the quartz plate. The differ-

ences of these spectra are due as before to the absorption of light in the quartz plate.

It is found on comparison that in such proofs all distinctions come more sharply to view than in those where the photographs are successively brought into the field of vision. For thicker plates this process is less suitable, since the breadth of the stripe of light increases with the thickness of the plate and becomes ultimately wider than the object of the photographs admits. The loss of light which the rays undergo by reflection from the plane parallel surfaces of the quartz plate was so trifling in my proofs that it could be disregarded without injury to the trustworthiness of my result.

As will be self-evident all the proofs have only a very relative value. For as the prism and the lenses of the spectroscope employed consist likewise of quartz the proofs do not represent merely the absorption of the plate of quartz inserted in the track of the rays, but those of a much thicker plate. The mean total thickness of the prism and the lenses of the apparatus is 21 m.m. My proofs have therefore been produced with an uncovered slit under the influence of a stratum of quartz of the thickness of 21 m.m., and their parallel proofs consequently show merely how much more light is absorbed by the quartz plate covering the slit. As to the real resistance of the quartz no one of these proofs gives a decision. For this purpose there would be required prisms and lenses of a material absolutely impervious to the ultra-violet rays.

I give subsequently only the results of plates of 3, 20, and 50 m.m. in thickness. They show in what degree the mass of quartz retards the action of the most refrangible rays.

Quartz plate 3 m.m. in thickness. Aluminium sparks. Width of slit, 0.080 m.m. Exposure, 2½, 5, 10, 20 secs. One proof at each with and without the quartz plate. Both series differ very little from each other, but the proofs with the plate are uniformly less intense than the others. This distinction is most distinct in the line No. 32, and as it is quite clear at all exposures it can be observed there better than in the other lines.

Quartz plate 20 m.m. in thickness. Aluminium sparks. Width of slit, 0.080 m.m. Exposure, 15, 30, 60, 90, 120, 180, 240, 300 seconds; a proof with the plate at each and a proof without the plate at 5, 10, 20, 40 seconds. In all the proofs the quartz plate has completely absorbed all the rays (Nos. 30, 31, 32), whilst without the quartz plate No. 32 appeared entirely, No. 30 only in 20 and 30 secs., and No. 31 with its less deflected component only in 30 seconds.

Quartz plate 50 m.m. in thickness. Aluminium sparks. Width of slit, 0.080 m.m. Exposure, 30, 60, 90, 120 secs.; one proof each with the plate, and 5, 10, 20, 40 seconds one proof each with the plate. No trace of the lines in question appeared, just as with the 20 m.m. plate.

All other proofs gave similar results.

Hence, in thick strata, quartz is to a great degree sparingly permeable for the most refrangible rays of the ultra-violet. My former proofs of the most refrangible ultra-violet had therefore been under the restraining influence of the prisms and lenses employed. Possibly their want of transparence was mainly to blame for the non-success of the proofs of the spectral region lying beyond 182  $\mu\mu$ . As long as I continued working with quartz I could scarcely expect better results than heretofore. To obtain prisms and lenses more permeable for the ultra-violet had hence become an absolute necessity. If I was not willing to occupy myself with the search for suitable materials, I was then restricted to fluor-spar. In fact all the subsequent proofs, even those which will be at once discussed, the absorption spectra of gelatin, have been executed with prisms and lenses of white fluor-spar.

Faultless fluor-spar in colourless crystals ranks among rarities. The coloured varieties which are less difficult to obtain are not sufficiently transparent to come into

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. ciii., Part II., April, 1893).

consideration for photographing the most refrangible rays. Moderately large specimens of the colourless material are never optically pure. Cracks, flaws, and other defects occur here and there, and interfere more or less with the optical effect of apparatus prepared from such materials, often, as I have myself repeatedly experienced, to such a degree as to render them useless where the production of clear images is required. It is not too much to say that to procure large faultless apparatus of white fluor-spar must now be classed among impossibilities. Quartz, or even calc-spar, may be found of faultless quality much more frequently than pure white fluor-spar. Under these conditions the procuring of fluor-spar for my spectroscopic apparatus would have been impracticable if Herr Carl Zeiss, of Jena, had not taken a profound interest in my work and assisted me in the most disinterested manner. Although he does not profess to supply fluor-spar apparatus, he has given me, besides a large prism ( $70^\circ$ ), the requisite lenses and closing-plates (plane parallel), all wrought of unusually pure fluor-spar, and with the refractive surfaces of the utmost perfection, for the extension of my observations on the ultra-violet. My permanent gratitude is due to Herr Zeiss for this active support, which has yielded in the sequel the most beautiful fruits.

(To be continued).

### RECENT ADVANCES IN AGRICULTURAL CHEMISTRY.

M. GEORGES VILLE, whilst upholding the main principles laid down in his works and in his earlier lectures, has not been idle. He has continued observing and experimenting, and has in particular developed his doctrine of "sideration." It has been proved, by careful experiments both in France and in other countries, that certain plants are capable of absorbing the free nitrogen of the air and of retaining it in their tissues. Such plants are those especially of the leguminous order—peas, beans, tares, clover, &c. These plants, as practical agriculturists are fully aware, do not require ammoniacal salts, nitrates, or other nitrogenous manures; they obtain the nitrogen needed for their growth from the air. Now, by "sideration," M. Ville understands the cultivation of these plants as a material for fertilising the soil for the benefit of subsequent crops, *e. g.*, of wheat or other plants which do not derive their supply of nitrogen from the atmosphere to any sufficient extent. M. Ville, and those who accept his views, sow, *e. g.*, clover, and plough it into the soil, as he has fully explained in his writings, such as "The Perplexed Farmer," an English version of which, from the pen of Mr. W. Crookes, F.R.S., has been published (Messrs. Longmans). The field of clover, &c., is thus made to play more conveniently and economically the part assigned by the old school of agriculture to cattle kept for the mere production of manure—"straw-treaders" as they are technically called.

With the exaggeration customary in controversy M. Ville has been accused of pronouncing cattle-keeping an error. This is by no means correct. Where there is at hand a good market for milk, butter, cheese, meat, or for wool, he upholds live stock as remunerative. But how, he asks, can any number of cattle at once supply manure to keep their pasture-land fertile, and at the same time supply manure for the arable land? The more his teachings are adopted the more shall we be delivered from the disgrace and the barbarism of "permanent pasture."

The keeping of stock for the manufacture of manure is one of the unhappy agencies which are depopulating the country and driving the peasantry to fester in the slums of our great cities under conditions no less demoralising than anti-sanitary.

It has been said that the man who makes two ears of

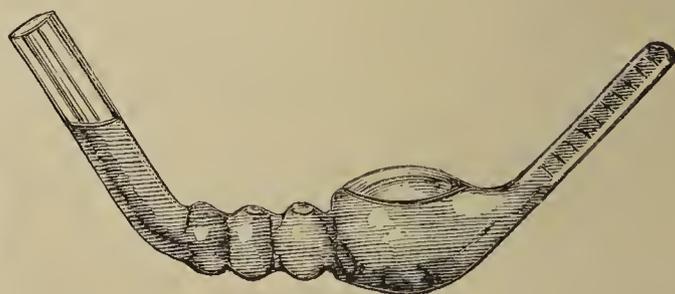
corn grow where formerly there grew only one is a benefactor to his species. The great naturalist Buffon said, in a very similar manner, "Where a loaf is created a man springs up," but he forgot to add, Woe to the nation where men arise without the loaves! Now M. Ville has shown practically how the supply of food may be vastly increased. For this he merits the highest honours. Painful it is to be compelled to add that he evidently does not meet with the recognition to which he is so fully entitled. Perhaps in a couple of centuries a statue to his memory will be erected amidst official acclamations! His view as to the benefit which France may derive from agricultural improvements is, however, over-strained. All the advances in farming which are possible in France are no less possible in Spain, in Hungary, South Russia, Canada, or Australia. Hence France can never dictate the price of wheat or other necessities of life; she must always be under-sold by countries where land is more abundant, the climate better, and local burdens less heavy.

### ON THE OCCLUSION OF GASES BY THE OXIDES OF METALS.\*

By THEODORE WILLIAM RICHARDS and ELLIOT FOLGER ROGERS.

In the course of an investigation upon the atomic weight of copper, recently conducted in this Laboratory, it was noted that cupric oxide prepared by the ignition of the nitrate always contains a considerable amount of occluded gas, which is composed mainly of nitrogen.† Cupric oxide prepared from the carbonate, on the other hand, appears to possess no such property of occluding gases. Since the material used by Hampe and others had all been made by the former method, it was at once evident that the occluded gas contained in the oxide was wholly responsible for the formerly accepted erroneous results for the atomic weight of copper.

The results of these experiments suggested the possibility that gases might be occluded by all oxides prepared in this way from the nitrates. It became a matter of much importance to test the point, for such oxides have often furnished the starting-point for determinations of atomic weights.



The method adopted in the present research was precisely similar to that used in the case of the cupric oxide. Since it is by no means certain that indefinite heating in a vacuum could drive out all the gas from the compact, often crystalline compound under examination, the material was dissolved in acids under such conditions that the gas set free could be measured and analysed.

The simple apparatus needed has been described and explained in the paper already quoted. The material to be investigated was placed in the largest bulb of the bulb-tube shown in the accompanying diagram, and the

\* Contributions from the Chemical Laboratory of Harvard College.

† Theodore W. Richards, *Proceedings of the American Academy of Arts and Sciences*, xxvi., 281. In 1868 Frankland and Ainsworth pointed out this fact; but their statement lacked definiteness, and has since been largely forgotten.

tube was about half-filled with cold water which had been thoroughly boiled. The whole was then connected with the water-pump, and freed from adhering air-bubbles by agitation in the partial vacuum, the water being allowed to boil gently under the reduced pressure. Subsequently the tube was filled with boiled water, and returned to its normal horizontal position. Pure acid was now run in from a pipette, a short piece of glass rod within the large bulb furnishing a means of agitating the oxide during its solution. The gas which was set free was finally collected and measured in the sealed end of the apparatus. In the concluding experiments, where greater accuracy was desired, the gas was transferred, and re-measured in a tube which had been carefully calibrated by means of mercury.

The gas was analysed with the help of a small Hempel's apparatus made for the purpose. The burette with which the first ten analyses were made was about 7 m.m. in internal diameter, and could be read to a 50th of a c.c., while that used for the later analyses was only 4 m.m. in diameter, and could be read with reasonable certainty to the rooth. The portion of the gas absorbed by caustic potash was assumed to be carbon dioxide, and the further portion which was absorbed by alkaline pyrogallol was assumed in like manner to be oxygen. The residue was perfectly inert, and was undoubtedly nitrogen. One sample of this residue obtained from zincic oxide was mixed with oxygen and subjected to the spark of an induction coil, without diminution in volume. The apparatus and chemicals were tested from time to time by analyses of air.

In every case the gas, while saturated with aqueous vapour, was measured at the ordinary temperature and atmospheric pressure of the room. The variations from the mean values of 22° and 76.0 c.m. were not sufficient to need attention in crude work of this kind, when working upon such very small quantities of gas.

#### *Zincic Oxide.*

Preliminary experiments with this substance gave results exactly corresponding to those obtained from cupric oxide. If the substance was prepared by ignition of the nitrate, very considerable amounts of gas were found to be occluded; while material of a similar grade of purity in every other respect, made by heating zincic carbonate, appeared to contain no trace of gas.

The oxide used in the first three experiments was made by treating so-called pure zinc with nitric acid, evaporating to dryness, re-dissolving the zincic nitrate in water with the addition of a little nitric acid, precipitating a small amount of iron with ammonia in slight excess, evaporating the filtrate, and igniting the residue. This gave a faintly yellow oxide.

For the second series a nearly neutral solution of fairly pure zincic chloride was precipitated while boiling by a solution of sodic carbonate. Part of the basic carbonate thus formed was ignited directly, the oxide thus produced containing no occluded gas (Experiment 4). The remainder was dissolved in nitric acid, evaporated to dryness, and ignited to the full heat of the blast lamp in an open porcelain crucible. Experiments 5, 6, and 7 are analyses of this yellowish sample.

For the third series a solution of "chemically pure" zincic nitrate was allowed to stand over an excess of zinc for some time. The filtered solution was evaporated until a portion of the nitrate had been converted into the basic salt. The whole was then poured into distilled water, and a solution of normal nitrate was thus obtained after the basic salt had been filtered off. This solution was treated a number of times with zincic hydrate—which had been precipitated by ammonia and washed until free from the salts of this base—and allowed to stand. The filtered solution was evaporated to dryness, and heated in a porcelain crucible to about 240° C. over a ring burner. Part of this was analysed at once (Experiment 8), part heated by a Bunsen burner (Experi-

ments 9 and 10), and part ignited at a very high temperature in a Hempel clay furnace with the blast-lamp and bellows (Experiments 11 and 12). Experiment 13 was made with a soft white oxide prepared from the basic nitrate.

Analyses 14 to 27 inclusive were made from oxide obtained as follows. Pure white zincic oxide of commerce was dissolved in nitric acid, and carefully washed zincic carbonate was added to this solution in slight excess. The whole was allowed to stand with occasional shaking for some time, and finally filtered and evaporated rapidly by boiling. This gave a sample of the oxide, which was very nearly white after intense heating in a double porcelain crucible.

In Experiments 22 and 23, pure oxygen was introduced into the flame of the blast lamp used for igniting the zincic oxide, the bottom of the outer crucible being melted where the flame struck it. The material analysed in Experiment 22 was taken from the layer nearest to the zincic silicate formed in the bottom of the crucible by fusion of the glaze, and that used in Experiment 23 was taken from the top. The zincic oxide of Experiment 24 was heated to bright yellow heat in the same way. All the edges of the porcelain were rounded, and the cover and the crucible itself were fused to the heavy iron supports on which they rested. After twelve minutes the iron itself began to burn and the ignition was stopped. The oxide was found to be "sintered together," and was of a greyish colour, as if it had been reduced in part. The inference was corroborated by the presence of zincic oxide on the cover of the crucible and on the sides of the stack of the furnace. The zincic oxide used in Experiment 25 was treated in a similar manner, but proved to be still darker in colour. It was afterwards ignited for some time in an atmosphere of oxygen in order that no reduced metal might be left.

The materials used in Experiments 26 and 27 were separate samples heated in a double crucible, with the cover of the inner crucible fitting inside the outer one, instead of covering both. This arrangement rendered less likely the entrance of reducing gases, and allowed freer play of air in the furnace. After the latter had been thoroughly heated by the ordinary blast lamp, oxygen was slowly turned on through a Y-tube to replace a large part of the air in the flame. This gave an intense white heat, which melted and burned the tip of a file in the fraction of a minute. In Experiment 27 the glaze of the inner crucible was fused, and the platinum which separated the two crucibles was cemented to the outer crucible. The crystalline residue of zincic oxide after this treatment was white, with the faintest trace of yellow, but no sign of grey. As the crucible would not stand a higher heat, and as any quantitative determination could scarcely be carried on at a higher temperature, no attempt was made to push the heat further.

The fifth series of determinations was made with the object of discovering whether the trace of silica and alkali dissolved from the glass and porcelain might be responsible for the occlusion of the gases. First, a sample of the purest zinc that could be obtained was treated with a small amount of pure nitric acid in a porcelain dish, and the solution evaporated to small bulk in the presence of an excess of zinc. Upon dilution the basic nitrate, which contained most of the impurities not deposited upon the zinc, was precipitated and removed by filtration. The solution was then evaporated to dryness, and the residue ignited in porcelain. (See Experiments 28 and 29). Another sample of zinc was dissolved in a similar way in platinum, and the resulting solution of the pure nitrate was divided into several portions. One portion was evaporated in glass and ignited in porcelain, the residue containing somewhat more gas than that which had been treated wholly in porcelain. (See Experiments 30, 31, 32, and 33). Another part was evaporated and ignited in platinum (Experiment 34). This sample was undoubtedly reduced in part by the diffusion of gases from the flame

No. of Expt.	Wt. of Zinc oxide. Grms.	Time and Temp. of heating.	Vol. of Gas evolved.	Vol. of Gas calc. for 10 gr. of ZnO. C.c.	Analysis of Gas by volume.
1.	1.375	Blast lamp.	1.6	12.0	
2.	1.19	"	1.45	12.2	
3.	1.225	"	1.53	12.5	
4.	1.1	"	0.00	00.0	
5.	1.05	"	2.1	20.	CO <sub>2</sub> = 1.2% O <sub>2</sub> =55.5 N <sub>2</sub> =42.5
6.	1.08	"	2.1	19.4	
7.	1.075	"	2.15	20.	
8.	1.27	240° C.	0.00	00.0	
9.	1.005	Bunsen flame.	0.70	7.0	
10.	1.065	"	0.78	7.3	
11.	1.22	Blast lamp. Hempel furnace.	0.58	4.7	
12.	1.91	"	0.92	4.8	
13.	1.05	Water blast. Hempel furnace.	0.20	1.9	
14.	1.07	Water blast furnace 30 mins.	0.75	7.0	
15.	1.00	"	0.71	7.1	
16.	1.02	Blast.	1.52	14.9	CO <sub>2</sub> = 1.3% O <sub>2</sub> =53.8 N <sub>2</sub> =44.8
17.	1.10	Water blast furnace 2 hrs.	0.35	3.2	
18.	1.20	" 3½ "	1.12	9.1	
19.	1.06	" 5 "	0.83	7.8	
20.	0.85	" 6 "	0.46	5.4	
21.	0.92	" 6½ "	0.53	5.8	
22.	1.07	{Furnace 6½ hrs. Oxygen flame, 15 mins.}	0.42	3.9	CO <sub>2</sub> = 0.0% O <sub>2</sub> =16.9 N <sub>2</sub> =83.1
23.	1.125	The same.	0.48	4.3	
24.	1.03	Oxy. fl. 15 mins.	0.24	2.3	O <sub>2</sub> =16.7% N <sub>2</sub> =83.3
25.	1.105	30 "	0.19	1.7	
26.	0.72	White heat 20 mins.	0.33	4.6	CO <sub>2</sub> =0 O <sub>2</sub> =24% N <sub>2</sub> =76
27.	1.0125	White heat 35 mins.	0.45	4.4	
28.	1.05	Water blast ½ hr.	0.42	4.0	
29.	1.019	1½ "	0.37	3.6	
30.	1.34	Bunsen flame 30 mins.	0.28	2.10	
31.	1.05	Water blast ½ hr.	0.97	9.2	
32.	1.0035	" 1 "	0.68	6.8	
33.	0.9765	" 1½ "	0.63	6.4	
34.	1.03	" ½ "	0.175	1.7	
35.	1.08	" ½ "	0.35	3.2	
36.	1.50	" 20 m.	0.82	5.46	
37.	1.004	" 1½ hr.	0.68	6.8	
38.	1.018	" 2 "	0.68	6.7	
39.	1.00		0.00	0.00	

## Remarks.

- No. 4.—From carbonate.  
 No. 8.—Gave test for nitrates.  
 No. 13.—Made from basic nitrate.  
 No. 14.—Fourth series.  
 No. 17.—Partly reduced.  
 Nos. 18—21.—Heated in double crucible by water blast in furnace. Samples removed from time to time.  
 No. 22.—Layer next the silicate.  
 No. 23.—Upper layer.  
 No. 24.—Partially reduced and re-oxidised.

- No. 25.—Reduced more than Ex. 24 and re-oxidised.  
 Nos. 26 and 27.—White after ignition.  
 No. 28.—Fifth series.  
 No. 30.—Probably contained nitric acid.  
 No. 34.—Partially reduced.  
 No. 35.—Less reduced.  
 No. 36.—Possibly reduced in part.  
 No. 39.—Prepared from carbonate.

(Erdmann, *Pogg. Annal.*, lxii., 611; Morse and Burton *Am. Chem. Journ.*, x, 311—321). Still another portion was ignited for a short time only in platinum, the ignition being completed in porcelain (Experiment 35). A fourth portion was ignited for a short time in an open platinum dish with free access of air (Experiment 36). Finally, the remainder of the solution of pure zincic nitrate was evaporated and ignited in a platinum vessel enclosed within one of porcelain. This specimen was not exposed to the action of reducing gases, and upon solution it evolved almost exactly the same amount of gas as the specimen which had been prepared in glass and ignited in porcelain. (See Experiments 37 and 38).

Experiment 39, using zincic oxide prepared from the carbonate, was made to test again the accuracy of the method.

The weight of zincic oxide taken for each individual experiment is tabulated in the second column of the accompanying Table, and the third column indicates approximately the conditions used for the ignition of the different portions. The volume of gas given off on the subsequent solution of the zincic oxide in sulphuric acid is recorded in the fourth column, while the fifth contains the same data reduced to the standard of ten grms. of zincic oxide. The sixth column contains a record of the analyses of the gases, and the seventh supplies information upon a few minor points connected with individual results.

It is evident that we are dealing here with a phenomenon similar both qualitatively and quantitatively to that observed in the case of copper. Zincic oxide prepared from the nitrate occludes a very appreciable quantity of nitrogen and a somewhat variable quantity of oxygen. Continued application of heat tends to drive out both gases, the oxygen being less firmly held than the nitrogen; but the highest heat which we were able to obtain was insufficient wholly to eliminate either gas. Under like conditions, specimens of zincic oxide made from zincic nitrate which had been obtained in a number of different ways appeared to hold approximately the same amounts of gas. It is almost, if not quite, impossible to prepare the oxide in this manner in a state wholly free from solid impurities taken from the containing vessel during the ignition of the purest possible zincic nitrate. The effort was made in the preceding series of analyses to prepare samples which must contain wholly different kinds of impurities. The fact that these different samples contained almost equal amounts of gas shows with reasonable certainty that the impurities are not responsible for the occlusion.

It is noticeable that the oxide obtained at a very low temperature, which still contained traces of zincic nitrate, contained little or no occluded gas (Experiments 8 and 30); also that six specimens which had been suspected of partial reduction contained much less gas than similar material free from this suspicion (Experiments 17, 24, 25, 34, 35, and 36).

(To be continued.)

The Use of Hydrometers. — Fr. Maly (*Zeit. f. Instrumenten Kunde*) — The author shows that accuracy in the use of these instruments depends on the state of the spindles. He cleanses first from coarse impurities, and then rubs with a damp (but not wet) cloth. Friction with a dry cloth is useless. The cleansed instrument is then allowed to lie for a time, so as to permit of the evaporation of any adhering moisture.

## THE ELECTROLYTIC SEPARATION OF THE METALS OF THE SECOND GROUP.\*

By SAMUEL C. SCHMUCKER.

OF recent years the determination of metals quantitatively by the methods of electro-chemical analysis has grown into great popularity. The exceedingly accurate results, the simple forms obtained, and the ease with which it is possible to determine the absolute purity of the deposits, all combine to make electrolytic methods highly desirable. Hitherto most of the operations have served simply to determine quantitatively the amount of one ingredient present, while comparatively less success has attended the separation of metals from each other. It is true that many valuable separations are known, the results of which have been published in the various chemical journals and in the few books devoted to the subject. But the list of separations of metals in the same group, and of separations of the different groups, is far from complete; and it is to this point that those chemists interested in electrolytic work are now giving their most earnest attention. Here the field seems at present likely best to repay the investigator.

As an example of a gap desirable to fill, I would cite the case of those metals known to analytical chemists as the *metals of the second group*, viz., arsenic, antimony, tin, mercury (ic), lead, bismuth, copper, and cadmium. We have no electrolytic method serving for the separation of the first three from any of the later members. An examination of the literature of the subject would disclose to the student of electrolysis that should he encounter, for instance, a mixture containing copper, arsenic, antimony, and tin, he would find himself advised to abandon the current and employ the usual gravimetric method of digestion with sodium sulphide to effect the separation of copper from the other constituents. Nor is this by any means a solitary example. It is true, individual separations have been made in this group. For example, Smith and Frankel (*Am. Chem. Journ.*, 12, 428) succeeded in separating copper from arsenic, both in cyanide solution and in ammoniacal solution in which the arsenic was in the form of pentoxide and there was much free ammonia. The results in this latter instance have been confirmed by McKay. Very recently, Smith and Wallace (*Journ. Anal. Appl. Chem.* vii., 4) have printed an account of their successful separation, in very varying proportions, of copper from antimony, in alkaline tartrate solutions. These are the first successful results where antimony was present as more than a bare trace. Copper has never been separated from tin. Cadmium has no recorded separation from either antimony or tin; it has, however, been separated by Smith and Frankel from arsenic in cyanide solution. The case is in no wise better with either lead or bismuth. Solutions of either of these with any of the other three (As, Sb, Sn) have defied separation. Concerning mercury (ic) there is little more to be said. If a mercuric solution contains also arsenic in the pentoxide form, and a decided excess of potassium cyanide, the mercury can be separated without difficulty. These results have suggested the question whether it is possible to find a general method suitable for the separation of any of the basic oxides of this second group from any or all of the acid oxides of the same group. This problem I have endeavoured to solve. The method employed by Smith and Wallace for the separation of copper from antimony, suggested that in the alkaline tartrates might lie the key to the situation; and the separations from arsenic suggested, also, that it would be well to have the acid oxides in their highest state of oxidation. The results have fully justified my utmost expectation, and so far as they have been prosecuted, have been uniformly accurate. Inasmuch as we already have a separation of

copper from arsenic, and of copper from antimony, my first attention was turned to the separation of—

*Copper from Tin.*

A solution of copper sulphate was made containing 0.0999 gm. of metallic copper in each portion measuring 10 c.c. About one-tenth of a gm. (varying from 0.1020—0.1057 gm.) of metallic tin was dissolved in hydrochloric acid, and bromine water added until the solution remained coloured with the bromine to insure complete oxidation. I was led to suspect the presence of iron in the tin, and as this metal is deposited by the current from an alkaline tartrate solution, it became necessary to secure its removal. The tin solution was accordingly evaporated to dryness, taken up with caustic soda, the solution diluted, the iron filtered off, and the filtrate containing the tin (as sodium stannate) was neutralised with tartaric acid. To this solution 4 grms. of tartaric acid were added and, as soon as this was thoroughly dissolved, 10 c.c. of ammonium hydroxide (sp. gr. 0.932). To this (after filtering off slight impurities brought in with the tartaric acid) 10 c.c. of the above-mentioned cupric solution (containing 0.0999 gm. copper) were added, the whole transferred to a platinum dish having a capacity of about 200 c.c., and the solution diluted to 175 c.c. with distilled water. A current, generated by five or six gravity cells, coupled in series, was run through the solution, the anode being a flat platinum spiral. There was a voltmeter also in the circuit. The precipitation was started at 4 p.m., and allowed to run during the night. The currents employed most successfully generated from 0.4 c.c. to 1.2 c.c. of electrolytic gas per minute. Immediately on interrupting the current, the liquid contents of the dish (which should smell quite strongly of ammonia) must be rapidly poured off, luke-warm distilled water poured into the dish, allow to flow around the inside and gently emptied out. The washing with warm water should be repeated three or four times quite rapidly, and be followed by similar washings with small quantities of absolute alcohol. The dish can then be carefully dried on the edge of a warm plate, allowed to cool, and weighed. Great care must be exercised during the drying to see that the dish does not get too warm, or the metal will readily oxidise, for the copper deposited from an alkaline tartrate solution does not have the lustrous sheen of that precipitated from solutions containing free acid or potassium cyanide; it has a velvety dark red appearance, but is thoroughly adherent to the dish. If the current is strong enough to generate 1 c.c. of electrolytic gas per minute, the precipitation is complete in five minutes. A decided excess of ammonia has no deleterious effect. The following examples will serve to illustrate the operation:—

*Experiment 1.*—0.1087 gm. of metallic tin was dissolved in hydrochloric acid, oxidised, evaporated to dryness, taken up with water and sodium hydroxide, filtered, neutralised with tartaric acid, 4 grms. of solid tartaric acid and then 10 c.c. of ammonium hydroxide added. 10 c.c. of the copper solution (0.0999 gm. copper) were added, the whole transferred to a platinum dish, diluted to 175 c.c., and the current applied. The current delivered 0.4 c.c. of electrolytic gas per minute, and was allowed to act for seventeen hours. The deposit of copper weighed 0.1001 gm.

*Experiment 2.*—0.1039 gm. was treated as above. 10 c.c. of copper solution were used, 4 grms. tartaric acid and 15 c.c. of ammonium hydroxide added, and a current generating 1 c.c. of electrolytic gas per minute acted for fifteen and one-half hours. The precipitated copper weighed 0.0997 gm.

*Experiment 3.*—0.1044 gm. of tin was treated as before. 4 grms. of tartaric acid and 20 c.c. of ammonium hydroxide added, together with 10 c.c. of the copper solution. A current generating 1.2 c.c. electrolytic gas per minute acted for five hours. The deposited metal weighed 0.0997 gm.

\* From the *Journal of the American Chemical Society*, vol. xv., No. 4, 1893.

It having now been found possible to separate copper from arsenic, from antimony, and from tin, my attention was next turned to the possibility of separating copper from the other three collectively.

#### *Copper from Arsenic, Antimony, and Tin.*

Here, guided by the experience of Smith, Frankel, and Wallace, I decided to have the three acid oxides in their highest state of oxidation. Accordingly the solutions were made up as follows:—A quantity of arsenious oxide weighing 3.3342 grms. was dissolved in nitric acid (sp. gr. 1.3), and the solution evaporated to dryness. The arsenic acid thus formed was taken up with water, any slight impurities filtered off, and the filtrate diluted to 250 c.c. with distilled water. This gave a solution containing 0.1009 gm. metallic arsenic in each 10 c.c. For the antimonious solution a portion of potassium antimonious tartrate,  $C_4H_4(SbO)KO_6 + \frac{1}{2}H_2O$ , was dissolved in water, diluted largely, and then boiled with addition of bromine water until the solution remained discoloured for a considerable time by the bromine, thus indicating the complete oxidation of the antimony. The addition of a small quantity of tartaric acid prevented the slight tendency to precipitation of oxysalts. The solution was filtered and diluted to 250 c.c., thus giving 0.1024 gm. metallic antimony in each 10 c.c. The tin solution was prepared as described under the section on copper and tin, and was made of such a strength as to contain 0.1031 gm. metallic tin to every 10 c.c. The copper solution was made by dissolving a little more than 20 grms. of copper sulphate and diluting to 500 c.c. Ten c.c. of this solution, as determined by direct trial, contained 0.1016 gm. metallic copper.

The solution which proved best for the separation contained 8 grms. of tartaric acid, 31 c.c. of ammonium hydroxide, and 10 c.c. of each of the solutions of copper, antimony, arsenic, and tin described above. Five hours proved sufficient time, and a current generating 0.8 c.c. electrolytic gas per minute proved of sufficient strength to effect a thorough precipitation of the copper entirely free from any of the other three metals. The copper has the same appearance as when separated from tin, and must be washed and dried in the same way. It is, however, absolutely necessary to keep the quantity of tartaric acid and of free ammonia as high as indicated, or antimony to the amount of fully one-half of that present will be precipitated. I give the following results:—

*Experiment 1.*—Eight grms. of tartaric acid were dissolved in water, 30 c.c. of ammonium hydroxide added, and the solution filtered. To this were added 10 c.c. of each of the solutions of arsenic, antimony, tin, and copper (0.1016 in 10 c.c.) previously mentioned, and the solution diluted to 175 c.c. The current generated 0.8 c.c. electrolytic gas per minute, and was allowed to act for five hours. The precipitated copper weighed 0.1019 gm.

*Experiment 2.*—Exactly the same quantities as in 1 were exposed with the same strength of current and for the same length of time. This resulted in the deposition of 0.1010 gm. of metallic copper instead of 0.1016 gm.

Having thus succeeded in the separation of copper, I next directed my attention to cadmium, and as antimony seemed to give the most trouble, I began with the separation of—

#### *Cadmium from Antimony.*

The antimony solution was the one previously described. The cadmium solution was the nitrate, and contained 0.0916 gm. of the metal in 10 c.c. of solution as determined by electrolytic deposition from the cyanide solution. There is only one difficulty presented in this separation, and that is that the current must be weak, or the deposited cadmium will be too spongy to wash. Accordingly, it is necessary to allow the current to act through the night. The deposit of metal shows a tendency to form spongy masses here and there. These can be washed without loss if care be exercised in pouring the wash water on and off. The dish containing the deposit is washed with water simply—the washing with alcohol

being unnecessary—and then dried on the edge of the hot plate. As actual results I give the following:—

*Experiment 1.*—Five grms. of tartaric acid were dissolved in hot water, 15 c.c. ammonium hydroxide were added, and the solution filtered free from impurities introduced by the acid. Ten c.c. of the antimony solution and 10 c.c. of the cadmium solution (0.0916 gm. metallic cadmium) mentioned above were added, the whole transferred to a platinum dish, diluted to 175 c.c., and the current allowed to act over night. The cadmium was washed with hot water and dried. It weighed 0.0920 gm.

*Experiment 2.*—The solution here was made up in the same way as in the preceding experiment. The current gave 0.3 c.c. electrolytic gas per minute. It acted over night. The cadmium deposit weighed 0.0925 gm.

*Experiment 3.*—The solution was just the same as in the last case. The current gave 0.4 c.c. electrolytic gas per minute, and acted for sixteen hours. The deposit of metallic cadmium weighed 0.0925 gm.

#### *Cadmium from Tin.*

In this case the tin solution was the same as that employed in the separation of arsenic, antimony, and tin from copper; and, indeed, throughout the rest of these trials the arsenic solutions (0.1009 gm. metallic arsenic in 10 c.c.), the tin solutions (0.1031 gm. metallic tin in 10 c.c.), and the antimony solutions (0.1024 gm. of antimony in 10 c.c.) are the same. The separation presents no difficulties, and the metal is deposited in good form if the precaution previously mentioned is observed, namely, to use a long-continued weak current. The metal should be washed with hot water only, and dried on the edge of a warm plate.

*Experiment 1.*—Five grms. of tartaric acid were dissolved in water, 15 c.c. of ammonium hydroxide added, then 10 c.c. of the tin solution, and 10 c.c. of the cadmium solution (0.0916 gm.). This was diluted to 175 c.c. in the platinum dish, and a current liberating 0.1 c.c. of electrolytic gas per minute allowed to act upon the mixture for eighteen and one-half hours. The cadmium deposit was washed with hot water, dried, and weighed. It equalled 0.0914 gm.

*Experiment 2.*—The conditions and quantities were here just the same as in the last experiment, save that the current delivered 0.2 c.c. of electrolytic gas and was allowed to act for eighteen hours. The cadmium weighed 0.0918 gm.

#### *Cadmium from Arsenic.*

The solutions employed in this case were those used previously. The amount of tartaric acid was 5 grms., and of ammonium hydroxide 15 c.c. This quantity proved the best for all separations where but two metals were present, and was adhered to under these circumstances throughout the rest of the work. When more than two elements are present it becomes necessary to increase the amounts of tartaric acid and of ammonium hydroxide to 8 grms. and 30 c.c. respectively. The tartaric acid was dissolved in water as before, the ammonium hydroxide added, followed by the arsenic and cadmium, the solution transferred to the platinum dish, diluted to 175 c.c., and then electrolysed. The deposit differed in no wise from that obtained in the separation of cadmium from tin.

*Experiment 1.*—Five grms. of tartaric acid were dissolved in water, 15 c.c. of ammonium hydroxide were added, followed by 10 c.c. of the cadmium solution (= 0.0916 gm. cadmium), and 10 c.c. of the arsenic solution. The mixture was introduced into a platinum dish, diluted to 175 c.c., and a current that gave 0.3 c.c. electrolytic gas per minute allowed to act for a period of sixteen hours. The cadmium deposit weighed 0.0913 gm.

*Experiment 2.*—Like quantities were taken and treated in the same manner, except that the current delivered 0.2

c.c. of electrolytic gas per minute. It acted sixteen hours. The cadmium deposit weighed 0.0921 gm.

*Cadmium from Arsenic, Antimony, and Tin.*

The solution was now made up by combining the arsenic, antimony, and tin with the cadmium. The tartaric acid was increased to 8 grms. and the ammonium hydroxide to 30 c.c. The cadmium separated from the three differed in no respect from that separated from any one. It had the same appearance, and washed and dried in the same way.

*Experiment 1.*—Eight grms. of tartaric acid were dissolved in water, 30 c.c. of ammonium hydroxide were added, followed by 10 c.c. each of arsenic, antimony, tin, and cadmium solutions. The current liberated 0.25 c.c. of electrolytic gas per minute and acted for eighteen hours. The metallic cadmium weighed 0.0915 gm.

*Experiment 2.*—The same quantities were used as in Experiment 1. The current gave 0.4 c.c. of electrolytic gas per minute, and acted sixteen hours. The deposit of cadmium weighed 0.0920 gm.

*Experiment 3.*—Same quantities were used. The current gave 0.3 c.c. of electrolytic gas per minute, and precipitated 0.0918 gm. cadmium.

Copper and cadmium having yielded thus easily to the current in the presence of arsenic, antimony, and tin in ammonium tartrate solutions, my attention was next turned to bismuth.

(To be continued).

## NOTICES OF BOOKS.

*On Sewage Treatment and Disposal.* For Cities, Towns, Villages, Private Dwellings, and Public Institutions. By THOMAS WARDLE, F.C.S., F.G.S. Manchester: Heywood. Large 8vo, pp. 408.

THE author of this volume has passed from the chemistry of colours and their application to that of sewage and its impurities. We are glad to find that he does not accept irrigation as the universal method of dealing with the sewage difficulty, but depends more upon chemical processes. Of these he describes many as carried out in different localities. He quotes the standards of the late Rivers' Pollution Commissioners, or rather of Professor E. Frankland, F.R.S., since his colleagues in that memorable and costly inquiry, being neither chemists nor physicians, must have accepted his guidance. Mr. Wardle expounds the part played by bacteria in the putrefaction of sewage and of imperfect effluents. This is a novel feature in works on the disposal of sewage. The Dibdin process, inherited by the London County Council from the late Metropolitan Board of Works, is not greatly approved of. This might be expected, as the material used is lime in the proportion of 3.7 grains to 1 grain of copperas. Hence the effluent is of necessity alkaline.

The "amines process," or, as it is facetiously called, the herring-pickle method, is described at great length, but with the remark that it does not seem to be received with popular favour.

Webster's electrical treatment seemed to us very satisfactory when it was tried at Crossness. An electrical process, substantially the same, is now in use at Rouen and Havre, but the credit of its invention is not given to Mr. Webster.

General Scott's process, the subject of an endless series of patents, turned on precipitation with lime and clay. The effluent was of course alkaline. The deposit was ignited in kilns and sold as cement. It has been abandoned at Birmingham, since the nitrogen and the phosphates were wasted, and since the cement was neither better nor cheaper than that made in the ordinary way without the addition of sewage-matters.

Hille's process is said to be destructive of fertilising properties.

The Committee of the Local Government Board on Sewage Treatment (1875) are accused of pronouncing Goodall's process "the twin of the A B C process," and declaring both a failure. Both analysis and observation prove that the A B C process is here unfairly treated.

The process now in use at Coventry is no longer that of Anderson (phosphates), but lime and iron, followed by irrigation.

At Kettering, since the author obtained his information, the sewage is sterilised by the injection of carbolic and cresylic acids emulsified with steam. The sewage is then precipitated with salts of alumina. The process seems to give great satisfaction, and is being adopted at Melton Mowbray.

Mr. Wardle's work will, we believe, do good service.

*Dangerous Trades for Women.* By Mrs. C. MALLET. London: W. Reeves. Small 8vo., pp. 22. 1893.

THIS pamphlet forms one of a series of publications issued by the so-called "Humanitarian League." No one can be more fully convinced than are we that whatever tends to sap the health and the vigour of the community should be at once and thoroughly rectified. But whilst keeping in view Earl Beaconsfield's grand maxim "Sanitas sanitatum et omnia sanitas," we must all the more insist that existing evils should be stated truthfully, without either exaggeration or distortion. Their exposure must be conducted in the pure interest of public health, and not in the intention of making political or socialistic capital.

We are led to make this remark from a distrust of the spirit of this pamphlet and of the motives of the writer and of her associates. Those who really wish to know the truth, and nothing but the truth, concerning dangerous trades had better be guided by the discourses of Professor Watson Smith than by the sensational letters which appear in a certain class of papers. It is all very well to talk of the "ignorant carelessness of the masters." If Mrs. C. Mallet were really acquainted with her subject she would know that employers have often great difficulty in enforcing sanitary regulations in their establishments. The steel and stone dust which now no longer "surrounds the Sheffield cutlers" (it was not the cutlers but the grinders who were exposed to this evil) was got rid of by boxing in the revolving stones in sheet-iron jackets traversed by a strong current of air. But the workmen resisted this improvement, and even destroyed the apparatus.

As far as our opinion may have any weight, we hold most decidedly that the use of white-lead as a pigment should at all hazards be abolished. Nor do we think that the use of phosphorus at all, white or red, is a necessity. It is possible to make matches without its presence.

The author's appeal to the "Women's Liberal Associations of Great Britain" shows at once the political bearing of this pamphlet.

Some of the other publications of the League—such as No. 2, "A Denunciation of the Queen's Buckhounds"; No. 3, on "Rabbit Coursing"; No. 4, "The Horrors of Sport"; and No. 5, "Behind the Scenes in Slaughter Houses"—seem to deserve attention. But to "Humanitarianism" the League adds Bestiarism, since one of the tracts deals with experimental physiology.

If they would denounce the massacre of harmless and beautiful birds at the behest of modistes they would be doing much better.

*The Use of the Electric Current as a Source of Heat in Dry Metallurgical Tests.*—W. Borchers (*Zeit. Angew. Chem.*).—The author points out the advantages of the current as a source of heat, and describes a kind of electric furnace.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

*Zeitschrift für Analytische Chemie.*  
Vol. xxxii., Part 4.

A New Method for the Quantitative Determination of Carbon in Iron and Steel.—Otto Pettersson and August Smith.—This paper, besides small figures introduced in the text, requires the two large plates at the end of the volume.

Critical Studies on Methods for Determining Sulphur. (II.).—L. Marchlewski.—The author examines the methods of Gröger or of Treadwell. He concludes that Gröger's method cannot be used commercially for the valuation of pyrites, and that it is unsuitable for determining sulphur in lead sulphate and analogous compounds. He is of opinion that Sawyer's method cannot compete with that of Lunge in sulphuric acid works on account of the greater rapidity of the latter. But if a product has to be examined which contains along with pyrites other fixed and insoluble compounds, such as calcium sulphate, only the method of Sawyer or the most recent modification of Treadwell's process can be used.

Distinction between Natural Butter and Margarine.—F. Gantter.—Already inserted.

Valuation of Hides for Glue.—F. Gantter.—Already inserted.

A New Volumetric Method of Determining the Value of Fowler's Solution and Tartar Emetic.—Dr. Stefan Györy.

Standardising Acids by means of Metallic Sodium.—Dr. Erich Neitzel.—A small beaker is filled to one-third with petroleum which has been heated above the boiling point of water, filtered through paper, and tared on the balance. A rectangular piece of about 0.6 to 1 gm. in weight is then cut with a penknife from a rod of sodium, so that it has freshly-cut surfaces on all sides, taken up with the forceps, and allowed to slide into the beaker. On weighing again, the difference shows the weight of the sodium taken. The weighed portion is then taken up with the forceps, and without regard to the adherent petroleum allowed to slide into a flask holding from 250 to 300 c.c., and containing 75 c.c. of alcohol of from 88 to 94 per cent. The neck of the flask is then closed with a perforated cork or caoutchouc stopper, through the aperture of which is thrust a glass tube previously rinsed with alcohol. The development of hydrogen takes place quietly. After the completion of the reaction a few c.c. of alcohol are poured through a cooling tube into the flask, the stopper is rinsed off, and the contents of the flask are diluted with about 100 c.c. of distilled water. After adding phenolphthalein or some other indicator we may at once proceed to titration. The weight of the sodium increased by the factor—

$$\frac{1000}{23}$$

gives the consumption of the acid (supposed to be normal) in c.c. We may therefore at once allow three-fourths of the calculated number of c.c. to flow into the solution of sodium hydroxide, adding the remainder drop by drop until the change of colour takes place.

Arrangements of the Electrolytic Laboratories of the Joint Stock Company at Stalberg, Westphalia.—H. Nissenon and C. Rüst.—This paper requires the four accompanying figures.

On Characterising Portland Cement.—R. Fresenius and W. Fresenius.—The authors assign the following limits for the properties of Portland cement:—1. Specific gravity, not ignited, at least 3.00. 2. Specific gravity,

ignited, at least 3.12. 3. Loss on ignition, at most 3.4. 4. Alkalinity of aqueous solution of 0.5 cement, not more than 7.2 c.c. of decinormal acid. 5. Consumption of permanganate for 1 gm. cement, not more than 2.8 m.g. 6. Proportion of magnesia, not above 3 per cent.

General Process for Determining Foreign Bodies in Liquids.—E. Gossart (*Chem. Zeit.*).—If a drop of a volatile liquid is caused to fall upon the surface of another liquid, curved by adhesion, if the drop and the subjacent liquid are both homogeneous it rolls for a time upon the lower liquid. But if the liquids are of unlike nature it sinks more or less rapidly into the lower stratum.

A Method of Securing Riders on Artificial Balances.—A. K. Markl.—This paper requires its three figures.

## 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.

Cocoa-nut Oil.—Will some correspondent kindly inform me—(1) What quantity and strength of soda ley is required to kill 1 cwt. of cocoa-nut oil for grease manufacture (not soap)? (2) What proportionate quantity of water will cocoa-nut oil carry as compared with palm oil?—J. I.

## MEETINGS FOR THE WEEK.

FRIDAY, 24th.—Physical, 5. "On the Magnetic Shielding of Concentric Spherical Shells," by Prof. A. W. Rücker, M.A., F.R.S., President. "On the Action of Electromagnetic Radiation on Films containing Metallic Powders," by Prof. G. M. Minchin, M.A.

## LECTURE NOTES

ON

## THEORETICAL CHEMISTRY.

BY

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THE CHEMICAL NEWS.

VOL. LXVIII., No. 1774.

ON THE  
TEACHING OF INORGANIC CHEMISTRY.

By MARGARET D. DOUGAL.

(Continued from p. 238.)

IN order to secure a well arranged plan and to divide the material uniformly, certain rules must be followed to determine which constituent of a compound is to be spoken of and described. We have the option of treating the salts either in connection with the metals which are contained in them, or in connection with the acids. Berzelius, as is well known, has tried both methods, and in the later editions of his books first gives a survey of the characteristic properties of the acids, and then describes the individual salts according to the metals. Those who have studied Berzelius's method, or any similar plan arranged from the modern standpoint, must see that the enumeration of all its salts in connection with a metal forms, not only an arbitrary, irregular, and imperfect association of the most varying types and formulæ, but also necessitates innumerable repetitions which waste time, and are, moreover, wearisome to the student. However worthy of commendation this arrangement according to the metals may be for analytical chemistry, it is little adapted for a general course of experimental chemistry. The attributes of the salts of a metal can be well characterised without describing all the salts one after another. Further, isomorphism among large groups of salts can be produced just as well by the change of the positive as of the negative constituent; but metals of the different families may replace each other without change of crystalline form, whilst the negative elements of isomorphous compounds belong, with few exceptions, to the same family. From these and similar considerations, Professor Lothar Meyer decides on treating the salts always in connection with their acids. As, however, the hydracids of the type HCl and H<sub>2</sub>S have already been described, this rule is not made to extend to them, but only to the oxyacids and the sulpho-salts analogous to them.

After the occurrence, mode of extraction, and properties of the elements of each family have been spoken of, their compounds are discussed in the same order as those of hydrogen: first with Family VII., F, Cl, Br, and I; and then with Family VI., O, S, Se, Te, together with the oxides, hydrates, and also the sulphhydrates. When they are of importance, the compounds with Family V., N, P, &c., and also with Family IV., C, Si, &c., are also treated. In this way, the position in the system of every compound is definitely determined. This uniformity does not, of course, compel a like treatment for all sections, but allows full freedom to discuss the more important in detail, whilst the less important are either only briefly mentioned or are omitted altogether.

Professor Meyer was formerly in the habit of introducing with the purely empirical discussion of each family the general formula of its compounds, and, from it, of deducing its valency, so as, by induction, to lead up to the knowledge of the general law. But, as he has noticed in the course of time, that the tendency in preparatory schools is to induce the student to assimilate the lecture-course more by memory than by reasoning, he now follows a more deductive and dogmatic procedure, and accordingly gives for every family first of all its typical formula, according to which its compounds are formed—as, for example, the alkali metals:—

I.—RCl, R<sub>2</sub>O, ROH, R<sub>2</sub>S, RSH, &c.,

and for the metals of the alkaline earths:—

II.—RCl<sub>2</sub>, RO, RO<sub>2</sub>H<sub>2</sub>, RS, RS<sub>2</sub>H<sub>2</sub>, &c., &c.,

so that, in this way, the student knows what to expect; and at the same time proofs are given for using for calcium chloride CaCl<sub>2</sub>, instead of Gmelin's formula CaCl.

Professor Lothar Meyer begins his systematic consideration with the Family of the alkali metals, taking the opportunity to introduce instructive incidents in the history of chemistry as well as explanations of important methods of research. Electrolysis, the stoichiometric determination of atomic and equivalent weights, acidimetry, and alkalimetry are demonstrated and described.

Attention is especially called to the increase of the positive character of the elements with the increase of atomic weight. From its association with the alkalis, ammonia is again referred to, its salts and their isomorphism with the potassium salts spoken of; and mention is now made of the compound salts, those of ammonia being particularly dealt with.

Family II. of the earth-metals—beryllium, magnesium, calcium, strontium, and barium—is so nearly analogous to Family I. that a brief comparison is sufficient. After the discovery, occurrence, and mode of extraction have been spoken of, special emphasis is laid, when describing their properties, on specific heat and on the law of Dulong and Petit, from which the divalency of the Family is inferred. Beryllium gives occasion to explain the exception to this law, and to deduce the proof of the divalency of the metal from the vapour-density of the chloride. As divalent bases, the hydrates offer opportunity to discuss the relations of equivalent to atomic weight, and to differentiate between them. Here, again, the increase of the positive character with atomic weight is noted. As types of intra-reaction with Family I., the preparation of the alkaline hydrates by means of those of the alkaline earths, as well as of the reverse operation, is experimentally shown. The peroxides are also discussed, especially barium peroxide; and, in addition, the earlier-mentioned hydrogen peroxide. With the sulphides the phosphorescent compounds are shown.

Family III.—boron, aluminium, scandium, yttrium, lanthanum, and the others for the most part grouped with the indefinite earth-metals—is conveniently treated in a somewhat different way. The type of compound is alike for all; but the properties of boron and its compounds differ so much from the others, in spite of their analogous composition, that it is advisable to describe them alone, and before the others. Boracic acid, or the trihydrate BO<sub>3</sub>H<sub>3</sub>, manifests such a great diminution of basic and positive character, as compared with LiOH and BeO<sub>2</sub>H<sub>2</sub>, that it is classed as a weak acid capable of forming salts. The weakness of the acid is shown in the decomposition of the borates by water, and in the formation of the anhydrous salts BO<sub>2</sub>Na, B<sub>4</sub>O<sub>7</sub>Na<sub>2</sub>, &c. The latter compound is more particularly described as a type of a frequently recurring phenomenon, so that later, or when a similar compound is formed in connection with other acids, it need only be mentioned.

Of the metals of this Family, aluminium is especially considered, and allusion is made to the analogies its compounds show to those of boron—particularly the chloride and hydrate with its weak acidic nature. The very rare members are briefly treated; at the same time it is mentioned that cerium in Family IV. is nearly related to lanthanum, and apparently all the insufficiently known elements between lanthanum and barium have the character of earth-metals. Whether didymium should be placed in Family V. is somewhat doubtful. Owing to the great similarity of these earth-metals to one another, it is convenient to discuss them all now, so far as this can be done in an elementary course.

As occasion offers during the consideration of this Family, as well as those preceding and following it, it is remarked that the elements of low atomic weight, as lithium, beryllium, and boron, occur but seldom; those

of higher weight to perhaps iron (at. wt. = 56), are, without exception, frequently and widely distributed; whilst all of higher weight than iron are much more rarely found on the earth's crust.

The elements of Family IV.—carbon, silicon, titanium, zirconium, cerium, thorium—are described together, by reason of the similarity of their properties, their occurrence, and modes of preparation. But the compounds of carbon exhibit such marked differences from those of the others that they are especially dealt with.

Of the halogen compounds of carbon only those of the type  $\text{CCl}_4$  are somewhat minutely described, the others being merely mentioned, and their fuller treatment referred to organic chemistry. The oxides of carbon are discussed in detail—particularly carbonic acid as well as its salts. The consideration of the carbonates gives occasion to compare them with the borates of Family IV. Since the normal hydrate of carbon should be  $\text{CO}_4\text{H}_4$ , all carbonates appear as anhydrous salts of the type  $\text{CO}_3\text{H}_2 = \text{CO}_4\text{H}_4 - \text{H}_2\text{O}$ . They are treated in groups, at first with the alkalis, then with the great isomeric family of calc-spars and aragonites, and of others allied to them so far as they are worthy of consideration. After carbonic acid, carbon monoxide, carbon bisulphide, phosphene, and urea are discussed briefly, the associated carbamic acid having been already shown and explained when dealing with the carbonates of the alkalis. Finally, the compounds of carbon and nitrogen are dealt with.

The compounds of the remaining elements of Family IV. are next described, first the fluorides, chlorides, &c.; then the oxides and hydrates, or anhydrides and acids. The silicates furnish numerous examples of the anhydrous salts of the polysilicic acids, which are grouped and characterised according to the type of metal with which they combine. As silicates, pottery, porcelain, and glass are here mentioned. Titanium, zirconium, and thorium are only briefly treated. Whether cerium really belongs to this Family remains doubtful; it has, however, been already spoken of.

Between Families IV. and V. a peculiar and sudden change of properties is manifest. From the hitherto infusible carbon we come to the gaseous and, up to now, difficult to liquefy nitrogen, and from the very difficultly fusible silicon to the easily-fused phosphorus. All the previously considered elements, moreover, have been distinguished by their great affinity for oxygen, all being difficult of reduction. This property is seen also in phosphorus, but not in nitrogen, whose oxides, as is known, readily yield oxygen. In comparison with titanium and zirconium we have vanadium and niobium, to which, as third member, tantalum is associated, whose analogue in Family IV. is yet to be discovered. If we include Family VI. we have the following grouping:—

C = 11.97	N = 14.01	O = 15.96
Si = 28.3	P = 30.96	S = 31.98
Ti = 48.0	V = 51.1	Cr = 52.0
Zr = 90.4	Nb = 93.7	Mo = 95.9
—	Ta = 182.0	Co = 183.6
Th = 231.9	—	U = 238.8

(To be continued).

**Burettes and Pipettes.**—A number of proposals put forward, for the most part merely slight modifications of forms already known. G. A. Le Roy (*Moniteur Scientifique*) describes an overflow burette and pipette, in which the zero-point of the graduation coincides with the upper end. The burette is filled from an elevated reservoir by means of a T-piece. The liquid running out above arrives into a glass jacket, inclosing the burette for its whole length and having at its lower end a lateral escape-pipe. The inclosure of the entire burette in a glass-jacket must certainly render the reading off less accurate.—*Zeitschr. Anal. Chem.*, xxxii., Part 4.

## THE ELECTROLYTIC SEPARATION OF THE METALS OF THE SECOND GROUP.\*

By SAMUEL C. SCHMUCKER.

(Concluded from p. 245).

### *Bismuth from Arsenic.*

THE solution was made by dissolving 5.8 grms. of bismuth nitrate in water acidulated with enough nitric acid to prevent the formation of basic salts. The solution was diluted to 400 c.c., and ten c.c. taken for the determination of the bismuth. The metal was precipitated from the alkaline tartrate solution and weighed 0.0518 gm. The practice had now become uniform of adding 5 grms. of tartaric acid and 15 c.c. of ammonium hydroxide when two metals were present, and 8 grms. of acid and 30 c.c. of ammonium hydroxide when four metals were in the same solution. The solution was made up as in all preceding cases, and the process differed in no way until the washing began. Bismuth does not form so compactly on the dish as cadmium does, or even as copper from the alkaline tartrate solution. Accordingly great care was necessary in the washing. In drying, too, it seemed to oxidise with very little heating. Therefore, when the deposition was complete, the anode was raised, the liquid gently but quickly decanted from the deposited bismuth, and the wash-water gently poured on and off. This latter was repeated three or four times, and was followed by three or four washings with absolute alcohol. The dish was placed on a very moderately heated plate and the evaporation of the alcohol facilitated by gentle blowing. It is best to use a long-continued weak current for bismuth or the deposit will be spongy and loose, rendering washing difficult.

*Experiment 1.*—The solution contained 5 grms. of tartaric acid, 15 c.c. of ammonium hydroxide, 0.1009 gm. metallic arsenic, and 0.0518 gm. of bismuth. It was diluted to 175 c.c. The current acted sixteen hours and gave 0.3 c.c. of electrolytic gas per minute. The precipitated bismuth weighed 0.0514 gm.

### *Bismuth from Antimony.*

Here the procedure was exactly similar to that described under the separation of bismuth from arsenic. The precipitated metal resembled that obtained in the preceding experiment.

*Experiment 1.*—The solution contained 5 grms. of tartaric acid, 15 c.c. of ammonium hydroxide, 0.1024 gm. of antimony, and 0.0518 gm. of bismuth. It was diluted to 175 c.c. The current gave 0.22 c.c. of electrolytic gas per minute. It acted sixteen and one-half hours. The deposit of metallic bismuth weighed 0.0513 gm.

### *Bismuth from Tin.*

The method of procedure was just the same here as in the separation of antimony, or of arsenic from bismuth. The precipitated bismuth was treated as heretofore and had the same appearance.

*Experiment.*—The solution contained 5 grms. of tartaric acid, 15 c.c. of ammonium hydroxide, 0.1031 gm. of metallic tin, and 0.0518 gm. of metallic bismuth. It was diluted with distilled water to 175 c.c. The acting current gave 0.2 c.c. of electrolytic gas per minute; time, sixteen and one-half hours. The bismuth deposit weighed 0.0514 gm.

### *Bismuth from Arsenic, Antimony, and Tin.*

The procedure was again just as before. The bismuth precipitated readily and in as clean a form as when separated from each of the metals singly.

*Experiment.*—The solution contained 0.0518 gm. of bismuth, 0.1009 gm. of arsenic, 0.1024 gm. of antimony,

\* From the *Journal of the American Chemical Society*, vol. xv., No. 4, 1893.

0.1031 gm. of tin, 8 grms. of tartaric acid, 30 c.c. of ammonium hydroxide, and was diluted to 175 c.c. The current gave 0.2 c.c. of electrolytic gas per minute, and was allowed to act for sixteen and one-half hours. The bismuth, after washing and drying, weighed 0.0513 gm.

The method adopted by me having proved successful in the separation of copper, cadmium, and bismuth from the metals forming acid oxides, I next applied it to the study of mercury in its bivalent form. About 7 grms. of mercuric chloride were dissolved in distilled water and diluted to 500 c.c. Ten c.c. of this solution proved to contain 0.0933 gm. of metallic mercury. I first undertook the separation of—

*Mercury from Tin.*

There was a doubt in my mind whether the mercuric compound could be made up in alkaline tartrate solution when there was so much free ammonia present. I found, however, that if the mercuric chloride solution be added to the tartaric acid solution before the addition of the ammonia there is little likelihood of trouble, though even then the double compound sometimes forms, especially if the solution be not dilute. But if care be exercised the mercuric salt may be added last. If the solution is well diluted and the mercuric salt added with constant stirring all remains in solution very nicely. The mercury and tin were then combined with the tartaric acid and ammonia, the solution diluted and the current passed. The precipitation is quite rapid even with a fairly weak current, and the metal separates as a lustrous coating having a very slight tendency to drops. The mercury is washed with very warm water three or four times, and then dried by keeping the dish in the warm hand and blowing gently into it to facilitate the evaporation. Any attempt to dry it on the plate is attended with very considerable risk of vaporising a portion of the mercury.

*Experiment.*—Ten c.c. of the mercuric chloride solution (=0.0933 gm. metallic mercury, 10 c.c. of tin solution, 5 grms. of tartaric acid, and 15 c.c. of ammonium hydroxide) were united and diluted to 175 c.c. The current gave 0.2 c.c. of electrolytic gas per minute and was continued for six hours. The mercury deposited weighed 0.0930 gm.

*Mercury from Arsenic.*

The solution contained 0.0933 gm. of mercury, 0.1009 gm. of arsenic, 5 grms. of tartaric acid, and 15 c.c. of ammonium hydroxide. It was diluted to 175 c.c. The current gave 0.33 c.c. of electrolytic gas per minute, acted for five hours, and deposited 0.0928 gm. of metallic mercury.

*Mercury from Antimony.*

*Experiment.*—The solution contained 0.1024 gm. of antimony in addition to the mercury, also 5 grms. of tartaric acid, and 15 c.c. of ammonium hydroxide. It was diluted to 175 c.c. with water. The current gave 0.5 c.c. of electrolytic gas per minute; it acted for six hours, and precipitated 0.0932 gm. of metallic mercury.

*Mercury from Arsenic, Antimony, and Tin.*

The solution was made up in the same manner as in the three preceding separations, save for the increase of tartaric acid and of ammonium hydroxide. There was, however, a difference in the nature of the deposited mercury. A part of it gathered, as in the other cases, in a lustrous coating on the sides of the dish, but in addition to this there was quite a considerable amount of mercury in the form of drops so small as to be almost pulverulent. This rendered washing exceedingly difficult. The fluid contents of the dish, after the anode had been raised, are carefully decanted from the powder, boiling water added, allowed to flow around the dish, and again very carefully decanted. This was repeated six or seven times, never draining off the last drops to avoid loss of the mercury. If this care is taken there is no difficulty about good results, but the slightest haste results in the loss of mercury. Naturally when that much water remains on the mercury

the evaporation from the heat of the hand is a most tedious, but the only safe, process.

*Experiment 1.*—The solution contained 0.0933 gm. of mercury, 0.1009 gm. of arsenic, 0.1024 gm. of antimony, 0.1031 gm. of tin, 8 grms. of tartaric acid, 30 c.c. of ammonium hydroxide, and was diluted to 175 c.c. The current gave 0.5 c.c. of mixed gases per minute. It acted for sixteen hours and precipitated 0.0935 gm. of mercury.

*Experiment 2.*—The conditions were the same as in the first experiment. The current gave 0.4 c.c. of electrolytic gas per minute and precipitated 0.0933 gm. of metallic mercury.

I made no attempt to separate lead from arsenic, antimony, or tin.

In conclusion, I would acknowledge my indebtedness to Prof. Edgar F. Smith, at whose suggestion and under whose supervision the above studies were brought to completion.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1893.

By WILLIAM CROOKES, F.R.S.,

and  
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,  
Professor of Chemistry at the University of Oxford.

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

London, November 10th, 1893

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the 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 October 2nd to October 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.

A comparison of the average composition of the five Thames-derived waters during last month with that of the same waters in October, 1892, shows a decided improvement in the amount of nitrates, in the oxygen required to oxidise the organic matter, and in the organic carbon. Notwithstanding a somewhat heavy rainfall, the composition of the waters during the last month is almost identical with that recorded in September, when the Thames waters were of a wholly exceptional degree of purity, the increase in organic carbon in October over that in September only amounting to one part in seven million parts of water, as will be seen by the following Table:—

*Averages of the Five Supplies derived from the River Thames.*

1893.	Common salt per gallon.	Nitric acid per gallon.	Hardness, degrees.	Oxygen required per gallon.	Organic carbon per gallon.	Organic carbon per gallon.	Colour.	
							Brown.	Blue.
	Means.	Means.	Means.	Means.	Means.	Maxima.	Means.	
Sep.	2.163	0.570	13.64	0.026	0.057	0.071	12.2 : 20	
Oct.	2.197	0.665	14.10	0.031	0.067	0.099	13.8 : 20	

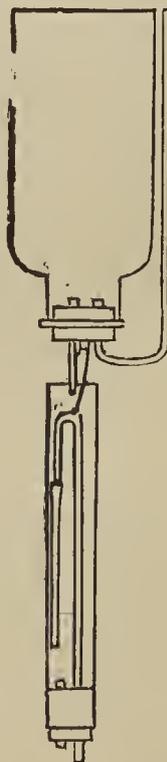
The rainfall in the month of October at Oxford\* was very near the mean fall for the month over an average of twenty-five years. The actual fall was 2.65 inches, while the mean is 2.56 inches. Most of the rain occurred in the early part of the month, 1.9 inch, or 72 per cent, falling in four days. Although this heavy rain immediately followed an exceptionally dry month, the self-purifying power of the running stream and the aerating and filtering arrangements of the Companies have proved amply sufficient to prevent any rise in organic matter, our analyses showing no variation in the uniform good quality of the water between the first and the second half of the month.

We are, Sir,  
Your obedient Servants,  
WILLIAM CROOKES.  
WILLIAM ODLING.

### AN AUTOMATIC EXTRACTOR.

By W. D. HORNE.

In the analysis of commercial fertilisers soluble phosphoric acid is separated by repeated washings of the mass with small quantities of water. Two grms. of the sample are treated on a ribbed filter with successive portions of water, about 10 c.c. at a time, until at least 250 c.c. have run through, each addition being deferred until the preceding has passed through.



Feeling that time might be saved by having this washing done automatically led to the device of a simple apparatus which mechanically delivers the required quantity of water at measured intervals in a gentle stream upon the material on the filter, stirring it up and leaching out the soluble matter without requiring any attention after the start.

One part of the apparatus consists of a wide-mouthed bottle of 250 c.c. capacity closed by a cork perforated by two glass tubes. One tube projects outward about 3 or 4 c.m. and tapers to a moderately fine point. The other

\* Oxford has been chosen in preference to London, as its rainfall more closely represents the average fall over that part of the gathering ground of the Thames valley which supplies the chief sources of the river.

tube, after emerging from the cork, curves directly over the edge of the cork and extends down the full length of the bottle on the outside. The bottle, being filled with water, is inverted, and the water drops from the end of the short tube, while the necessary air enters by the long bent tube, and bubbles up through the column of water in the bottle. As the rate of flow or dropping depends principally upon the fineness of the point of the dropping tube and the freedom of the air's access through the longer tube, any desired rapidity of flow can be obtained by varying the size of either tube. It is more advantageous to use the same dropper and to regulate the air supply by plugging more or less loosely the upper end of the air tube with an appropriate stopper.

So much for the water supply. In order to convert this into an intermittent washing stream it flows into a tube suspended below, provided with a capillary syphon tube within, whose longer limb passes through a stopper at the bottom of the outer tube, something like the Adams fat extractor.

To make this part of the apparatus, cut the bottom off of a test-tube 15 m.m. in diameter and 15 c.m. long, close one end with a rubber stopper with one hole, and within the test-tube put a 3 m.m. tube bent double by a sharp curve, with one limb about 15 c.m. long and the other about 3 c.m. The longer limb passes through the hole in the stopper at the bottom of the test tube, while on the shorter limb is put a piece of rubber tubing of variable length, according to the quantity of water that is to be syphoned off at each delivery. To the loop of the syphon fasten one end of a short wire, whose other end terminates in a hook to catch in a wire eye inserted in the cork of the inverted bottle.

Thus suspend the syphon apparatus to the water supply, having the dropping-tube inside the test-tube. When the water is allowed to drop the test-tube slowly fills, until the water, rising in the syphon's short arm, passes beyond the bend and syphons over. The operation then repeats itself.

The speed of dropping from the reservoir must be such as to allow each syphoned portion to pass completely through the filter before the next flows on. And the quantity which syphons over each time is to be regulated by varying the length of the rubber tube which extends from the short limb of the syphon. The lower end of this rubber tube is cut off diagonally to ensure complete emptying of the syphon at each delivery.

These things once arranged, they need little attention afterwards.

Only a moment is required to fill the bottle, attach the syphon tube, and hang the inverted bottle in its rack with the filter containing the fertiliser below it in a funnel resting in a flask.

The washing is done regularly, without attention and without loss of time. A few supplementary washings by hand may be well to get the material all into the point of the filter, although experiments have shown that the mechanical washing is thorough and gives results identical with the tedious hand method.—*Journal of the American Chemical Society*, xv., No. 5.

### ON THE OCCLUSION OF GASES BY THE OXIDES OF METALS.\*

By THEODORE WILLIAM RICHARDS and ELLIOT FOLGER ROGERS.

(Concluded from p. 242).

#### *Nickelous Oxide.*

THE series of experiments with nickelous oxide led to results not unlike those with zincic oxide. In this case sulphuric acid proved unsatisfactory as a solvent, and

\* Contributions from the Chemical Laboratory of Harvard College.

hydrochloric acid was adopted. A solution containing about 20 per cent of hydrochloric acid gas was freed from air by continued boiling, rapidly cooled, and run into the tube containing the oxide of nickel. On account of the very slow action of the cold acid the tube was warmed after exhausting the air as usual. The gas set free was measured as before.

In order to prove the accuracy of the method a grm. of zincic oxide prepared from the carbonate was dissolved in hot hydrochloric acid in precisely a similar way. No trace of gas was evolved during this solution.

It was thought unnecessary to make a series of experiments as elaborate as that made with the zincic oxide. Nickelous nitrate was evaporated to dryness in porcelain and ignited 15 minutes in a blast lamp and then a number of hours over a Bunsen burner in the furnace. (Analysis 1, below).

A part of the nickelous oxide remaining was further ignited for two hours in the furnace by means of the water-blast. This was used for the second analysis. A portion of the latter was ignited again in the furnace at the highest temperature we could obtain, by the addition of oxygen to the flame for about 15 minutes, until the bottom of the outer crucible as well as the platinum foil between the two crucibles was melted away. The arrangement of data in the Table is similar to that already described.

No. of Expt.	Weight of Oxide. Grms.	Vol. of Gas evolved. C.c.	Vol. of Gas calc. for 10 gr. NiO. C.c.	Analysis of Gas by volume. Per cent.
1.	1.14	0.469	4.11	{ O <sub>2</sub> =12.25 N <sub>2</sub> =87.75
2.	0.997	0.34	3.41	
3.	1.13	0.35	3.09	{ O <sub>2</sub> = 8.8 N <sub>2</sub> =81.2

*Magnesium Oxide.*

The experiments with the oxide of magnesium led to very unexpected results, the amount of gas evolved upon the solution of this compound being five to twenty times as much as was obtained from zincic oxide, and over twenty-five times as much as from the oxide of nickel. More difficulty was found in decomposing the nitrate than before, and the remaining oxide was in a much harder and more compact state, and consequently more difficult to pulverise. The process used was similar to that employed in the case of the other oxides.

No. Expt.	Wt. of Oxide used. Grms.	Time and Temp. of heating.	Vol. of Gas evolved. C.c.	Vol. of Gas calc. for 10 gr. of MgO. C.c.	Analysis of Gas.
1.	0.50	Blast lamp 30 mins.	5.45	109.	{ O <sub>2</sub> =66.6% N <sub>2</sub> =33.4
2.	1.0 (about)	,, 1 hr.	0.05	0.5	
3.	0.50	,, 1 1/4 ,,	5.86	117.2	{ CO <sub>2</sub> = 5.98 O <sub>2</sub> =53.7 N <sub>2</sub> =40.29
4.	0.25	,, 2 1/4 ,,	2.31	92.4	{ O <sub>2</sub> =47.6 N <sub>2</sub> =52.4
5.	0.25	,, 3 1/4 ,,	2.31	92.4	{ CO <sub>2</sub> = 2.2 O <sub>2</sub> =38.9 N <sub>2</sub> =58.9
6.	0.25	Oxygen blast, 20 mins.	2.04	81.6	{ O <sub>2</sub> =34.3 N <sub>2</sub> =64.2
7.	0.25	Water blast, 1 1/2 hr.	2.31	92.4	{ CO <sub>2</sub> = 1.5

*Remarks.*

No. 2.—Made from carbonate.

Nos. 3 to 6.—Analyses made from one sample of oxide heated under different conditions. 1, 3, and 4 gave tests for nitrates with ferrous sulphate; 5 and 6 did not.

Magnesium nitrate made from pure nitric acid and magnesian carbonate of commerce was evaporated to dryness in porcelain. The residue was pulverised in an agate mortar, heated by means of the blast lamp in a covered porcelain crucible, and cooled over calcic chloride. For a parallel experiment, a portion of the original carbonate was converted into the oxide by simple ignition, the magnesia formed in this way evolving only an extremely small amount of gas upon solution (Expt. 2).

A third portion of magnesium nitrate was made from pure magnesium ribbon and pure nitric acid, and the oxide was obtained from this salt by evaporation and ignition in porcelain as usual (Expt. 7).

Sulphuric acid was used for the solution of the magnesian oxide, as in the case of zincic and cupric oxides. The preceding Table explains itself.

The amount of gas occluded by magnesian oxide is thus far more than that occluded by the oxides of copper, zinc, and nickel. The quantities of carbon dioxide recorded in the Table are undoubtedly far from accurate, since the gas was collected over water. It is interesting to note that the amount of nitrogen evolved by the oxide upon going into solution was slightly increased up to a certain point by the increasing time and heat of the ignition, while the amount of oxygen was rapidly diminished.

No. of Expt.	Vol. of Nitrogen found in 1 grm. of MgO. C.c. Gas.	No. of Expt.	Vol. of Oxygen found in 1 grm. of MgO. C.c. Gas.
1.	3.6	1.	7.2
3.	4.72	3.	6.3
4.	4.84	4.	4.4
5.	5.44	5.	3.6
6.	5.24	6.	2.8

*The Oxides of Cadmium, Mercury, Lead, and Bismuth.*

These oxides, the only other suspected ones which could be easily analysed by the method in hand, all yielded negative results. The oxide of cadmium was distinctly crystalline, and contained only the merest trace of gas. The oxides of mercury, lead, and bismuth obtained by the ignition of the corresponding nitrates also appeared to contain no occluded gaseous impurity.

Unfortunately the oxides of antimony, iron, and a number of other metals are not sufficiently soluble in acids to test with ease their power of occlusion by this method. It seems probable that interesting results might be obtained from them; hence in the near future other methods will be tried here, with the hope of determining if these oxides also occlude gaseous impurity.

*Theoretical Considerations.*

From the fact, observed with both copper and zinc, that oxides which still contain a trace of nitrates, as well as those made from the carbonate, retain no imprisoned gas, it is readily inferred that the decomposition of a trace of nitric acid is alone responsible for the impurity. It is natural that this last trace of nitric acid should be confined below the surface, whence the gases resulting from its ultimate decomposition would find it hard to escape. On this supposition it is not unnatural that zincic oxide which has been partly reduced, and hence somewhat disintegrated, should contain less occluded gas than that which has not been thus reduced. Moreover, since magnesian nitrate is harder to decompose than the other nitrates, and the oxide is more compact, we should expect to find more gas occluded in this case than in the others. All these inferences agree with the facts. The difference in the rate of expulsion of the oxygen and of the nitrogen is interesting and less easy to explain.

The negative results observed with a number of metals lead one to conclude that the physical condition of the oxides in these cases was so porous that even the last traces of nitrogen were allowed to escape. Indeed, cupric and zincic oxide made from very finely divided basic nitrates, obtained from aqueous solution, contained much

less gas than samples which were obtained in a more compact condition by the direct ignition of the normal nitrate. This fact shows how much depends upon physical conditions.

It must be borne in mind that the occlusion of gases noted in this paper is a very different phenomenon from the retention of undecomposed oxides of nitrogen alluded to by Marignac,\* Morse and Burton, and others. Nitrogen present in the state of gas could of course give no test with sulphanic acid and naphthylamine, or any other test for oxidised nitrogen. It is evident that the phenomenon we are now studying, like the other just spoken of, may be a very serious cause of error in many of the published determinations of atomic weights; these would hence appear lower than their true value, because of the extra material which is calculated as oxygen.† Before any quantitative results obtained in this way can be accepted as authoritative, definite proof must be brought forward of the absence of this source of error. It is to be hoped that the able experimenters who have recently worked upon zinc, nickel, magnesium, and similar metals, have preserved typical specimens of their final products. If this is the case, nothing could be easier than to determine the amount of occluded gas, if any is present, and to apply the necessary correction.

As long ago as 1887 one of us was engaged, through the suggestion of Professor Cooke, upon an investigation of the atomic weight of zinc depending upon the analysis of zincic bromide. The work was discontinued because of the many publications upon this subject which appeared before it could be completed. Since the results recorded in this paper appear to indicate that the last word has not yet been said upon the subject, the investigation of zincic bromide and chloride is now being continued in this Laboratory.

### ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.‡

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 240).

THAT my expectations depending on the greater transparency of fluorite were realised only to a limited extent in that part of the spectrum which has been already observed with quartz, and in the region beyond it not at all, may be here mentioned only in a preliminary manner, and because the following proofs might otherwise readily lead to erroneous conclusions.

**B. In Dry Gelatin.**—In principle and in arrangement the experiment resembled the foregoing. Much time was taken up with the production of the gelatin film, the absorption of which was to be determined.

Soret made use of a watery solution of gelatin, which he placed between the slit and the source of light in a closed trough with parallel sides of quartz; a means equally convenient and certain of obtaining gelatin media of every desired thickness, but applicable only when the presence of water does not interfere. Water, even if recently distilled, is not indifferent in its behaviour with the most refrangible rays. When Soret placed in the

track of the rays a trough of 10 m.m. in width, the line No. 32 disappeared entirely; whilst after emptying the trough, when there remained merely the absorption of the two quartz sides, it was visible again (*Archives des Sci. Phys. et Nat.*, vol. lxi., p. 336, 1878). For my purpose, therefore, the use of gelatin in solution was not admissible.

I made use of dry films of gelatin, which I made from a solution of gelatin in water. The stouter films of 0.1 m.m. in thickness and upwards were used without support, but the thinner films were placed upon a plate of quartz parallel to their plane. My observations were limited to thicknesses of gelatin suitable for silver bromide gelatin. But attention was principally given to such thicknesses as probably occur between the several particles of silver bromide of the coating of the plate.

We calculate in practice for a plate of 13 and 18 c.m. side-lengths and 10 c.m.<sup>2</sup> of emulsion fit for pouring, which contained in 100 parts by weight of water 5 parts by weight of gelatin. According to this proportion I covered with a 5 per cent solution of gelatin a plate of quartz placed in a level position. This plate was subsequently used for all films, and also for taking the absorption spectra. I dried it carefully, and then measured the gelatin film which I had taken off the middle of the plate with a micrometer capable of showing 0.01 m.m. From a number of measurements the thickness was found to be 0.020—0.021 m.m., which agreed well with measurements made on emulsion plates by others. On this thickness, which for the sake of simplicity I will assume as 0.020 m.m., is founded the thickness of all the thinner films, which will be referred to below. I did not disguise to myself the fact that the method, according to which I have determined here and subsequently the thickness of the films, might be open to various objections, but I held the degree of accuracy thus obtained completely sufficient for the purpose in view. I then made solutions containing in 100 parts by weight of water 2.5, 1, 0.5, 0.125, 0.100, 0.063, 0.100, 0.063, 0.004, 0.002 parts by weight of gelatin (Heinrich's hard emulsion gelatin). I poured with a pipette containing 1 c.m.<sup>3</sup> up the above-named quartz plate the same quantity as before, and spread the solution uniformly to the edge of the plate by means of a thin glass rod. The coating was dried in heat, and without any current of air, which, as I had ascertained in preliminary experiments, gives in solutions poor in gelatin layers which become thicker towards the middle of the plate.

The moistened plate, which had previously been carefully levelled, lay on a plate of mirror glass, which rested a few m.m. above the water-surface of a hot water-bath, and rested on the edge of the vessel. Above, on the plate of glass, there stood a spacious metal pipe open at both ends and several c.m. high, closed above with a second glass plate. The coating of the quartz plate dried consequently in an atmosphere of watery vapour. For the escape of the steam, the loose connection between the pipe and its glass cover was sufficient. The thickness of the films thus obtained was, on the basis of the above-made assumption, 0.010, 0.004, 0.002, 0.001, 0.0005, 0.0004, 0.00025, 0.00008, 0.00004 m.m. I laid bare the dried plate in its middle by means of a clean cut for some m.m. in length, and placed it in the camera in such a manner that the slit was covered for half its length with the coated plate, and for the other half for the part of the plate which had been laid bare. Each exposure then gave two spectra, and the difference between the two corresponded to the absorption of the gelatin film. As the source of light there were used Leyden jar sparks of cadmium, zinc, aluminium, thallium, and tungsten. The exposure began with a single spark (opening spark), and was never continued longer than three minutes. The plates this time were those of Dr. Schleumer, of Frankfort-on-Main; the development was as before. The proofs (276) were distributed on 60 plates.

(To be continued.)

\* "Il est probable que l'oxyde de zinc et la magnésie ne sont pas les seuls oxydes qui retiennent aussi énergiquement des composés nitreux, lorsqu'on les prépare par la calcination de leurs azotates."—*Annales de Chimie et de Physique*, Series [6], i., p. 311, footnote.

† The following are the metals whose atomic weights have been determined by means of the oxide made through action of nitric acid:—Hydrogen (cupric oxide), Magnesium, Aluminium, Vanadium, Manganese, Nickel, Cobalt, Copper, Zinc, Gallium, Selenium, Tin, Antimony, Tellurium. See Meyer and Seubert, "Atomgewichte," pp. 17 to 42; also "Nickel," Krüss, *Zeit. Anorg. Chem.*, ii., 235; "Zinc," Morse and Burton, *Amer. Chem. Journ.*, x., 311—321; "Magnesium," Burton and Vorse, *CHEM. NEWS*, lxi., p. 267.

‡ From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following are abstracts of papers received during the vacation, and published in the *Transactions* :—

56. "*Peri-derivatives of Naphthalene.*" By R. MELDOLA, F.R.S., and F. W. STREATFEILD. (*Trans.*, 1893, 1054).

A description is given of the preparation of 1 : 1', or peri-nitronaphthylamine by nitrating  $\alpha$ -naphthylamine in presence of sulphuric acid, and of the preparation from this compound of benzylidene-1 : 1'-nitronaphthylamine, 1 : 1'-nitrobromonaphthalene, 1 : 1'-bromonaphthylamine, 1 : 1'-bromonaphthol, and 1 : 1'-dibromonaphthalene.

57. "*Note on Lead Tetracetate.*" By A. HUTCHINSON, M.A., Ph.D., and W. POLLARD, B.A. (*Trans.*, 1893, 1136).

It is shown that the compound which crystallises from a solution of red-lead in glacial acetic acid, described by Jacquelin, in 1851, is *lead tetracetate*,  $Pb(C_2H_3O_2)_4$ . A corresponding propionate has been obtained. On adding ammonium chloride to a solution of the tetracetate in chlorhydric acid, a precipitate of the characteristic double salt of ammonium chloride and lead tetrachloride is produced.

58. "*Resolution of Lactic Acid into its Optically Active Components.*" By T. PURDIE, Ph.D., B.Sc. (*Trans.*, 1893, 1143).

Inactive lactic acid has already been resolved into its active components by two of the three general methods discovered by Pasteur, namely, by selective fermentation, and by crystallisation of salts of the alkaloids. The author finds that the third method, that of spontaneous resolution by crystallisation, can also be applied with success.

In the course of an investigation on the resolution of lactic acid into its active components by crystallisation of the strychnine salts (Purdie and Walker, *Trans.*, 1892, 754) an active zinc ammonium lactate was encountered, which possessed in a marked degree the property of forming supersaturated solutions when dissolved in a syrup of active ammonium lactate, and of separating from these solutions in comparatively large, well-defined crystals. It was also observed that a strong solution of ordinary ammonium lactate dissolves large quantities of ordinary zinc lactate, forming a syrup from which an inactive zinc ammonium lactate does not at once crystallise, but which readily deposits zinc lactate when slightly diluted. These observations suggested the idea that possibly the active double salts might be present in such a solution in a state of supersaturation, and that they might be separately crystallised from it under suitable conditions of temperature and concentration by adding the proper crystalline nuclei.

It is found that by heating a solution containing certain definite proportions of ammonium lactate, zinc lactate, and water, and then cooling, a supersaturated solution is obtained, from which either of the active salts or the inactive salt can be separated at will by adding traces of the respective salts as nuclei. By alternately dropping into such a solution dextrogyrate and lævogyrate nuclei, and adding fresh inactive zinc lactate to the exhausted mother-liquor, it is possible to obtain successive crops of the oppositely active salts in quantity. By re-crystallisation, products are readily obtained containing over 90 per cent of the active substances. The admixture of inactive salt can be eliminated by crystallisation of the zinc lactate prepared from the double salts. Determinations of the specific rotations of the zinc lactates thus obtained gave numbers agreeing with those given by Wislicenus for zinc sarcocollate at similar concentration. When equal quantities of 8 per cent solutions of the oppositely active zinc ammonium salts are mixed,

inactive zinc lactate is precipitated. The inactive zinc ammonium salt was also prepared, and was found to have the composition represented by the formula—



while that of the active salts is—



The salts also differ considerably in properties.

59. "*The Colouring Principles of Rubia sikkimensis.*" By A. G. PERKIN and J. J. HUMMEL. (*Trans.*, 1893, 1157).

The authors have separated both purpurin and munjistin or purpuroxanthincarboxylic acid from this root; they point out that the results show that it is nearly identical as regards colouring principles with the closely allied *Rubia munjistin*.

60. "*The Colouring and other Principles contained in Chay Root.*" By the same. (*Trans.*, 1893, 1160).

Chay root is the root of *Oldenlandia umbellata*, and is used as a dye-stuff in India; a large number of distinct products were isolated by extracting it either with an aqueous solution of sulphurous acid, or with lime-water, alcohol, and other solvents, viz., two substances of the formula  $C_{16}H_{12}O_5$ , both of which are shown to be anthragalloldimethyl ethers; a monomethyl ether of alizarin crystallising in orange needles melting at 178—179°; a resinous yellow substance, possibly an isomeric methyl ether, of alizarin in an impure form; metahydroxyanthraquinone; a yellow substance melting at 141°, which yields alizarin when heated with sulphuric acid; ruberythric acid; rubichloric acid; alizarin; a wax of the formula  $(C_{10}H_{18}O)_2$ , melting at 87—88°; and cane-sugar.

61. "*Phenyl-naphthalenes. I.  $\alpha$ -Phenyl-naphthalene.*" By F. D. CHATTAWAY, B.A. (*Trans.*, 1893, 1185).

It is shown that  $\alpha$ -phenyl-naphthalene can be synthesised in several ways, but that the yield in all cases is unsatisfactory. The best method is by the action of  $\alpha$ -chloronaphthalene on benzene in the presence of anhydrous aluminium chloride.  $\alpha$ -Phenyl-naphthalene is obtained as a thick, oily liquid, which solidifies on long standing, affording a fatty-looking mass without definite crystalline form. It boils at 324—325°, and is readily soluble in alcohol, ether, and benzene, but cannot be obtained crystalline from these solutions, being deposited on evaporating them in oily drops. It volatilises with steam, and possesses a peculiar odour resembling both naphthalene and diphenyl.

62. "*The Vapour Pressures, Molecular Volumes, and Critical Constants of Ten of the Lower Ethereal Salts of Acids of the Acetic Series.*" By SYDNEY YOUNG, D.Sc., F.R.S., and G. L. THOMAS, B.Sc. (*Trans.*, 1893, 1191).

The authors' chief object was to ascertain how far the generalisations of Van der Waals regarding "corresponding" temperatures, pressures, and volumes, are true for the members of a group of allied compounds. It has already been shown by one of them that the generalisations hold good, with a close approximation to accuracy, in the case of the four mono-haloid derivatives of benzene, but that when compounds of different chemical character are compared much greater deviations are to be observed, more especially as regards the absolute temperatures (boiling points) at corresponding pressures. It has also been shown that among the substances so far studied the deviations are greatest in the case of acetic acid and the alcohols, and it becomes therefore of additional interest to examine the behaviour of the salts formed by the interaction of the fatty acids and alcohols. The critical and other constants of a number of these have been determined by several observers, but the results are far from concordant, owing probably to imperfect purification of the substances examined. Two samples of each etherea salt were employed: one was prepared from the acid or anhydride and the alcohol; the other was obtained

from Kahlbaum. All were carefully purified, and their purity was proved both by the constancy of their boiling-points and by the agreement between the boiling-points, relative densities, and critical temperatures and pressures of the two samples.

The investigation shows that, although the results obtained with the ten compounds are in fair agreement with the generalisation of Van der Waals,—in close agreement so far as the molecular volumes of liquid are concerned,—yet the deviations observed are related to their composition.

The ratios of the absolute temperatures to the absolute critical temperatures at any series of corresponding pressures are clearly dependent on the molecular weights, though this is apparently not the case with the ratios of the molecular volumes of either liquid or saturated vapour to the critical volumes.

The composition of the isomeric ethereal salts appears, however, to influence all the ratios, those for the formates being lowest when the absolute temperatures or volumes of saturated vapour are compared and highest in the case of the volumes of liquid. The ratios for the acetates, on the other hand, are highest in the case of the absolute temperatures and of the volumes of saturated vapour, and lowest for the volumes of liquid.

The presence of the iso-group in methylic isobutyrate appears to have a distinct influence on the ratios. The ratios of the actual critical densities to the theoretical densities (for a perfect gas) show a maximum variation of 2 per cent; the mean value, 3.91, is somewhat higher than that (3.76) for the majority of substances previously studied; it is, however, lower than for the alcohols and for acetic acid.

The ratios of the absolute temperatures and of the volumes of liquid and saturated vapour at corresponding pressures to the critical constants, also the values of PV/T at the critical points, are compared with those of the substances previously studied, and it is found that the ethereal salts form a separate group.

The twenty-two compounds for which data are available fall into four groups:—(1) The ethereal salts, (2) the alcohols—methyl alcohol being especially abnormal, (3) acetic acid, (4) ether, benzene and its haloid derivatives, carbon and tin tetrachlorides.

63. "The Fermentation of Dextrose, Rhamnose, and Mannitol by a Lævolaetic Ferment." By GEORGE TATE, Ph.D.

In studying the micro-organisms that attack ripe pears the author has had occasion to isolate an organism that under aërobic conditions brings about lævolaetic fermentation of the hexoses, dextrose, mannose, and galactose, and also of mannitol, but an inactive lactic fermentation of the methylpentose rhamnose (isodulcitol).

The products of the fermentation of dextrose, mannitol, and rhamnose have been quantitatively determined: nine molecules of dextrose are found to yield two molecules of alcohol, one of succinic acid, seven to eight of lævolaetic acid, and smaller molecular proportions of formic and acetic acids.

Mannitol yields the same products, but in different proportions, there being a greater yield of alcohol and slightly greater yield of lævolaetic acid.

Neither alcohol nor formic acid was found among the products of the fermentation of rhamnose; nine molecules of this sugar afforded approximately five molecules of acetic acid and four molecules of optically inactive lactic acid.

The action of the organism as a lævolaetic ferment of dextrose was found to be unchanged after cultivating the parent cells in fluids containing rhamnose, inactive acid being formed.

The organism which is referred to as a lævolaetic ferment from its action upon the typical sugar dextrose belongs to the class of ascobacteria, and can develop so as to produce two forms of growth, widely differing in

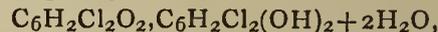
macroscopic appearance—one in which rods and cocci predominate, a second in which the organism propagates as an ascobacterium.

64. "Derivatives of Quinone containing Halogens. Part III. Derivatives of Quinhydrone." By ARTHUR R. LING and JULIAN L. BAKER. (*Trans.*, 1893, 1314).

Quinhydrone melts at 170—171°. The authors have obtained a compound having the composition of a *monochloroquinhydrone*, which melts at 145°, by gently heating a solution of quinone and monochloroquinol in chloroform; under somewhat similar circumstances Clark (*Amer. Chem. Journ.*, xiv., 574) obtained a small amount of quinhydrone. They have also obtained an isomeric compound melting at 132—133° by evaporating an ethereal or alcohol solution of quinol and monochloroquinone. When either of these isomerides is boiled with light petroleum they dissociate, and their constituents then interact, giving rise to dichloroquinhydrone, which is dissolved by the light petroleum, and quinhydrone, which remains undissolved.

*Dichloroquinhydrone*,  $C_6H_3ClO_2, C_6H_3Cl(OH)_2$ , is obtained by mixing solutions of monochloroquinone and monochloroquinol, and also by partially oxidising a solution of monochloroquinol with ferric chloride. It crystallises from water in dark violet needles containing one molecular proportion of water, melting at 70—72°; these are rendered anhydrous when kept over concentrated sulphuric acid, and then melt at 93—94°.

*Tetrachloroquinhydrone*,—



was described by Städeler in 1849. It is obtained in the form of dark violet needles by triturating paradichloroquinone and paradichloroquinol with water, and also by partially oxidising a solution of paradichloroquinol; the authors find that it melts between 105° and 140°, but has no definite melting-point. They confirm Städeler's observations that it loses its water of crystallisation when kept over concentrated sulphuric acid, becoming light yellow; the crystalline form of the anhydrous compound appears to be the same as that of the hydrated compound. An isomeride is obtained when metadichloroquinol and an excess of metadichloroquinone are boiled with a mixture of benzene and light petroleum; it separates from the filtrate in long, brown, prismatic needles, and melts at 135°.

*Hexachloroquinhydrone*.—A substance of the composition  $C_{12}H_4Cl_6O_4 + \frac{1}{2}H_2O$  is obtained by triturating trichloroquinone and trichloroquinol with water; it melts at 115—117°, and does not alter in weight when kept over concentrated sulphuric acid.

The authors failed to obtain octochloroquinhydrone, and conclude, from numerous experiments which are described, that this compound is non-existent.

*Dibromoquinhydrone*,  $C_6H_3BrO_2, C_6H_3Br(OH)_2$ , crystallises from water in anhydrous, dark, bronze-coloured needles, and melts at 98°.

*Tetrabromoquinhydrone* is obtained by boiling an aqueous solution of paradibromoquinol with an excess of paradibromoquinone; it separates, when the filtrate is rapidly cooled, in dark violet needles of the composition  $C_6H_2Br_2O_2, C_6H_2Br_2(OH)_2 + 2H_2O$ , and melts at 145—150°. It loses its water of crystallisation, and becomes light-coloured when kept over concentrated sulphuric acid.

*Dichlorodibromoquinhydrone*, prepared from paradichloroquinone and paradibromoquinol, crystallises from water in bluish-black needles containing two molecular proportions of water; it melts at 130—135°, and loses its water of crystallisation, becoming light yellow coloured when kept over concentrated sulphuric acid. An isomeride is obtained from paradibromoquinone and paradichloroquinol; it resembles the last-described compound and becomes pale brownish-yellow, losing its water of crystallisation when kept over concentrated sulphuric acid.

Ordinary Meeting, November 2nd, 1893.

Dr. ARMSTRONG, President, in the Chair.

MESSRS. Edmund Lamb, James A. Audley, Henry Bailey, and Charles Mills were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick Edmund Bowman, Ash Leigh, Bowdon, Cheshire; Henry Fielden Briggs, Roseneath, Torquay; Frank Browne, Government Civil Hospital, Hong Kong; John Dixon Brunton, Wire Mill, Musselburgh; Charles March Caines, 11, Clockhouse Road, Beckenham, Kent; Thomas Petson Carswell, 369, Scotswood Road, Newcastle-on-Tyne; Harry J. Chaney, 29, Chalcot Crescent, Regent's Park, London; Allan Thomas Cocking, 39, Lister Street, Rotherham; John A. Craw, 2, Millgate, Cupar Fife; Charles Sordes Ellis, 17, Bloomsbury Square, W.C.; Alexander M. Forrester, 22, Scotia Street, Glasgow; Henry Garnett, 2, Bartholomew Villas, Kentish Town, N.W.; William Hotton Grieve, 226, Friern Road, East Dulwich; Harry Edwin Hadley, The School of Science, Kidderminster; Henry Ormsby Hale, Oundle School, Northamptonshire; Harold Harris, Denmark House, Tuffley Avenue, Gloucester; William Hesketh, B.A., School House, Ferriscoverles, Blackburn; Harold B. Holthouse, 42, St. Ann's Valley, Nottingham; Alexander Sinclair Hughson, 12, Myrtle Crescent, South Shields; Bertram Hunt, F.I.C., 5, Queen's Crescent, Glasgow; Richard Savory Ladell, 155, Praed Street, Hyde Park, London; William Fred Mawer, 16, Fentiman Road, S.W.; J. R. Morgan, Leydenburgh, Port Hall Street, Brighton; Frederick Morton, 101, Quarumby Road, Huddersfield; George F. Payne, M.D., Atlanta, Georgia, U.S.A.; Thomas Beilby Rawlins, 2, Levan Street, Pollokshields, Glasgow; George Percival Rees, Ely House, Basford, Stoke-on-Trent; Thomas Anderson Reid, Lostock Gralam, Northwich; Herbert Santer, Albion Brewery, Caledonian Road, N.; Philip Schidrowitz, 102, Oxford Gardens, Notting Hill, W.; W. Edgar Sims, B.Sc., Stafford House, Longsight, Manchester; Frederick Shapley, Whittier, Fuller, and Co., San Francisco; Frederick Spencer, Rose Villa, Uttoxeter, Staffs.; Robert Curling Styles, Knockhall, Greenhithe, Kent; Jocelyn Field Thorpe, Gloucester House, 20, Larkhall Rise, Clapham; William Herbert Walden, 55, Clapham Road, S.W.; Frank Ernest Welchman, 16, Carlton Road, Putney Hill, S.W.; William Gilchrist White, Lamb Roe, Whalley, Lancashire; Edward Humphreys Winder, 37, Vincent Square, S.W.; Stanley Wyndham, Ph.D., Judson, Florida, c/o Trenton Phosphor Co.

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

\*65. "The Action of Bromine on Azobenzene." A correction. By HENRY E. ARMSTRONG.

It was pointed out by me in a recent note (*Proc. Chem. Soc.*, 1892, p. 194) that a compound represented by a formula such as is assigned to azobenzene, Ph·N:N·Ph, did not come within my "colour rule"; at the same time I drew attention to Werigo's colourless tetrabromazobenzene, and stated that Mr. Mills, at my request, had undertaken to further study the bromo-derivatives of azobenzene, and had already confirmed Werigo's observation.

According to Werigo, tetrabromazobenzene melts at 320°; the product obtained by Mr. Mills charred at a high temperature without melting; when boiled with tin and muriatic acid, it gave a tetrabromobenzidine, which was readily purified by crystallisation from boiling xylene; this melted at 285° (uncorr.), and proved to be identical with that prepared from benzidine, following the directions of Claus and Risler. This benzidine derivative was converted into a tetrabromodiphenyl melting at 189° (uncorr.), from which a small quantity of dimetabromobenzoic acid was obtained by oxidation.

During the course of the experiments, Mr. Mills was

gradually led to notice that the original product from azobenzene was very similar to tetrabromobenzidine, and he eventually satisfied himself by repeatedly crystallising it from xylene that it was, in fact, nothing but impure tetrabromobenzidine. The difference in composition between tetrabromazobenzene and tetrabromobenzidine is so small that it is practically impossible to decide by analysis which compound is under examination; and the fact that tetrabromobenzidine is destitute of basic properties renders its differentiation difficult. Werigo's tetrabromazobenzene must therefore be struck off the list of known compounds; and no argument as to the constitution of azobenzene can be based on its behaviour with bromine.

\*66. "The Origin of Colour. (X.) Coloured Hydrocarbons." By HENRY E. ARMSTRONG.

Graebe, in a recent note (*Ber.*, 1893, 2354), adduces what appears to be satisfactory evidence that the acenaphthylene, C<sub>12</sub>H<sub>8</sub>, discovered by Behr and Van Dorp, is actually a yellow hydrocarbon, and contends that the colour of this hydrocarbon and also that of the red hydrocarbon from fluorene (*cf. Proc. Chem. Soc.*, 1892, 192) is to be regarded as, in the first instance, conditioned by the presence of the group >C:C<. He ascribes the non-appearance of colour in ethylene derivatives generally to a secondary influence exercised by the groups displacing the hydrogen atoms in ethylene.

The problem is of such importance that I will venture to point out that in the case of coloured substances generally, the type of the series is itself always coloured—the only exception which I can call to mind being iodoform (*cf. Proc. Chem. Soc.*, 1893, 62). Acenaphthylene, no doubt, cannot well be represented otherwise than by the formula—



but if possessed of an ethenoid structure akin to that of anthracene, an "explanation" of its colour may be given similar to that which I have put forward in the case of anthracene and of certain coloured quinoline derivatives (*Proc. Chem. Soc.*, 1893, 63). On inspecting the formula—



it will be seen that the carbon atoms of the one nucleus are attached to the benzene nucleus on the left in ortho-positions and by ethenoid linkages; in other words, the hydrocarbon is an orthoquinonoid derivative. The external coupling is, in a measure, comparable with that which occurs in compounds such as methylene blue, &c., and it is this circumstance, perhaps, which causes the colour of the hydrocarbon to be so much more intense than that of anthracene, for example.

(To be continued).

#### PHYSICAL SOCIETY.

Ordinary Meeting, November 10th, 1893.

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

MR. R. S. COLE was elected a Member of the Society.

A paper on the "Separation of Three Liquids by Fractional Distillation," by Prof. F. R. BARRELL, M.A., B.Sc., G. L. THOMAS, B.Sc., and Prof. SYDNEY YOUNG, D.Sc.,

F.R.S., was read by Prof. Young. Accepting the results obtained by F. D. Brown in his experiments on the variation in the composition of the distillate from a mixture of two liquids, viz., that the relative quantities of the two substances in the vapour at any instant are proportional to the weights of the substances in the still, multiplied by the ratio of their vapour pressures, the authors write Brown's equation in the form—

$$\frac{d\xi}{d\eta} = c \frac{\xi}{\eta}$$

where  $\xi$  and  $\eta$  are the weights of the two liquids in the still and  $c$  the ratio of their vapour pressures. Taking  $c$  as constant, the above equation is integrated, and from the resulting expressions curves are plotted showing the changes in composition that take place during the distillation. Assuming that a similar law holds for three liquids, A, B, and C, viz.—

$$\frac{1}{a} \frac{d\xi}{\xi} = \frac{1}{b} \frac{d\eta}{\eta} = \frac{1}{c} \frac{d\zeta}{\zeta}$$

the composition of the distillate at any instant is calculated.

Taking  $a=4$ ,  $b=2$ , and  $c=1$  (numbers nearly proportional to the vapour pressures of methyl, ethyl, and propyl acetates) numerous curves are plotted showing the progress of the separation at various stages of fractionation. These curves show distinctly that, although fractions containing large proportions of the liquids A and C, of lowest and highest boiling-points respectively, can be easily separated, the middle substance, B, is much more difficult to obtain in a state of purity. Consideration of these curves led the authors to see that by carrying out the fractionation in a particular way it was possible to separate the mixture into two portions, one containing only A and B, and the other B and C. These mixtures of two liquids would then be fractionated in the usual manner. This process was carried out on a mixture of methyl, ethyl, and propyl acetates, the results of which are given in considerable detail in the paper. The remarkable agreement between the densities of the ethyl acetates obtained respectively from the mixtures (A+B) and (B+C), as well as the fact that the densities of the separated liquids were the same as before the mixing, shows conclusively that the method employed was highly successful.

Prof. RAMSAY said the paper was a most valuable one, and would be a great aid to chemists. Distillations were usually carried out by "the rule of thumb," with the result that absolutely pure liquids could rarely be obtained.

The PRESIDENT enquired whether the curves representing the progress of distillation could be constructed from the very complete experiments made, and so test the assumed law.

Prof. YOUNG thought this not possible from the numbers obtained. To test the law in this way would be very laborious.

A "Note on the Generalisations of Van der Waals regarding 'Corresponding' Temperatures, Pressures, and Volumes" was read by Prof. S. YOUNG. In November, 1891, the author read a paper on the same subject (*Phil. Mag.*, Feb., 1892), and gave the critical molecular volumes of some twelve substances as calculated by M. Mathias. Since then a few small errors have been found in the calculation, and the author's corrected values are now given. The vapour pressures, molecular volumes, and critical constants of ten esters (methyl formate, acetate, propionate, butyrate, and isobutyrate; ethyl formate, acetate, and propionate; and propyl formate and acetate) have recently been determined (*Trans. Chem. Soc.*, lxiii., p. 1191). In the present paper the absolute temperature and volume of the twelve substances are given in terms of their critical constants, and tables given showing respectively the ratio of boiling-points (abs. temps.) at corresponding pressures, to absolute critical temperatures; the

ratios of volume of liquid at corresponding pressures to the critical volume; and ratios of volume of saturated vapour at corresponding pressures to critical volume; for the halogen derivatives of benzene, carbon tetrachloride, stannic chloride, ether; methyl, ethyl, and propyl alcohols; and acetic acid; and the extreme values for the ten esters previously mentioned. Whilst showing fair agreement with each other, the differences between them exceed errors of experiment. The ratios also indicate that the substances can be arranged in four groups, thus tending to show that molecular weight and chemical constitution have some influence on the results. The differences found would probably result from the presence of complex molecules such as are known to exist in acetic acid.

If Van der Waals's generalisations were strictly true, the ratio  $\frac{PV}{T}$  at the critical point should be constant for

all substances, as also the ratio  $\frac{D}{D'}$ , of the actual to the theoretical density (for a perfect gas) at the critical point. On comparing these quantities only a rough approximation is found, but the grouping of the compounds is again well marked.

Prof. RAMSAY was not sure that the existence of complexes would alter the molecular volume in the liquid state; for liquids seem very compact. Experiments on the surface energy of liquids had proved that complex molecules do exist in the alcohols and acetic acid. Dr. Young's conclusion was, therefore, confirmed by experiments of an entirely different nature.

Prof. HERSHEL was gratified to see Van der Waals's theory so well borne out in liquids, and hoped to see it extended to solids. The recent researches of Prof. Roberts-Austen on alloys seemed to point in this direction.

Mr. ROGERS said molecular complexes do exert an influence on the properties of substances, as had been shown by Prof. Thorpe's viscosity experiments. Van der Waals's generalisations should therefore be looked at from a chemical as well as a physical point of view.

The PRESIDENT thought the numbers brought forward showed fair agreement, especially when it was remembered that Van der Waals took no account of the complex molecules. Contrary to Prof. Ramsay, he would rather expect aggregation to affect the molecular volumes in the liquid state, for only about one-fifth the space was supposed to be occupied by matter. On the other hand, the relatively small contraction of liquids on cooling did not support this view.

"An Instrument for Drawing Conic Sections" was exhibited and described by Mr. J. GILLET, B.A.

This consists of a spindle inclined to a plane board, and a tube fixed to the spindle at an angle. A pencil which passes through the tube traces out a cone in space as the spindle is turned, and on sliding the pencil through the tube so as to keep its point against the plane, the point traces out a conic—the section of the cone made by the plane of the board. A circle, ellipse, parabola, or hyperbola can be drawn according to the inclination of the spindle to the board.

Prof. HENRICI said a similar instrument had been described in an Arabian manuscript 1000 years old, and had been independently re-invented by both a German and an Italian mathematician. He thought the fact of angle between the spindle and the tube in Mr. Gillett's instrument not being adjustable, was a disadvantage.

Mr. Inwards and Prof. Herschel also took part in the discussion, to which Mr. Gillett replied.

Zero-point in Measuring Pipettes.—Ch. O. Curtman (*Pharm. Rundschau*).—The author places the zero-point at the meniscus of the last drop retained by capillary attraction.

CORRESPONDENCE.

PREPARATION OF HYDROGEN.

To the Editor of the Chemical News.

SIR,—With regard to Mr. Ball's recent discovery (CHEM. NEWS, vol. lxxviii., p. 284) I beg to refer him to the new German edition of Graham Otto's "Compendium," vol. i., p. 99, published as early as 1878, where he will find the following note:—

"More powerfully still (than the metal) acts one drop of platinum chloride. . . . An action similar to platinum have solutions of gold, copper, silver, zinc, antimony, bismuth, and lead, and it is said that an addition of the chloride of either cobalt or nickel still surpasses the action of platinum."—I am, &c.,

H. KEMP.

St. Xavier's College, Bombay,  
October 28, 1893.

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. cxvii., No. 18, October 30, 1893.

The Yield of the Vine in the Season 1893.—M. Chambrelent.—The vintage this autumn in the Gironde and the Camargne has been unusually early and exceptionally good both in quantity and quality.

Carboxylated Derivatives of Dimethylaniline (Dimethylamidobenzoic Acids).—Charles Lauth.—The introduction of the group CO.OH in dimethylaniline in substitution for an atom of hydrogen, and the position which it occupies with reference to the amidogen in the molecule, gives to each of the isomers obtained peculiar properties, especially as regards the production of colouring substances. When the position occupied is ortho we obtain carboxylic colouring substances soluble in alkalis and capable of dyeing with metallic mordants. If it is para we obtain colouring-matters not carboxylic, and identical with those of dimethylaniline itself. When the position is meta the aptitude to form tinctorial substances has almost entirely disappeared.

Temperature of Baking Bread.—Aimé Girard.—Referring to M. Balland's paper (*Comptes Rendus*, October 16, 1893), the author states that the temperature in the middle of the dough is 101°, not in some, but in all cases.

No. 19, November 6, 1893.

A New Method of Preparing Methylamine, and on the Constitution of Hexamethylene-tetramine.—MM. Trillat and Fayollal.—If we reduce by means of zinc and hydrochloric acid the aqueous solution of the ammoniacal compound of formaldehyd, and heat the product in presence of soda, there is evolved a strong odour of methylamine. 100 grms. of formic aldehyd at 33 per cent are mixed in the cold with an aqueous solution of ammonia until no more heat is evolved. We then add at once 200 grms. zinc powder, and there is then allowed to flow gently into the mixture 750 grms. ordinary hydrochloric acid. This addition is made in the cold, and should be effected in the space of from eight to ten hours. To the liquid there is added a large excess of sodium carbonate, and it is distilled by a current of steam. The distillate is received in dilute hydrochloric acid. Ammonia passes over first, and then methylamine. We obtain thus a mixture of the two hydrochlorates, which are evaporated,

dried, and separated by absolute alcohol in heat. It may be considered as para.

Alkaline Methyltartrates and Ethyltartrates.—J. Fayollal.—The author describes the preparation of the lithium, sodium, potassium, and ammonium methyltartrates, and of the lithium, sodium, potassium, barium, and calcium ethyltartrates. He subjoins their specific rotatory powers in the form of a table.

Researches on the Homologues of Gallanilide. Preparation of Galloparatoluide.—P. Cazeneuve.—The author conjectured that as gallanilide, the anilide of gallic acid, is obtained by the action of aniline upon tannin, homologues of gallanilide might be obtained by analogous methods. Experience showed that only paratoluidine behaves like aniline, forming galloparatoluide.

*Zeitschrift für Analytische Chemie.*  
Vol. xxxii., Part 4.

The Annular Vernier Burette.—C. Meinecke (*Chem. Zeitung*).—This is a burette which permits of very accurate readings by means of a very fine auxiliary burette. The graduation is carried round the entire circuit of the burettes. The experimentalist titrates as usual, and if the liquid does not exactly stand at a degree it is allowed to flow into the vernier burette as far as the next degree, by which means it is possible to read to hundredths of a c.c.

Weight Burette.—M. Ripper (*Chemiker Zeitung*).—The liquid consumed is determined, not by volume, but by weight. This principle, first proposed by Hager and F. H. Morgan, is especially recommended in case of rather concentrated solutions. The equivalent is contained, not in 1 litre, but in 1 kilo. Ripper's apparatus is a shortened and proportionately expanded glass cock burette, which can be suspended to the balance by means of a wire, or clamped by its neck and its lower end to a stand. The author enumerates the following advantages of weighing as compared with measuring:—1. Independence of the temperature of the standard solutions. 2. Independence of correct graduation. 3. No errors in reading off. 4. No errors from the adhesion of the standard solutions to the sides of the tubes. 5. Equal degree of accuracy on using different quantities of liquid.

Sublimation of Iodine, Benzoic Acid, &c.—J. Hertkorn (*Chemiker Zeitung*).—The author uses, to contain the substance to be sublimed, a flat capsule of enamelled iron provided with a channel-shaped margin, into which fits a cone of enamelled iron closed with a doubly perforated cork. The channel is filled with mercury, oil, melted paraffin, &c. The stopper closing the upper orifice of the cone has two apertures. Through one of these there passes an escape tube, which can be closed by means of a caoutchouc pipe and a pinch-cock. Through the other perforation passes a long pear-shaped refrigerator extending into the cone.

Apparatus for the Fractionated Distillation of Liquids.—M. Ekeberg (*Chemiker Zeitung*).—This arrangement is adapted for the distillation of liquids boiling between 100° and 250°. The pipe for conveying away the vapours is coiled spirally and passes through an air-bath, the temperature of which can be kept constant to 0.2° by means of an electric thermo-regulator.

Safety Arrangement Against Explosions.—P. Altmann (*Chemiker Zeitung*).—The object is to prevent the danger of explosions from the sudden extinction of gas-flames left without supervision. A ring composed of two metals having different coefficients of expansion is applied to the burner in such a manner that the one end is close to the flame, and is heated accordingly. The ring is thus expanded, and a lever fixed at its other end slides over the arm of a cock which it carries along when the ring cools and contracts, and thus turns off the gas.

Photography as a Substitute for Direct Observation in Polarising.—Chauvin and Charles Fabre.—*Comptes Rendus*, cxiii., p. 691.

Table for Calculating the Proportion of Phosphoric Acid from the Weight of Magnesium Pyrophosphate.—Fr. Scheiding (*Chemiker Zeitung*).—The author assumes that if 0.5 grm. of the substance is taken, direct percentages of phosphoric anhydride are obtained. The table is not inserted.

Arrangement for Determining the Quantity of a Volatile Ingredient Present in any Substance.—O. Pettersson (*Chemiker Zeitung*).—Already inserted.

Proposal for the Composition of Normal Weights for Analytical and Physical Weighings.—A. Gawalowski (*Oel und Fett-Industrie*).—The author has found the subjoined alloy very suitable for the production of weights to resist gases, moist air, &c.:—Aluminium, 80.0; fine gold, 8.0; fine silver, 2.5; platinum, 4.0.

Proposals for Standardising in Acidimetry and Alkalimetry.—E. Brentel (*Oest. Chem. Gesellschaft and Zeit. Anorganische Chemie*).—Already inserted.

Comparisons of Various Methods for Standardising Normal Acids and Normal Alkalies.—C. L. Parsons.—From the *Journal of Analytical Chemistry*.

Standardising Normal Acids, especially for the Kjeldahl's Nitrogen Process.—F. C. Wells.—From the *Journal of Analytical Chemistry*.

Testing Burettes and other Measuring Vessels.—H. L. Payne.—From the *Journal of Analytical Chemistry*.

Burettes with Automatic Adjustment for the Zero-point.—H. R. Procter (*Chemiker Zeitung*) and St. Krawczynski (*Berichte*).—Procter's instrument is quite similar to that formerly proposed by J. Stumpf (*Zeit. Anal. Chemie*, 29, 590).

Pipettes for Poisonous Liquids.—Al. F. Reid.—From the *CHEMICAL NEWS*.

A Cock-pipette.—Carl Meissner (*Chemiker Zeitung*).—This instrument requires the accompanying figure.

## 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.

Decomposition of Salt by Electrolysis.—Can any reader inform me where I shall find the latest results that have been obtained on the practical scale in the decomposition of salt by electrolysis?—J. W.

## MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8. (Cantor Lectures). "The Art of Book and Newspaper Illustration," by Henry Blackburn.

WEDNESDAY, 29th.—Society of Arts, 8. "The Regulation of Street Advertising," by Richardson Evans.

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THE CHEMICAL NEWS.

VOL. LXVIII., No. 1775.

VEGETATION IN AN ATMOSPHERE DEVOID OF OXYGEN, AND CONSIDERATIONS ON THE DAWN OF ANIMAL LIFE.

By Dr. T. L. PHIPSON, F.C.S.,  
Graduate of the Faculties of Science and Medicine of the University of Brussels, Member of the Chemical Society of Paris, &c.

IN various papers published in the CHEMICAL NEWS during the present year, I have endeavoured to show that in the earliest ages of the earth, when life first made its appearance, plants (*anærobies*) must have been formed before animals (*aërobies*), as the presence of unoxidised substances in the primitive rocks prove that free oxygen was absent from the primitive atmosphere. The experiment on vegetation in hydrogen, which I published not long since (CHEM. NEWS, vol. lxvii., p. 303), shows that free hydrogen could not have existed in the primitive atmosphere any more than it can exist for any length of time in the atmospheric air of our days without becoming water.

On account of its feeble affinities, nitrogen alone could have formed the atmosphere in the earliest ages of our planet's history; and, previous to the advent of life, this primitive atmosphere was charged with carbonic acid and vapour by volcanic action, such as we see manifested to a considerable extent at the present time.

Hence the earlier vegetation of the globe developed in an atmosphere devoid of free oxygen, consisting of nitrogen, carbonic acid, and vapour, and *the whole of the oxygen now present in the earth's atmosphere is due to vegetation extending over immense periods of time.*

As the ancient plants were evidently anærobic, it was interesting to ascertain whether the plants of the present time were essentially of the same nature, and my experiments have shown me that they are; also that they must have preceded animal life—the latter resulting from the gradual transformation of anærobic cells into aërobic cells, *as a consequence of the changing conditions*; that is, the oxygen constantly poured into the air by vegetation.

At what precise geological period oxygen became present in sufficient quantity to allow of animal life might appear an interesting problem for the geologist, but *no such period will ever be determined*, because the change must have been very gradual; and the study of the lower forms of vegetable and animal life show us that there is no hard and fast line between the two kingdoms. There is no such thing to be discovered as "the first vestiges of animal life." As the oxygen evolved from the anærobic cells became gradually a greater factor in the composition of the air, these cells had to accustom themselves to it, until some became aërobic, and by their vital functions actually supplied carbonic acid to the air instead of oxygen.

In addition to the experimental notes I have already published to demonstrate the truth of these considerations, I may call attention to one experiment made with *Convolvulus arvensis* (a plant I have often used for this purpose) vegetating in an atmosphere devoid of free oxygen; whilst two other plants of the same species were growing alongside the apparatus in ordinary atmospheric air. It will be seen that the plants of the present day are anærobic, like those of the older periods, and that free oxygen in the air is not essential for their existence.

This experiment with *C. arvensis* vegetating in what may be termed a "primitive atmosphere," is typical of what occurs with all the phanerogamic plants mentioned in my previous papers, and with all the green *Alga*, such

as *Protococcus pluvialis* and the minute *Microcystis*, or "green matter of Priestley," that develops in spring water exposed for some weeks to the light.

The nitrogen in my former experiments was obtained from pure sulphate of ammonia, but more recently I have got it by the action of potash and pyrogallol on atmospheric air. It will be seen, however, by what follows, that *the same volume of nitrogen may be used over and over again* as it undergoes no alteration in volume or properties except those due to the oscillations of temperature and pressure. The apparatus consists simply of a graduated tube, wide enough to admit the plant easily, standing over water containing minute quantities of all the substances known (or supposed) to be useful to vegetation, and kept supplied with carbonic acid. Alongside of the graduated tube stands another smaller tube full of water; into this carbonic acid is introduced, at first, once a day; it displaces the water, but in the course of twenty-four hours or so, the water has absorbed this gas, and the tube is again full of water. Carbonic acid is again passed into it the next day, and the water displaced, saturated with carbonic acid, thus finds its way to the roots of the plant. In this manner the water of the basin in which stand the two tubes is kept supplied with a good quantity of carbonic acid. The whole is exposed to a constant northern light, such as is used by artists, which I have found preferable to a southern aspect or to the direct rays of the sun; the temperature of the room has varied from 15° to 32° C. One-half of the water in the little basin is covered to procure darkness for the roots, and a certain quantity of carbonic acid is also let into the graduated tube from time to time.

In this primitive atmosphere of nitrogen, carbonic acid, and watery vapour, vegetation is tolerably prosperous in spite of the confined condition of the air. The carbonic acid is absorbed and replaced by free oxygen, so that after a certain lapse of time the gas in the graduated tube approaches the composition of atmospheric air, and *can even be made richer than the latter in oxygen.* I have already shown that in pure carbonic acid a plant does not prosper long, but with a basis of nitrogen and vapour of water it will prosper with a large amount of carbonic acid for a considerable time, and will transform this carbonic acid into oxygen, volume for volume, until there is more oxygen in the gas than in common air.

First, 75 c.c. of pure nitrogen (reduced to 0° C. and 30 inches barometer) is introduced, and the plant being put in makes the whole 102 c.c. Then, a certain amount of carbonic acid is let in, and the volume of gas oscillates during the experiment from 102 to 127 or 130 c.c., according to the temperature and pressure, and the quantity of carbonic acid above the water at the time of observation.

The little plant was introduced on July 25, its height being then 30 divisions of the tube. On the 26th it had grown to 37 divisions; on the 28th, to 44 divisions; on the 29th, to 48; and on the 30th, to 51 divisions, when it began to curve. On July 31 it had formed a new leaf and was curving, occupying 52 divisions. On August 1 it had curved considerably, as all plants of the *Convolvulus* genus do, and measured only 50 divisions in height; but on the second it had shot up again to 64 divisions. It appeared very healthy. On August 3 it attained to 68 divisions. On the 5th there were new leaves formed, and the plant measured 70 divisions. During August 6, 7, 8, and 9, the plant was healthy and two more leaves had formed. The water being well supplied with carbonic acid, and a little introduced into the graduated tube, I left the experiment till September 18. On September 18 it had grown to 90 divisions, and by the 30th of the month to 94—nearly to the top of the graduated tube.

On October 2 it began to turn yellow, as did the two plants of the same species growing in the water outside the apparatus, as "witnesses." They all put on their autumnal tints at the same time, and were all dead by October 30.

The gas in the graduated tube (reduced to 0° C. and 30

inches barometer) measured 95 c.c. It was analysed on the 30th, and gave exactly—

Nitrogen	.. ..	75
Carbonic acid	.. ..	none
Oxygen	.. ..	20

Total .. .. 95 c.c.

In the course of three months and seven days, or ninety-eight days, the plant had grown from 30 to 94 divisions, not counting the curve natural to the *Convolvulus*, and had converted all the carbonic acid into oxygen, leaving the nitrogen exactly as it was at the commencement of the experiment. At the end of these fourteen weeks, the atmosphere of the graduated tube was thus found to be *richer in oxygen than ordinary atmospheric air*, which shows what would happen to the earth's atmosphere if there were an excessive supply of carbonic acid and vegetation did not deteriorate: *the oxygen of the air, due to plant life alone, would increase year by year.*

In the present state of things there is a kind of equilibrium *apparent* (not real), as during the last fifty or sixty years no excess of oxygen has been detected by analysis of the air. But what are fifty or sixty years compared to the thousands of centuries by which Nature counts her periods?

Hotham Villa, Putney,  
Nov. 14, 1893.

#### ON THE TEACHING OF INORGANIC CHEMISTRY.

By MARGARET D. DOUGAL.

(Concluded from p. 248).

ALTHOUGH vanadium is very nearly related to phosphorus as regards its compounds, there is, nevertheless, much to be said against the above grouping, particularly when we consider the corresponding members of Family VI. Even if it were possible to separate phosphorus from arsenic in order to place it in association with vanadium, nobody would separate selenium from sulphur in order to place the latter in association with chromium. It is therefore obvious that we are not able to use the above arrangement. A somewhat nearer consideration at once makes evident the reason for this apparent difficulty.

Titanium and zirconium are not quite analogous to silicon. On the curve of atomic volume they stand on the descending line, whilst the two first members—carbon and silicon, together with boron and aluminium—are represented on the lowest point of the curve. Still greater is the difference between phosphorus and vanadium, for the former is on the ascending line, and is accordingly easily fusible and volatile, and the latter is on the descending line as a very difficultly fusible element. We have, therefore, along with nitrogen and phosphorus, the volatile, easily fusible elements arsenic, antimony, and bismuth to combine in one family, and to treat in like manner the two following families. Accordingly, from Family V., the main groups, consisting of four or five members, are formed of the easily fusible and readily reducible, and the sub-groups of the more infusible and difficultly reducible elements:—

N = 14.01	O = 15.96	F = 19.06
P = 30.96	S = 31.98	Cl = 35.37
V = 51.1	Cr = 52.0	Mn = 54.8
As = 74.9	Se = 78.87	Br = 79.76
Nb = 93.7	Mo = 95.9	—
Sb = 119.6	Te = 125.0	I = 126.54
Ta = 182.0	W = 183.6	—
Bi = 208.9	—	—
—	U = 238.8	—

In the description of these groups attention is drawn to the peculiarity that the chemical value, with respect to positive and negative elements, is now different, namely:

		In IV.	In V.	In VI.	In VII.
Towards positive	.. ..	4	3	2	1
„ negative	.. ..	4	5	6	7

In consequence of the negative character of these elements, their affinity to other negative elements is so feeble that they frequently are unable to hold in stable union the number of negative atoms, *e.g.*, of chlorine, corresponding to their chemical value. For instance, of the members of Family V., only P, Nb, Sb, and Ta form normal chlorides of the formula  $RCl_5$ , whilst  $NCl_3$ ,  $VCl_4$ , and  $BiCl_3$  cannot take up a further quantity of chlorine. Still more striking is this in Family VI., where only one normal chloride,  $WCl_6$ , is known, and even this readily parts with chlorine; and in VII., where, up to the present, no chloride,  $RCl_7$ , has been prepared. In order to allow the student more thoroughly to understand these intricate relations, the lower chlorides are somewhat more fully discussed:—



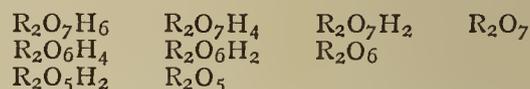
The degree of detail in which the individual members are treated depends on their relative importance.

The oxides and hydrates offer fewer irregularities; nevertheless, their composition is more difficult to grasp than those occurring in the first four Families.

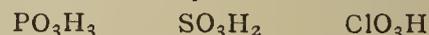
The hydroxyl compounds are regarded as anhydroacids:—

IV.	V.	VI.	VII.
$RO_4H_4$	$(RO_5H_5)$	$(RO_6H_6)$	$(RO_7H_7)$
$RO_3H_2$	$RO_4H_3$	$(RO_5H_4)$	$RO_6H_5$
$RO_2$	$RO_3H$	$RO_4H_2$	$RO_5H_3$
		$RO_3$	$RO_4H$

The poly-acids are represented in an analogous manner:—



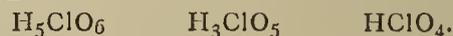
The composition of the acids poorer in oxygen is easily made clear in a similar way:—



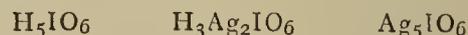
These regular formulæ are certainly more comprehensive than the representations in many text-books, as, for example, the representation of the different perchloric acids by the formulæ—



instead of by the typical formulæ corresponding to their behaviour—



But the periodic acids and their silver salts of the regular composition—



are regarded as molecular additions of silver oxide and water to  $AgIO_4$  or  $HIO_4$ , although their behaviour in no sense agrees with such a representation.

Dr. Meyer again takes up the consideration of the elements in detail. In Family V., as nitrogen and its compounds differ so very much in their properties from the following substances, it is advisable to speak of this element once more. After the explosive halogen compounds have been mentioned, of the oxygen compounds, nitric acid and the nitrates are fully described; and from their products of decomposition the lower oxides follow. The other elements of the group are then dealt with: their occurrence, modes of extraction and properties, their halogen compounds, their oxides, hydrates, oxychlorides, sulphides, &c., chiefly in the same order as hitherto adopted.

Of Family VII. oxygen is the first member. As it has already been fully discussed, it only remains to deal with ozone. The chloroxides could be, indeed, regarded as chlorides of oxygen were it convenient to do so.

The following elements—sulphur, selenium, and tellurium—are spoken of together, as well as their compounds, with special mention of sulphur. The halogen compounds afford a striking example of the change in affinity strength with atomic weight, inasmuch as their stability increases from those of sulphur over selenium to tellurium. The consideration of oxygen compounds begins conveniently with sulphur dioxide, which leads up to the description of the manufacture of sulphuric acid. The sulphates are again—as the carbonates, nitrates, &c.—arranged in isomorphous groups.

The elements of Family VII.—fluorine, chlorine, bromine, and iodine—have, in connection with their preparation from their hydrogen compounds, been somewhat fully described, so that little now remains to be added. The compounds they form by their mutual union are likewise soon dismissed, but it is again indicated that in the cases of elements of very similar properties the mutual affinity appears to be weakened, so that the number of the halogen atoms frequently remains below the particular number denoted by the chemical value. The consideration of the oxygen compounds of the salt-formers conveniently begins with the lowest oxides and hydrates, inasmuch as these form the starting-point for the preparation of the higher oxides. That the latter correspond to the heptad elements of the type has already been mentioned.

The main groups of Family VII. having been discussed, there remain only the sub-groups. Formerly Dr. Meyer treated them in the same order as the main groups; latterly, however, he has adopted what he believes to be a better arrangement based upon the nature of the elements.

After Family V. the easily reducible elements have been dealt with as the main groups of the families, whereas in the first four families they constituted the sub-groups; so between IV. and V., as already mentioned, there is a discontinuity, which is obvious from the following classification:—

IV.	{	Main group ..	C, Si, Ti,	Zr,	—	Th,
		Sub-group ..		Ge,	Sn,	Pb,
V.	{	Main group ..	N, P,	As,	Sb,	Bi,
		Sub-group ..	V,	Nb,	Ta,	--

Accordingly, it is advisable to begin the consideration of the sub-groups with those of Family V., and to conclude with those of IV. We thus obtain the following series:—

V.	VI.	VII.	VIII.	I.	II.	III.	IV.
V,	Cr,	Mn,	Fe, Co, Ni,	Cu,	Zn,	Ga,	Ge.
Nb,	Mo,	—	Ru, Rh, Pd,	Ag,	Cd,	In,	Sn.
Ta,	W,	—	Os, Ir, Pt,	Au,	Hg,	Tl,	Pb.

This arrangement allows of the oxy-acids of the phosphorus, sulphur, and chlorine groups to be connected up with the isomorphous acids of vanadium, chromium, manganese, and their related acids, whilst the lower oxides of these groups form the natural link with those of the iron group, whose compounds rich in oxygen are generally very unstable.

The elements and compounds of these three sub-groups, V., VI., and VII., are then described and discussed; chromium and manganese, owing to their importance, being dwelt upon at greater length than the others.

The metals which are usually classed together as Family VIII., namely, the difficultly fusible heavy elements, Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt, are conveniently described in two divisions; first, Fe, Co, and Ni; and then the platinum metals. There remain, in conclu-

sion, still a dozen somewhat easily fusible heavy metals, the description of which is much simplified when similar ones are compared together. The treatment of their compounds is rendered easy by reference to the main groups of the same families to which they are analogous. We have, for example, for the normal chlorides the series:—

CuCl	ZnCl <sub>2</sub>	GaCl <sub>3</sub>	GeCl <sub>4</sub>
AgCl	CdCl <sub>2</sub>	InCl <sub>3</sub>	SnCl <sub>4</sub>
AuCl	HgCl <sub>2</sub>	TlCl <sub>3</sub>	(PbCl <sub>4</sub> )

Naturally, the variations from these types as shown by CuCl<sub>2</sub> and AuCl<sub>3</sub> are clearly pointed out. At the same time the weakness of the affinities is indicated by the fact that TlCl<sub>3</sub> is readily split up into TlCl and Cl<sub>2</sub>, whilst PbCl<sub>4</sub>\* cannot exist, at least, in an isolated condition.

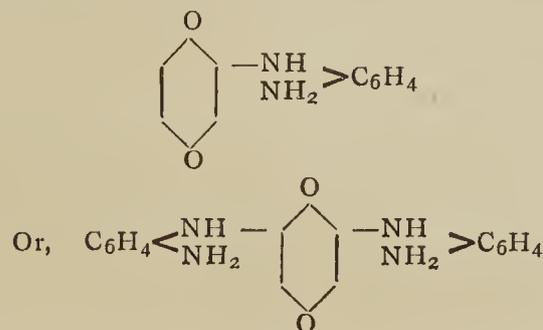
Such is Professor Lothar Meyer's mode of presentation of the subject-matter of Inorganic Chemistry. He gives it as not the only one possible, and it is doubtless capable of modification in certain particulars; nevertheless it must be obvious that it is the outcome of much thought and experience, and as such, is well worthy of the attention and careful study of all who are concerned in the Teaching of Inorganic Chemistry.

### THE INTERACTION OF QUINONES AND ORTHO- NITRANILINE AND NITROPARATOLUIDINE.†

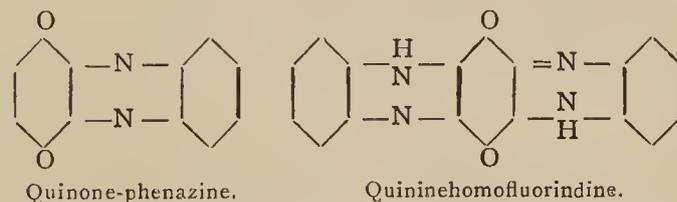
By Dr. JAMES LEICESTER, Ph.D., F.C.S.,  
Lecturer on Chemistry and Metallurgy at the Merchant Venturers'  
Technical School, Bristol.

It is known that quinone and aniline interact, forming quinone-anilide, and the constitution of these compounds appears to be established.

It was to be supposed that by an analogous interaction of orthodiamines and quinones substances would be obtained such as are represented by the following formula—



Or that action might proceed so far that quinone-phenazines or even quinone-fluorindine would result—



Actually the interaction of orthophenylene diamine and quinone is found to give rise to a mixture of substances which are exceedingly difficult to isolate; therefore, in order to fully determine the nature of the action, a series of experiments have been carried out with orthonitro-bases and quinones.

\* Lead tetrachloride, PbCl<sub>4</sub>, has been recently isolated by H. Fried- rich as a translucent, yellow, highly refractive liquid, readily decom- posable into lead dichloride and chlorine. The much more stable lead tetracetate, Pb(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>4</sub>, has lately been obtained by Hutchin- son and Pollard. A corresponding propionate is also known.

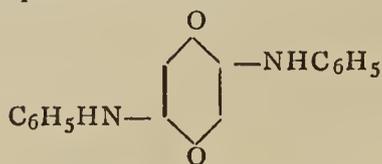
† *Ber. d. Deutsch. Chem. Gesell.*, xxiii., 2793; *Chem. Soc. Journ.*, Abstr., 1890, 1445.

*Quinone-orthodinitranilide.*

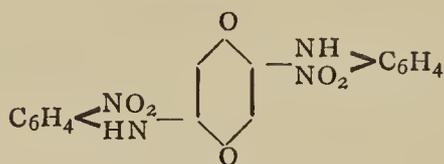
A solution in glacial acetic acid of three parts of quinone with 2.5 parts of orthonitraniline was heated for about two hours, the liquid being allowed to boil gently. On cooling the solution red crystals deposited, which were filtered off, and having been washed with a little glacial acetic acid and then with alcohol and ether were re-crystallised from hot absolute alcohol; thus obtained the products consisted of long red needles, melting at 305° C., with decomposition. On analysis it gave the following results:—

	Found.	Theory, C <sub>18</sub> H <sub>12</sub> N <sub>4</sub> O <sub>6</sub> .
C .. ..	57.3 p.c.	56.8 p.c.
H .. ..	3.1 "	3.1 "
N .. ..	14.8 "	14.7 "

This substance is to be regarded as the orthonitro-derivative of quinone-anilide—



Quinone-anilide.



Quinone-orthonitranilide.

*Quinone-homofluorinidine.*

If the orthonitroquinoneanilide be heated under pressure with alcoholic ammonium sulphide to 100° C. in a close tube, colourless crystals are noticed, which are probably orthoamidoquinoneanilide. When these crystals are exposed to the air they become a bluish black colour.

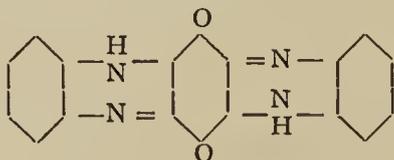
The mass is boiled with water and then re-crystallised from a mixture of methyl alcohol and benzene, from which mixture it separates in the form of dark green plates, which yield a violet-coloured powder having the same appearance as the homofluorindine of O. Fisher.

This blue colour and fluorescence with acetic acid, which is increased by adding a little alcohol, shows it to be a fluorindine. It is not, however, identical with homofluorinidine, as it contains oxygen.

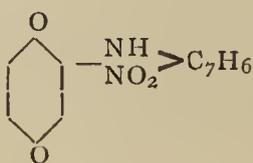
On analysis it gave the following result:—

	Found.	Theory, C <sub>18</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub> .
C .. ..	68.5 p.c.	68.7 p.c.
H .. ..	3.9 "	2.3 "
N .. ..	17.7 "	17.8 "

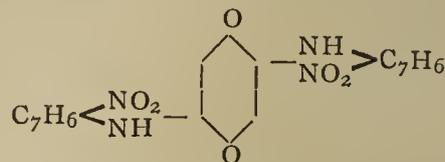
Assuming it to be quinone-homofluorinidine it would have the following constitution:—

*Orthonitrotoluidoquinone.*

When quinone and metanitroparatoluidine interact in a solution of glacial acetic acid the chief substance formed is a mononitrotoluidoquinone—



which yields a red crystalline mass when re-crystallised from absolute alcohol, while the dinitro-compound—



crystallises in bronze-coloured leaves and is harder to dissolve in absolute alcohol. The ortho-nitro compound decomposes at about 300° C.

	Found.	Theory, C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> .
N .. ..	11.03 p.c.	10.85 p.c.

The dinitrotoluidoquinone decomposes at 140° C.

	Found.	Theory, C <sub>20</sub> H <sub>16</sub> N <sub>4</sub> O <sub>6</sub> .
N .. ..	13.6 p.c.	13.7 p.c.

(To be continued).

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 252).

I OBTAINED still stronger films in a similar manner, but with the difference that I removed them from the plate after drying; and as they were not quite uniform among themselves, I sought them out of a suitable thickness with the aid of the above-mentioned micrometer; cut them in slips of 0.5 m.m. in width, and fixed these slips in series, according to their thickness, across the slit—5 m.m. long and 1 m.m. wide—of a small opaque screen, and at a mutual distance of 1 m.m. In this manner there was formed a grating serving as a filter for the rays, the rods of which had the thickness of 0.13, 0.07, 0.058, 0.04, 0.03, 0.02, 0.01. When I covered the slit with this grating, each exposure gave seven different absorption spectra, separated from each other according to the distance of the neighbouring slips, by unfeebled line-shaped spectra, which in reading off the data of absorption proved to be useful means of orientation. Three such proofs, each of a different time of exposure, were always produced on a plate of 20 m.m. in width. Such spectral series, on account of their compactness, afford an excellent general view. Even when magnified six times, all the forty-five spectra of such a plate can be brought simultaneously into the field of view.

Layer of gelatin, 0.13 m.m. in thickness. Cadmium sparks. Width of slit, 0.020 m.m. Length of exposure, 1, 4, 9 sparks, 1, 4, 9, 16 . . . 81.

The absorption extends to the entire ultra violet. It begins to a scarcely perceptible degree at the margin of the visible spectrum, increases gradually to the line 18,

rises very rapidly from here, and reaches the maximum between the lines No. 18 and No. 23, close by the line 246.93 μμ.

This line appeared in all proofs which required more than nine seconds exposure, but invariably as a mere trace. Its intensity did not perceptibly increase even on an exposure of eighty-one seconds.

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

Gelatin layer, 0.02 m.m. in thickness. Arrangement of the experiment exactly as in the 0.13 m.m. The absorption begins with the line No. 12, increases very gradually as far as the cadmium line  $241.85 \mu\mu$ , and after a more rapid increase reaches its maximum near the wave-length  $230.70 \mu\mu$ . The line No. 23 is of equal intensity in all exposures of longer than nine seconds, but it is everywhere very pale. The marginal line of these proofs,  $230.70 \mu\mu$ , is rather more strongly deflected, but it can be recognised merely as a trace.

Gelatin layer, 0.01 m.m. in thickness. Arrangement of the experiment as in the foregoing. The transparence is here considerably greater than in the previous case. The absorption becomes perceptible only at the wave-length  $288.01 \mu\mu$ . It increases at first slowly, but after  $241.85 \mu\mu$ , rapidly. The most refrangible lines of these proofs merit especial attention. Up to No. 23 they are all very intense, but beyond No. 23, as also the line  $230.70 \mu\mu$ , they again become strikingly pale and dim. The longest illumination, eighty-one seconds, led this time to a more intense and extensive proof. Hence it is prolonged rather further into the ultra-violet than all the rest. It ends with the line No. 24, wave-length  $226.55 \mu\mu$ , which appears as a trace.

Layer of gelatin, 0.002 m.m. in thickness. Cadmium sparks. Width of slit, 0.010 and 0.020 m.m. Exposure, 1, 2, 3, 4, 5, 6 jar-sparks; 42, 4, 8, 16, 32, 96 seconds. The absorption begins with the line No. 17, scarcely increases perceptibly as far as No. 18, more strongly up to No. 23—on very short exposure No. 23 appears merely as a trace—and increases then so suddenly that all the lines only become efficient on prolonged exposure, but then powerfully. No. 24 concludes the spectrum, and—which is very uncommon—as a very intense line. There is not a trace of the refrangible lines Nos. 25 and 26.

Layer of gelatin of 0.001 m.m. in thickness. Cadmium and zinc sparks. Otherwise as for the thickness of 0.002 m.m. The transparence makes here notable advances. Up to No. 24 the spectrum appears almost in full force. Nos. 25 and 26, which were previously absent, now appear on short exposure, though feebly, and even the most refrangible lines of zinc can be traced to the last, which is a mere trace.

Layer of gelatin, 0.0004 m.m. in thickness. Zinc, aluminium, and tungsten sparks. Otherwise as at the thickness of 0.002. The absorption takes place quite uniformly, as is best shown with the tungsten spectrum. It begins with No. 23, is considerable at No. 27, increases from these progressively, and becomes complete near the aluminium line No. 30, traces of which may already be recognised.

Layer of gelatin, 0.00025 m.m. Zinc and aluminium sparks. Width of slit, 0.040 m.m. Exposure as for the thickness of 0.002 m.m.

The transparence extends strikingly further towards the more refrangible side. All the aluminium lines appear as traces, No. 32 stronger than the rest.

Layer of gelatin, 0.00008 in thickness. Aluminium, thallium, and tungsten sparks. Width of slit, 0.020 also 0.080 m.m. Exposure, 1, 2 jar-sparks; 1, 2, . . . 120 seconds. All the lines of aluminium appear paler than without the gelatin layer. The influence of absorption can be followed even in such thin films up to line No. 26.

(To be continued).

**The Nitrification of Meadow Soils.**—J. Dumont and J. Crochetelle.—The authors conclude from their researches that—(1) In soils rich in humus nitrification is intensified by the addition of small quantities of potassium carbonate (2 to 3 per 1000), but in larger doses the carbonate is injurious. (2) Potassium sulphate favours the production of nitrates in proportions of 7 to 8 parts per 1000. (3) Potassium chloride exerts only a moderate action. (4) Sodium carbonate does not appear to favour nitrification.—*Comptes Rendus*, cvii., No. 20.

## THE ACTION OF ZINC AND MAGNESIUM UPON METALLIC SOLUTIONS, AND THE DETERMINATION OF POTASSA.

By A. VILLIERS and F. BORG.

THE electrolytic methods which enable us to determine, and often, indeed, to separate, metals are becoming more and more utilised in analytical chemistry. It seems, however, at first sight that we might in a great number of cases substitute for them a more rapid method, which consists in displacing metals by another metal, such as zinc or magnesium.

In reality, this latter procedure is applicable only in a very limited number of cases (copper, gold, platinum). The metals are not, in general, precipitated in a state of purity, but as alloys containing larger or smaller quantities of magnesium or zinc.

The proportion of these latter varies with the acidity of the liquids and with the weight of the metal employed. Another cause has also a remarkable influence upon this proportion—the degree of purity of the metal. It is thus that the weights of platinum displaced by equal weights of different specimens of zinc in equal volumes of one and the same solution of platinum chloride, have been 100.92, 100.39, 119.12 per cent; that is to say, the platinum has been precipitated with excesses of 0.92, 10.39, and 19.12 per cent. The first specimen of zinc had been obtained by the electrolysis of an ammoniacal solution of pure zinc sulphate; the second was a distilled zinc, containing no impurities except traces of sulphur not determinable by the balance; the third was commercial zinc, containing 1.1 per cent of impurities, of which 0.44 was fixed matter.

These results show that zinc cannot be used for the determination of platinum even after a correction for the impurities. When the zinc is impure, the presence of the impurities, even in an infinitely slight quantity, occasions the fixation of a very notable quantity of this metal upon the platinum. Electrolytic zinc gives results which are merely approximate.

Magnesium, as it is found in commerce in the form of ribbons, is, on the contrary, quite suitable for the determination of copper, gold, and platinum; and, consequently of potassium, after a precipitation as double platinum-potassium chloride.

*Determination of Copper.*—When copper is accompanied by no other metals except the alkaline and earthy metals, it may be determined very quickly and easily in the metallic state by treating its solutions with magnesium. The copper is thus liberated, in a slightly acid liquid, in the form of a granular precipitate very easy to wash. The washing is finished with alcohol; the metal is dried at  $100^\circ$  and weighed.

We may make use of a weighed filter, or more simply deposit the reduced copper in a small weighed capsule.

The process is not applicable in presence of metals like zinc easily acted on by hydrochloric acid; there are produced alloys even if the liquids are very acid.

*Determination of Potassium.*—If we determine potassium in the double platinum chloride, the precipitate is collected, after desiccation, on a weighed filter. Or we incinerate the filter, ignite the precipitate in hydrogen, and determine the platinum in the residue, after having removed the potassium chloride with water. The former method presents the causes of error inherent in the use of weighed filters. The latter method is tedious, and involves the successive incineration of two filters.

The following method is very rapid and very accurate. The double chloride, obtained in the ordinary manner, is washed with a mixture of equal volumes of alcohol and anhydrous ether, in the capsule in which it has been produced, until the filtrate runs through absolutely colourless—a result obtained with a small volume of the mixture. The residual salt is dissolved in boiling water, collecting the solution in a conical vessel. We add to it a

little pure hydrochloric acid, and introduce gradually fragments of magnesium, until the liquor is completely decolourised and the magnesium dissolves without its surface becoming tarnished.

The platinum thus deposited is very easy to wash, and does not adhere to the sides of the capsule. It is brought upon a filter without folds; the filter, after desiccation, is incinerated, and the platinum is ignited. Its weight, multiplied by 0.3939 or by 0.4747, gives the corresponding weight of potassium or potassa.

This method is very advantageous in the determination of potassa in presence of soda and other substances, except ammoniacal salts. It is sufficient to substitute this method of liberating the platinum for that proposed by Corenwinder and Contamine in their method for the determination of potassa in mixtures such as salines or refined potash.

By the use of magnesium we have obtained exactly 100 per cent of the potassa contained in potassium sulphate mixed with large quantities of sodium phosphate and sulphate, calcium, magnesium, and iron chloride, and aluminium sulphate, if we employ for the precipitating and washing the chloroplatinate a mixture of equal volumes of anhydrous alcohol and ether.

In presence of bromides, the precipitate produced by platinum chloride may contain more or less bromine replacing an equivalent quantity of chlorine. Still, a determination of the weight of the platinum will give in this case an exact result.

We must not forget to transform the potassium salts into chloride if the acids are volatile, or, in the contrary case, to acidulate with hydrochloric acid.—*Bull. de la Soc. Chim. de Paris*, Series 3, ix. and x., p. 602.

### THE INFLUENCE OF FREE NITRIC ACID AND AQUA REGIA ON THE PRECIPITATION OF BARIUM AS SULPHATE.\*

By PHILIP E. BROWNING.

THE fact demonstrated by Dr. F. W. Mar (*Amer. Journ. Sci.*, xl., 283), in an interesting series of experiments, that free hydrochloric acid even in large quantities does not interfere with the complete precipitation of barium as sulphate when sulphuric acid is present in sufficient excess, but rather renders the precipitate more crystalline, and therefore more easily and quickly filtered, suggested a similar series of experiments having as their object an investigation of the influence of free nitric acid on the same precipitation. Certain qualitative preliminary experiments showed a similar effect to that brought about by hydrochloric acid as regards the crystalline form and rapid settling of the precipitate. It therefore remained to determine whether the nitric acid present had any solvent effect upon the precipitate. Accordingly a standard solution of barium nitrate was prepared, free from alkali, by precipitating a soluble barium salt with ammonium carbonate, washing thoroughly with hot water and dissolving in nitric acid, care being taken to avoid an excess of the acid, and making up to measure. Definite portions of this solution were drawn from a burette into counterpoised beakers, and weighed as a check on the burette reading. Several precipitations of the barium in the form of sulphate were made, both in the presence of free hydrochloric acid and in neutral solution, and the mean of closely agreeing determinations was taken as the value of the standard solution. The mode of procedure in the testing was simple and may be outlined as follows:—Into a counterpoised beaker a definite amount of the standardised solution of barium nitrate was drawn and the weight taken as before described; the amount of nitric acid to

\* *American Journal of Science*, xlv., 1893.—Contributions from the Kent Chemical Laboratory of Yale College.

SERIES I.									
	BaSO <sub>4</sub> equivalent to Ba(NO <sub>3</sub> ) <sub>2</sub> taken.	BaSO <sub>4</sub> found.	Error in terms of BaSO <sub>4</sub> .	Averages.	Time between pre- cipitation and fil- tration.	Per cent by volume of strong HNO <sub>3</sub> .	Total volume.		
	Grm.	Grm.	Grm.	Grm.	Hours.		C.m. <sup>3</sup>		
1.	0.2540	0.2336	0.0004—	0.0006—	12	5	100		
2.	0.2489	0.2483	0.0006—		"	"	"		
3.	0.2495	0.2489	0.0006—		"	"	"		
4.	0.2492	0.2482	0.0010—		"	"	"		
5.	0.2486	0.2483	0.0003—		0.0002—	6	"	"	
6.	0.2490	0.2490	0.0000		"	"	"		
7.	0.2555	0.2546	0.0009—		0.0006—	1	"	"	
8.	0.2538	0.2534	0.0004—		"	"	"		
9.	0.4067	0.4057	0.0010—	0.0006—	12	10	"		
10.	0.2540	0.2533	0.0007—		"	"	"		
11.	0.2492	0.2489	0.0003—		"	"	"		
12.	0.2493	0.2488	0.0005—		"	"	"		
13.	0.2494	0.2488	0.0006—		"	"	"		
14.	0.2492	0.2492	0.0000		0.0002—	6	"	"	
15.	0.2490	0.2489	0.0001—		"	"	"		
16.	0.2489	0.2484	0.0005—		"	"	"		
17.	0.2540	0.2524	0.0016—		0.0016—	1	"	"	
18.	0.2529	0.2515	0.0014—		0.0007—	12	15	100	
19.	0.2534	0.2522	0.0012—			"	"	"	
20.	0.2533	0.2531	0.0002—			"	"	"	
21.	0.2538	0.2532	0.0006—			"	"	"	
22.	0.2497	0.2490	0.0007—			"	"	"	
23.	0.2489	0.2487	0.0002—			"	"	"	
24.	0.2542	0.2528	0.0014—			0.0006—	6	"	"
25.	0.2486	0.2486	0.0000			"	"	"	
26.	0.2492	0.2487	0.0005—	"		"	"		
27.	0.2547	0.2532	0.0015—	0.0015—		1	"	"	
28.	0.2489	0.2478	0.0011—	0.0008—	12	20	"		
29.	0.2486	0.2475	0.0011—		"	"	"		
30.	0.2548	0.2546	0.0002—		"	"	"		
31.	0.2548	0.2542	0.0006—		"	"	"		
32.	0.2496	0.2486	0.0010—		"	"	"		
33.	0.2539	0.2527	0.0012—		0.0008—	6	"	"	
34.	0.2488	0.2475	0.0013—		"	"	"		
35.	0.2497	0.2497	0.0000		"	"	"		
36.	0.2486	0.2477	0.0009—		0.0007—	12	25	"	
37.	0.2491	0.2490	0.0001—			"	"	"	
38.	0.2494	0.2484	0.0010—			"	"	"	
39.	0.2538	0.2535	0.0003—			0.0008—	"	"	"
40.	0.2492	0.2484	0.0008—			"	"	"	
41.	0.2487	0.2471	0.0016—			"	"	"	
42.	0.3414	0.3407	0.0007—	"		"	"		
43.	0.2489	0.2481	0.0008—	0.0007—		6	"	"	
44.	0.2485	0.2478	0.0007—	"		"	"		

be used was then added, and the whole volume brought up to 90 c.m.<sup>3</sup> by the addition of water. This acid solution was then brought to the boiling point and 10 c.m.<sup>3</sup> of the dilute sulphuric acid added, and the whole was allowed to stand for the length of time shown by the Table before filtering on asbestos, igniting, and weighing. It will be seen that the total volume of liquid taken in each determination was uniformly 100 c.m.<sup>3</sup>, the percentage of acid by volume being thus easily regulated. In no case did the amount of barium salt present exceed 0.4 gm. considered as the sulphate, and consequently the uniform amount of 10 c.m.<sup>3</sup> of dilute (1:4 by volume) sulphuric acid employed was always enough to assure the excess which Fresenius (*Zeitschr. f. Anal. Chem.*, xxx., 455) has shown to be necessary in the precipitation of barium as the sulphate in the presence of hydrochloric acid. By

SERIES II.

	BaSO <sub>4</sub> equivalent to Ba(NO <sub>3</sub> ) <sub>2</sub> taken. Grm.	BaSO <sub>4</sub> found. Grm.	Error in terms of BaSO <sub>4</sub> . Grm.	Averages. Grm.	Time between precipitation and filtration. Hours.	Per cent by vol. of strong aqua regia. (3HCl:1HNO <sub>3</sub> ). C.m. <sup>3</sup>	Total volume. C.m. <sup>3</sup>	
1.	0.2539	0.2534	0.0005 -	0.0002 -	12	5	100	
2.	0.2540	0.2538	0.0002 -		"	"	"	
3.	0.2490	0.2490	0.0000		"	"	"	
4.	0.2491	0.2492	0.0001 +		"	"	"	
5.	0.2488	0.2484	0.0004 -		0.0001 -	6	"	"
6.	0.3419	0.3421	0.0002 +		"	"	"	"
7.	0.2491	0.2487	0.0004 -	0.0006 -	12	10	"	
8.	0.2486	0.2482	0.0004 -		"	"	"	
9.	0.2549	0.2539	0.0010 -		"	"	"	
10.	0.2543	0.2538	0.0005 -		"	"	"	
11.	0.2487	0.2485	0.0002 -		0.0002 -	6	"	"
12.	0.3416	0.3415	0.0001 -		"	"	"	"
13.	0.3417	0.3420	0.0003 +	0.0003 +	1	"	"	
14.	0.2547	0.2544	0.0003 -	0.0003 -	12	15	"	
15.	0.2492	0.2492	0.0000		"	"	"	
16.	0.2489	0.2479	0.0010 -		"	"	"	
17.	0.3412	0.3412	0.0000		"	"	"	
18.	0.3418	0.3417	0.0001 -		0.0001 -	6	"	"
19.	0.3413	0.3412	0.0001 -		"	"	"	"
20.	0.3411	0.3402	0.0009 -	0.0009 -	1	"	"	
21.	0.2492	0.2484	0.0008 -	0.0005 -	12	20	"	
22.	0.2486	0.2480	0.0006 -		"	"	"	
23.	0.2491	0.2485	0.0006 -		"	"	"	
24.	0.3412	0.3411	0.0001 -		"	"	"	
25.	0.3417	0.3418	0.0001 +		0.0000 -	6	"	"
26.	0.3417	0.3417	0.0000		"	"	"	"
27.	0.3414	0.3404	0.0010 -	0.0010 -	1	"	"	
28.	0.2491	0.2485	0.0006 -	0.0003 -	12	25	"	
29.	0.1701	0.1697	0.0004 -		"	"	"	
30.	0.1708	0.1705	0.0003 -		"	"	"	
31.	0.1710	0.1710	0.0000		"	"	"	
32.	0.3415	0.3410	0.0005 -		0.0003 -	6	"	"
33.	0.3418	0.3418	0.0000		"	"	"	"
34.	0.3412	0.3405	0.0007 -	0.0007 -	1	"	"	

SERIES III.

	Impurity present to the amount of 5 grms.	BaSO <sub>4</sub> equivalent to Ba(NO <sub>3</sub> ) <sub>2</sub> taken. Grm.	Apparent amount of BaSO <sub>4</sub> found. Grm.	BaSO <sub>4</sub> after purification. Grm.	Error after purification. Grm.	Percentage of strong HNO <sub>3</sub> by volume.
1. Ammonium nitrate		0.1710	0.1800	0.1702	0.0008 -	10
2. " "		0.3415	0.3440	0.3410	0.0005 -	"
3. " citrate		0.3412	0.3442	0.3407	0.0005 -	"
4. Sodium "		0.1360	0.1730	0.1366	0.0006 +	"
5. Metaphosph. acid		0.3461	0.3511	0.3470	0.0009 +	"

reference to Series I. it is evident that in the presence of 5 per cent of nitric acid very little solvent action is shown, and it appears also that the sulphate may be safely filtered after an hour's time. In the presence of 10 to 15 per cent of the acid the solvent effect is very small when the solution is allowed to stand six hours or more. With 20 to 25 per cent of acid present we find the solubility to be slightly increased, but even then the average loss is less than 0.001 gm.

Having shown that free nitric acid, even though present in considerable amount, has only a slight solvent influence upon barium sulphate, it seemed interesting to try the effect of the combination of nitric and hydrochloric acids mixed in the proportion to form aqua regia (3HCl:1HNO<sub>3</sub>). The experiments recorded in Series II. show that aqua regia has even less effect as a solvent than nitric acid alone. In fact it seems to act like hydrochloric acid alone, which practically has no solvent effect, as shown by Dr. Mar's work previously cited.

In this connection I append the results of a few experiments made to determine the effect of the presence of a considerable amount of free nitric acid, on the precipitations of barium as sulphate in cases where certain substances are present which under ordinary conditions tend to hold up the precipitate. Fresenius (*Zeitschr. f. Anal. Chem.* ix., 62) has demonstrated this property in the case of ammonium nitrate, Scheerer and Rube (*Fourn. Prakt. Chem.* lxxv., 113-116) have shown that metaphosphoric acid acts similarly, and Spiller (*CHEM. NEWS.* viii., 280-281) notes the same general effect where alkaline citrates are present. Series III. shows the results obtained by precipitating definite portions of the standard solution of barium nitrate in the presence of stated amounts of the substances just mentioned. The total volume in every case was 100 c.m.<sup>3</sup>, the amount of dilute sulphuric acid used 10 c.m.<sup>3</sup>, and the time between precipitation and filtration twelve hours. Upon filtering, igniting, and weighing the barium sulphate, an excess of weight, due undoubtedly to contamination of the precipitate, was found. It became necessary, therefore, to purify the precipitate as first weighed in order to determine whether all the barium was actually precipitated or whether a partial loss was covered by the amount of included impurity. The method of purification employed was that successfully applied by Dr. Mar in the work previously mentioned. The contaminated sulphate, collected on paper and treated according to the familiar method (on account of the difficulty attending the complete removal of the precipitate from asbestos for purposes of purification), was dissolved in warm concentrated sulphuric acid, and evaporated quickly and without spattering by means of the Hempel burner, the barium sulphate being left after this treatment in coarse granular crystals. The crystallised sulphate was warmed with a little water containing a drop of sulphuric acid, filtered upon an asbestos felt contained in a perforated platinum crucible, the crucible and felt having been previously ignited and weighed.

The results show that in the presence of nitric acid amounting to one-tenth by volume of the entire liquid these salts exert no apparent interference with the precipitation of the barium.

The entire work would seem to show that the presence of an excess of nitric acid or aqua regia amounting to 10 per cent by volume of the liquid treated is not only not to be avoided in estimating barium as the sulphate, but is actually beneficial. Ordinarily the advantage is found in the tendency of the precipitate to fall coarsely crystalline under the conditions. In certain special cases in which certain substances mentioned, which would otherwise exert solvent action, are present, the precipitation is made complete. The contaminating effect of such substances when complete precipitation is induced may be corrected by dissolving the precipitate in sulphuric acid and recrystallising by evaporation.

Royal Institution.—The annual Christmas Course of Lectures for Children will this year be delivered by Prof. James Dewar, F.R.S. The subject will be "Air, Gaseous and Liquid," and the first lecture will be delivered in the theatre of the Royal Institution, Albemarle Street, on Thursday, December 28. The next General Monthly Meeting of the Members will take place on Monday next at 5 o'clock.

## PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

Ordinary Meeting, November 2nd, 1893.

Dr. ARMSTRONG, President, in the Chair.

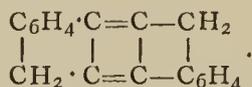
(Concluded from p. 255).

\*67. "The Formation of the Hydrocarbon 'Truxene' from Phenylpropionic Acid and from Hydrindone." By F. STANLEY KIPPING, Ph.D., D.Sc.

The further study of the hydrocarbon obtained from phenylpropionic acid (*Proc. Chem. Soc.*, cxii., 107; cxvii., 216) has led to the following results:—

The hydrocarbon is formed when hydrindone is heated either with phosphoric anhydride or with moderately concentrated sulphuric acid; it is also produced when a condensation product of hydrindone of the composition  $C_{18}H_{14}O$  is heated with either of these dehydrating agents.

This condensation product will be described in a future paper; the fact that it is readily converted into the hydrocarbon proves that the latter has the formula  $C_{18}H_{12}$ , and not  $C_{27}H_{18}$ , and is also evidence in favour of the view that the constitution of the hydrocarbon is expressed by the formula—



This view affords a simple explanation of the formation of the hydrocarbon from phenylpropionic acid and of its relation to other compounds.

The hydrocarbon in question is evidently identical with a compound obtained by Hausmann (*Ber.*, xxii., 2019) by heating hydrindone with concentrated chlorhydric acid, the study of which he did not continue. It is also identical with "truxene," a hydrocarbon prepared by Liebermann and Bergami (*Ber.*, xxii., 782) by reducing "truxone" with iodhydric acid; this is proved by the fact that both compounds are converted into Gabriel and Michael's "tribenzylenebenzene" (*Ber.*, x., 1557) on oxidation with chromic acid.

The author discusses the constitution of "truxene" and of "truxone," and points out that the formulæ assigned to them by Liebermann and Bergami (*Ber.*, xxiii., 317) do not accord with the facts of the case, and are not to be reconciled with the formation of truxone from  $\alpha$ -truxillic acid,  $C_{18}H_{16}O_4$ . It is also shown that the only evidence which led Liebermann and Bergami to assume that "truxene" is a "tribenzylenebenzene," namely, its conversion into "tribenzylenebenzene," is of little, if of any, value.

The constitution of "tribenzylenebenzene," being based on its conversion into triphenylbenzene, cannot be regarded as established, as it is first fused with potash at a high temperature and the product of this treatment is distilled over lime in order to bring about the change. It follows, therefore, that the conversion of the hydrocarbon from phenylpropionic acid into "tribenzylenebenzene" does not show that the former (truxene) has the molecular formula  $C_{27}H_{18}$ , but that "tribenzylenebenzene," which was hitherto supposed to have the molecular formula  $C_{27}H_{12}O_3$ , is, in reality,  $C_{18}H_8O_2$ ; this view is not refuted, but is rather corroborated by a study of the methods of forming "tribenzylenebenzene."

The behaviour of truxene with nitric acid and with bromine and its oxidation to nitrophthalic acid—



are described; attention is also drawn to a characteristic colouration which the hydrocarbon gives with ordinary concentrated sulphuric acid, and to its very peculiar decomposition by boiling nitrobenzene.

68. "The Action of Aluminium Chloride on Heptylic Chloride." By F. STANLEY KIPPING, Ph.D., D.Sc.

The fact that hydrindone is formed in large quantities on treating phenylpropionic chloride with aluminium chloride (*Proc. Chem. Soc.*, cxvii., 216) led the author to investigate the action of the latter on heptylic chloride, as it appeared possible that methylketohexamethylene, ethylketopentamethylene, or some other closed-chain compound might be formed.

After many unsuccessful experiments, in which almost the whole of the heptylic chloride was recovered as heptylic acid, it was found that under suitable conditions a large proportion of the acid chloride was converted into a neutral oil which was isolated by distillation in steam, but which proved to be a mixture; on cooling the fractions of highest boiling-point collected between  $290^\circ$  and  $310^\circ$ , a considerable quantity of colourless crystals was deposited which, when freed from oil, melted at about  $41^\circ$ . Analyses of this crystalline product gave results (I.,  $C = 82.2$ ,  $H = 10.2$ ; II.,  $C = 82.0$ ,  $H = 10.0$  per cent) corresponding to the formula—



It yields an oily hydroxime. On analysing this (found  $C = 75.4$ ,  $H = 10.0$ ,  $N = 6.7$ ; required  $C = 76.7$ ,  $H = 9.6$ ,  $N = 6.4$ ), the percentage of carbon found was somewhat lower than corresponds to the formula  $C_{14}H_{20}NOH$ , doubtless owing to the fact that the oil could not be purified.

It would seem, therefore, that the crystalline substance is a ketone, as was, in fact, to be expected.

The experiments which have been carried out up to the present with the object of determining its constitution, although few in number, have already afforded results of considerable interest. Fractions of the crude oil collected between  $280^\circ$  and  $310^\circ$ , when oxidised with nitric acid, gave a mixture of several acids, one of which was characterised by sparing solubility, and was, therefore, easily isolated; analyses of this acid gave results pointing to the formula  $C_{13}H_{10}O_6$  (found  $C = 59.4$ ,  $H = 3.9$ ; required  $C = 59.5$ ,  $H = 3.8$ ), and an analysis of its silver salt,  $C_{13}H_7O_6Ag_3$  (found  $Ag = 55.1$ ; required 55.5 per cent) confirmed this view. Whether this acid is an oxidation product of the ketone  $C_{14}H_{20}O$ , or whether it is produced from some other constituent of the oil, has not yet been determined, but in any case its indirect formation from heptylic acid is certainly rather extraordinary, as, to judge from its composition, it is a closed-chain compound.

The investigation of the behaviour of acid chlorides with aluminium chloride is being extended, and some progress has already been made with experiments with the chlorides of butyric, benzoylpropionic, and hippuric acids.

\*69. "The Inertness of Quicklime. II. The Interaction of Chlorine and Lime." By V. H. VELEY.

The author has ascertained by synthetical and analytical methods that no appreciable action takes place between dry chlorine and quicklime below  $300^\circ$ ; above this temperature a partial displacement of oxygen is effected by the chlorine: the interaction is thus analogous to that of baryta and chlorine not specially dried and at ordinary temperatures.

\*70. "Note on Hyponitrites." By D. H. JACKSON, M.A., B.Sc.

The author has conducted experiments for the purpose of obtaining alkali hyponitrites, hitherto known only in solution, in a solid state. He confirms the experience of previous observers that, contrary to the statement of Menke, hyponitrite is not formed when sodium nitrate is heated with metallic iron. Reduction of a solution of sodium nitrate with aluminium or with barium amalgam does not furnish hyponitrite. For the production of hyponitrites, the author employs Divers' method of reducing a solution of sodium nitrate with sodium amalgam. He finds that the best yield of hyponitrite results from the

use of an amalgam weak in sodium acting at a low temperature; owing to the violence of the action, no hyponitrite is obtained when sodium alone is used as the reducing agent. The origin of the metallic silver which generally contaminates silver hyponitrite produced by the usual process is traced to the reduction of silver hyponitrite by the hydroxylamine acetate contained in the solution in which precipitation is effected. In order to avoid loss of hyponitrite from this cause, it is recommended to add mercuric oxide to the alkaline solution resulting from the reduction. This destroys the hydroxylamine, and therefore the silver hyponitrite subsequently produced does not darken in the liquid. Although an aqueous solution of sodium hyponitrite quickly decomposes into sodium hydroxide and nitrous oxide, it was found that in the presence of much sodium hydroxide considerably less decomposition takes place. A strongly alkaline solution of sodium hyponitrite, prepared by reducing a strong solution of sodium nitrate, when spontaneously evaporated over sulphuric acid in a vacuum during several weeks, deposited crystals of sodium hyponitrite, which could be freed from hydroxide by washing with alcohol, in which the hyponitrite is very sparingly soluble. The crystals may also be obtained by precipitating a strong aqueous solution of the salt prepared by the interaction of silver hyponitrite and sodium chloride with alcohol. A determination of the sodium in these crystals showed that they possessed the composition of sodium hyponitrite.

Ammonium hyponitrite was obtained in groups of long needles by decomposing silver hyponitrite with an alcoholic solution of ammonium sulphide, and evaporating the filtered liquid over sulphuric acid in a vacuum. Like the sodium salt, this compound is difficult to obtain in any quantity, and this circumstance prevented the author from further investigating the properties of these hyponitrites.

71. "The Interaction of Hydrogen Chloride and Potassium Chlorate." By W. H. PENDLEBURY, M.A., and Mrs. MCKILLOP.

The authors have determined the amount of oxidising gases (whether chlorine or its oxides) removed on passing a given volume of air at a given rate through an aqueous solution of potassium chlorate and hydrogen chloride kept at a constant temperature, and have compared the amount removed with that present in the liquid. The evolved gases were received in a solution of potassium iodide, and at the end of each half hour the amount of iodine liberated was determined.

The following results were obtained at 30° with a mixture containing 30 grms. of potassium chlorate and 18.823 grms. of hydrogen chloride in 800 c.c.; the half-hourly determination of iodine was not performed during 41½ hours, 5.5 hours after mixing.

Hours after mixing.	Mass of iodine liberated.	Hours after mixing.	Mass of iodine liberated.
2.0	0.0021	47.5	0.0028
2.5	0.0032	48.0	0.0025
3.0	0.0038	48.5	0.0022
3.5	0.0035	68.0	0.0012
4.0	0.0034	69.0	0.0015
4.5	0.0028	69.5	0.0016
5.0	0.0025	70.0	0.0015
5.5	0.0022	71.5	0.0016
47.0	0.0023	72.0	0.0015

In a second set of observations twice the amount of hydrogen chloride was used (KClO<sub>3</sub> : 4HCl) (see first Table, next column).

100 c.c. portions were withdrawn at regular intervals from a solution of the same strength as that used in the second set of experiments kept at 30°, and the amount of iodine liberated thereby was ascertained.

A comparison of the two sets of observations shows that only a portion of the oxidising gases is removed by the passage of the air.

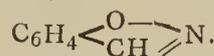
Hours after mixing.	Mass of iodine liberated.	Hours after mixing.	Mass of iodine liberated.
0.5	0.012	35.0	0.042
1.0	0.017	40.0	0.048
1.5	0.018	44.5	0.045
2.0	0.022	45.0	0.040
2.5	0.026	45.5	0.040
3.0	0.022	50.0	0.039
3.5	0.024	53.5	0.030
4.0	0.028	54.0	0.033
4.5	0.026	65.0	0.030
5.0	0.029	65.5	0.032
5.5	0.024	66.0	0.030
6.0	0.029	66.5	0.031
6.5	0.028	70.0	0.032
24	0.042	90.0	0.033

Hours after mixing.	Iodine liberated.	Hours after mixing.	Iodine liberated.
1	0.0021	24	0.0031
2	0.0022	28	0.0036
3	0.0024	29	0.0036
4	0.0022	31	0.0041
5	0.0023	32	0.0041
6	0.0024	46	0.0055
7	0.0029	47	0.0054
8	0.0033	76	0.0045
22	0.0032	77	0.0045
23	0.0031	94	0.0047

Observations are referred to showing that a solution—such as was used in these experiments—which, after exposure during forty-six hours in subdued light, liberated iodine to the extent of 0.0055 gm. per 10 c.c., after exposure at a window to bright sunlight during thirty minutes, liberated only 0.0038 gm. per 10 c.c.; after one hour's exposure the amount liberated had fallen to 0.0023, but no further reduction took place after three hours and a half's exposure. On removal into subdued light, the iodine-liberating power increased, being 0.0035 after four hours, and rising to 0.0048 after twenty hours in the dark. As solutions of the oxides of chlorine lose in oxidising power on exposure to light, the change observed in the chlorate solution is probably due to their destruction.

72. "The Formation of Indoxazen Derivatives." By WM. A. BONE, Ph.D.

The author has investigated the behaviour of orthochloronitrobenzaloxime towards alkalis with a view to isolating nitrindoxazen,—



Orthochlorobenzal chloride was converted by the action of fuming sulphuric acid into the corresponding aldehyd, which was then nitrated, and the nitrated aldehyd was converted into the hydroxime; on subjecting this to the action of caustic potash at 130°, ammonia was evolved, and hydrogen chloride was split off. On acidifying the solution, a white precipitate was thrown down, which, after re-crystallisation, melted at 222°; it possessed acid properties, and gave a red colour with ferric chloride solution. Analysis of the silver salt showed it to be 1:2:5-nitrosalicylic acid.

The hydroxime was then heated at 120° with a solution of sodium carbonate; hydrogen chloride was split off, but no ammonia was evolved. On acidifying the liquid, beautiful yellow needles appeared, melting at 189°.

The properties of the product (especially the facts that it gave a red colour with ferric chloride, and on heating with caustic potash yielded 1:2:5-nitrosalicylic) pointed to the conclusion that it was 1:2:5-nitrosalicylonitril, isomeric with nitrindoxazen, a molecular change having occurred during the interaction. In order to decide the question, the hitherto unknown nitriles of 1:2:5-nitrosalicylic acid were investigated. Several attempts were

unsuccessfully made to prepare these by well-known interactions; at last, by heating salicylaldehyde with acetic anhydride, and subsequently hydrolysing with dilute caustic potash, an almost quantitative yield of salicylonitril was obtained.

On nitrating salicylonitril with fuming nitric acid, the 1 : 2 : 3 : 5-dinitronitril was obtained crystallised in yellow plates, melting at 175°; unlike other members of the salicylic series, it gave no colouration with ferric chloride.

On using ordinary nitric acid, and conducting the nitration below 0°, the 1 : 2 : 5-mononitronitril was obtained. This crystallises in long pale yellow needles melting at 190°; it gave a red colouration with ferric chloride, and was found to be identical with the product obtained from orthochloronitrobenzaldehyde and sodium carbonate.

Derivatives of these nitriles were prepared and studied, notably their amidoximes. That of the mononitronitril is a weak base; its hydrochloride crystallises in yellow tablets melting at 215°. That of the dinitronitril is a neutral substance, crystallising in orange tablets melting at 204°.

The author, finally, attempted to prepare nitromethylindoxazen. Indoxazen itself is evidently exceedingly unstable, but it was thought that a methyl derivative would be more stable, and it seemed likely that orthochloronitroacetophenone would yield nitromethylindoxazen.

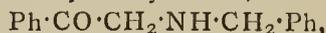
The hitherto unknown orthochloroacetophenone was prepared by the action of orthochlorobenzoyl chloride on ethylic acetosodacetate, and subsequently hydrolysing the product. All attempts to prepare orthochloronitroacetophenone from this failed, however, owing to the fact that nitration was accompanied by simultaneous oxidation.

Orthochloroacetophenone is a colourless oil which boils at 235—240°.

Orthochloronitroacetophenone was prepared by the action of orthochloronitrobenzoyl chloride on ethylic acetosodacetate, and subsequently hydrolysing the product. It is a very thick syrup, becoming crystalline on standing. The author was unsuccessful in preparing the hydroxime from this, although experiments were made under various conditions (at ordinary temperatures, at 100°, and under pressure at 130°); in all cases the ketone was unaltered, owing, probably, to the very negative character of the C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)Cl group.

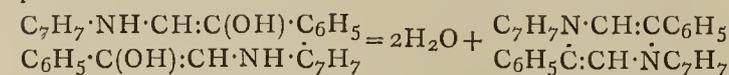
73. "The Interaction of Benzylamine and Phenacyl Bromide. Synthesis of Piazine Derivatives." By ARTHUR T. MASON, Ph.D., and GOODLATTE WINDER, Ph.D.

Phenacyl bromide and benzylamine easily interact, forming monophenacylbenzylamine,—

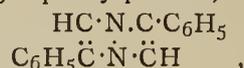


and diphenacylbenzylamine, (Ph·CO·CH<sub>2</sub>)<sub>2</sub>N·CH<sub>2</sub>·Ph.

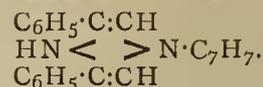
These compounds were isolated in the form of hydrobromides, as on setting the bases free molecular changes take place; in the case of monophenacylbenzoylamine, 2 molecules combine to form 1 : 4-dibenzyl-2 : 5-diphenylpiazine dihydride, the condensation being analogous to that which takes place in the case of isoamidoacetophenone:—



On heating the dihydride to the boiling-point toluene is eliminated and 2 : 5-diphenylpiazine,—

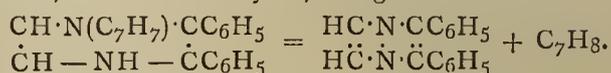


is formed, the product being identical with that from isoamidoacetophenone (*Ber.*, xxi., 1269). When diphenacylbenzylamine is set free it is probably converted into an oxazine derivative. Cold alcoholic ammonia converts the hydrobromide of diphenacylbenzylamine quantitatively into an amide, (C<sub>6</sub>H<sub>5</sub>·C(OH)·CH)<sub>2</sub>N·C<sub>7</sub>H<sub>7</sub>, which, at 100°, loses one molecule of water, 2 : 6-diphenyl-4-benzylpiazine dihydride being formed,—

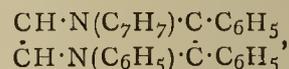


The same condensation occurs on warming the amide with dilute chlorhydric acid, the hydrochloride of the dihydride being formed.

When further heated, the hydride, as well as its hydrochloride, yields 2 : 6-diphenylpiazine, toluene, or benzyl chloride, as the case may be, being eliminated.



Aniline and benzylamine act on diphenacylbenzylamine hydrobromide, forming the dihydride,—



and 1 : 4-dibenzyl-2 : 6-diphenylpiazine dihydride.

On heating the latter compound with concentrated chlorhydric acid at 170°, two atoms of hydrogen are eliminated; the product is devoid of basic properties and unaltered by benzoyl chloride and acetic anhydride, and is probably 2 : 6-diphenyl-3 : 5-dibenzylpiazine. If, however, 1 : 4-dibenzyl-2 : 6-diphenylpiazine dihydride be heated alone at 260—270°, toluene is eliminated, and the remaining benzyl radicle probably "wanders" from nitrogen to carbon, 2 : 6-diphenyl-3-benzylpiazine being found.

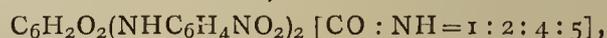
These transformations are comparable with those occurring when toluidine and xylydine are formed by heating the hydrochlorides of monomethyl- and dimethyl-aniline.

On treating the dihydride with an alcoholic solution of ferric chloride and chlorhydric acid, it yields 2 : 6-diphenyl-4-benzylpiazine dihydride.

74. "The Interaction of Quinones and Metanitrilanilide and Nitroparatoluidine." A Preliminary Note. By JAMES LEICESTER, Ph.D.

The relationship between quinonedianilide and azophenine has been pointed out by O. Fischer and E. Hepp (*Ber.*, 1888, 683), who also prepared fluorindine from the latter compound (*Ber.*, 1890, 2789).

In a previous paper (*Ber.*, 1890, 2793); *Proc. Chem. Soc.*, Abstracts, 1890, 1445) I gave the results of an investigation of the action of orthonitrilanilide and metanitrilanilide on quinone, toluquinone, and naphthaquinone, and showed that in principle the interaction was the same as in the case of aniline and quinone; for example, orthonitrilanilide and quinone combine to form quinonediorthonitrilanilide,—



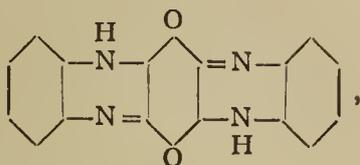
which on reduction with ammonium sulphide yields quinonehomofluorindine.

In addition to the quinonefluorindines, certain quinonephenazine derivatives were obtained; these are formed from the nitro compounds corresponding to quinone-anilide, quinoneorthonitrotoluidide - yielding quinone-orthomethylphenazine. I have now prepared a number of other quinonephenazines and quinonefluorindines; in fact, the interaction appears to be a general one in the case of paraquinones. The constitution of these compounds may be inferred partly from the manner in which they are formed and partly from their similarity in properties to the corresponding fluorindines. A number of crystalline compounds have also been obtained by the reduction of the anilides and toluides with magnesium; the products are, however, of a somewhat complex nature and their further investigation is proceeding.

Quinonedimetanitrilanilide is prepared by heating a solution of quinone and metanitrilaniline in glacial acetic acid; it crystallises from a mixture of methyl alcohol and benzene, and melts at 295°.

Quinonemetanitrilanilide is obtained together with the dianilide as a bronze-coloured powder melting at 135°.

Quinonemetahomofluorindine,—

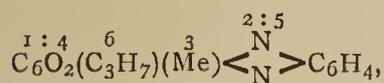


is formed by the reduction of the dianilide with ammonium sulphide; it is a brownish black powder melting above 360°. It affords a brown colour with acetic acid, changes to slaty green, and finally to mauve, on the gradual addition of sulphuric acid.

Quinoneparanitrotoluide is obtained in a similar manner as a bluish black crystalline powder; on reduction with ammonium sulphide it yields a slate-coloured compound which decomposes at about 300°.

Quinonediparanitrotoluide is a bronze-coloured substance; on reduction it yields a substance which melts at 320°, and dissolves in alcohol, benzene, or acetic acid, forming a dark greenish yellow coloured liquid, exhibiting a green fluorescence.

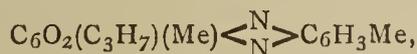
Thymoquinodiorthonitranilide, from thymoquinone and orthonitraniline, crystallises from alcohol and ether in straw-coloured needles melting at 125°. The phenazine,—



derived from it, forms grey needles melting at about 320°.

Thimoquinodiparanitrotoluide is deposited from absolute alcohol in yellowish red plates melting at 112°; it also crystallises in needles.

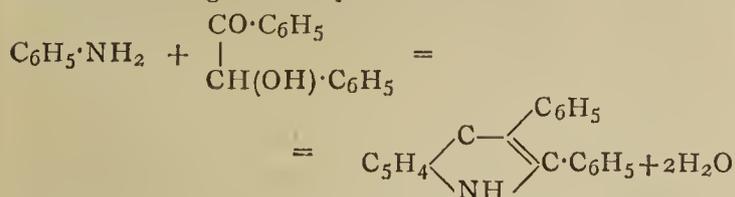
Thymoquinorthomethylphenazine,



is a greyish white crystalline powder which sublimes at 325°, and dissolves in acetic acid and ether, forming a yellow coloured liquid.

75. "Preparation of  $\alpha$ - $\beta$ -Diphenylindoles from Benzoin and Primary Benzenoid Amines." By R. JAPP, F.R.S., and T. S. MURRAY, D.Sc.

The authors have found that a mixture of benzoin, aniline, and zinc chloride yields E. Fischer's  $\alpha$ - $\beta$ -diphenylindole according to the equation—



By employing in place of aniline, orthotoluidine, paratoluidine,  $\alpha$ -naphthylamine, and  $\beta$ -naphthylamine, they obtained respectively  $\alpha$ - $\beta$ -diphenylorthotoluidole (m. p. 136°),  $\alpha$ - $\beta$ -diphenylparatoluidole (m. p. 153°),  $\alpha$ - $\beta$ -diphenyl- $\alpha$ -naphthindole (m. p. 141°), and  $\alpha$ - $\beta$ -diphenyl- $\beta$ -naphthindole (m. p. 166°).

Their work had proceeded thus far when a paper appeared by Bischler and Fireman (*Ber.*, xxvi., 1336), in which the preparation of these indoles (with the exception of  $\alpha$ - $\beta$ -diphenyl- $\alpha$ -naphthindole) by a different method was described. This method consists in first acting on cold desyl bromide with a primary benzenoid amine so as to obtain a desylanilide, thus,—



and then boiling this compound with an excess of amine, when, according to Bischler and Fireman, it is converted into an indole.

The authors now show :—

1. That the desylanilides described as new by Bischler and Fireman are, in reality, identical with the anilbenzoin series obtained by Voigt (*J. Pr. Chem.*, [2], xxxiv., 2) by

heating benzoin with aniline, paratoluidine, and  $\beta$ -naphthylamine respectively. The constitution assigned to the compounds by Bischler and Fireman, which differs from that given by Voigt, is, however, correct.

2. That these desylanilides, contrary to the statement of Bischler and Fireman, are not converted into indoles by boiling them with amines. In order that this transformation may occur, it is necessary that the hydrochloride or hydrobromide of the amine should also be present. The desylanilides used by these authors were, from the mode of preparation, doubtless contaminated with aniline hydrobromide.

3. That the foregoing indoles, with the exception of  $\alpha$ - $\beta$ -diphenyl- $\beta$ -naphthindole can be most readily obtained by boiling benzoin with a mixture of primary benzenoid amine and its hydrochloride.  $\alpha$ - $\beta$ -Diphenyl- $\beta$ -naphthindole is best prepared by the zinc chloride method.

The authors also find that all these indoles when crystallised from acetone form definite compounds with 1 mol. of acetone ("acetone of crystallisation"). In the case of  $\alpha$ - $\beta$ -diphenyl- $\alpha$ -naphthindole, similar compounds with ethyl methyl ketone and diethyl ketone were prepared.

Research Fund.

A meeting of the Research Fund Committee will be held in December. Fellows desiring grants are requested to make application before December 9th.

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. cxvii., No. 20, November 15, 1893.

Determination of the True Atomic Weight of Hydrogen.—G. Hinrichs.—The author, taking the atomic weight of oxygen as exactly = 16, calculates the value of H as 1.00025.

The "Emetic" of Barium.—E. Maumené.—(French chemists give the name "emetics" to a number of compounds of which the antimony-potassium tartrate is the type). M. Maumené considers that the atomic weight of tartaric acid ought to be raised. The composition of the barium "emetic" ought to be  $\text{C}_8\text{H}_4\text{O}_{10}, \text{SbO}_2, \text{BaO}$ , which would require 2.75 per cent BaO. The analyses of Dumas and Piria do not agree with this formula.

Production of Saccharose during the Germination of Barley.—L. Lindet.—The extracts obtained by the author contain, along with saccharose, reductive sugars, the quantity of which increases in a regular manner from the beginning to the end of germination from 2.72 to 6.28 per cent calculated on the barley. The only substance which decreases progressively during the germination of barley is starch. We cannot but be struck with the relation between the decrease of the starch and the increase of the saccharose. We have here a confirmation of the view of Brown and Morris that under certain circumstances saccharose is produced at the expense of starch.

*Zeitschrift für Analytische Chemie.*

Vol. xxxii., Part 4.

Top-pieces for Distillation.—MM. Greiner and Friedrichs (*Zeit. Angew. Chemie*).—The details of the construction are not given.

Blast for Blow-pipe Work.—W. Hamlet.—From the CHEMICAL NEWS.

**A Test-tube for obtaining Stratified Reactions.**—E. Besemfelder (*Chemiker Zeitung*).—This paper requires the accompanying figure.

**Self-acting Apparatus for Washing Precipitates.**—Konrad Haack (Inaugural Dissertation).—This paper cannot be intelligibly reproduced without the accompanying plate.

**Preparation and Properties of Pure Iodine.**—C. Meinecke (*Chemiker Zeitung*).—This memoir will be inserted in full.

**Separation of Antimony and Arsenic.**—According to Fischer the chlorine compounds of both metals are reduced by ferrous chloride, and the arsenious chloride is volatilised by repeated distillation with 20 per cent hydrochloric acid. This method has been modified by Hufschmidt (*Zeit. Anal. Chemie*, xxiv., 255), who effects the distillation in a current of gaseous hydrochloric acid, and further by A. Classen and R. Ludwig (*Berichte*, xviii., 1112), who use ferrous sulphate or ammonio-ferrous sulphate for the reduction of the chlorides. Whilst in these methods a determination of the antimony can only be effected gravimetrically in the residue from the distillation, the antimony can also be determined volumetrically if, according to the proposal of Gooch and Danner, we effect the reduction of the chlorides with hydriodic acid. In this case the antimony, after the arsenious chloride has been distilled off, is determined according to the usual iodometric method. The excessive hydriodic acid does not interfere.

**Determination of Barium as Sulphate and Separation of the Alkaline Earths.**—F. W. Mar.—From the *American Journal of Science*.

**Separation of Strontium from Lime.**—P. E. Brown.—From the *American Journal of Science*.

**Determination of Barium in Presence of Calcium and Magnesium.**—F. W. Mar.—From the *American Journal of Science*.

**Determination of Antimony and of its State of Oxidation.**—F. A. Gooch and H. W. Gruener.—From the *American Journal of Science*.

**Colour Reactions of certain Aromatic Trioxy-compounds.**—J. Stahl (*Pharm. Centralhalle*).—Already inserted.

## MEETINGS FOR THE WEEK.

MONDAY, 4th.—Society of Arts, 8. (Cantor Lectures). "The Art of Book and Newspaper Illustration," by Henry Blackburn.

— Society of Chemical Industry, 8. "Application of Air in Motion to Chemical Industry, by H. G. Watel (Adjourned Discussion). "Note on the Copper Mines of Singhbhoom," by H. Harris. "The Product of the Action of Mercuric Chloride upon Metallic Silver," by Chapman Jones.

WEDNESDAY, 6th.—Society of Arts, 8. "An Artist's View of Chicago and the World's Fair," by Frederic Villiers.

— Society of Public Analysts, 8. "On the Estimation of Beef Stearine in Lard," by W. F. K. Stock. "An Improvement in Richmond's Milk Scale," by Charles E. Cassal and B. H. Gerrans. "Leffman-Beam Method of Fat Estimation in Milk," by H. Droop Richmond and L. K. Bosely. "On Vinegar," by Edward Collens.

THURSDAY, 7th.—Chemical, 8. Ballot for the Election of Fellows. "An Apparatus for the Estimation of Gases Dissolved in Water," by Dr. Truman. "Metallic Oxides and the Periodic Law," by R. M. Deeley.

FRIDAY, 8th.—Physical, 5. "A Potentiometer for Alternating Currents," by J. Swinburne. "The Specific Resistance of Sea-Water," by W. H. Preece, F.R.S. "The Coefficient of Self-Induction of a Circular Current and The Magnetic Field of a Cylindrical Coil," by Prof. G. M. Minchin, M.A.

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## LECTURE NOTES

ON

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FERDINAND G. WIECHMANN, Ph.D.,

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THE CHEMICAL NEWS.

VOL. LXVIII., No. 1776.

INTERACTION OF QUINONES AND ORTHONITRANILINE AND NITROPARATOLUIDINE.\*

By Dr. JAMES LEICESTER, Ph.D., F.C.S.,  
Lecturer on Chemistry and Metallurgy at the Merchant Venturers'  
Technical School, Bristol.

(Concluded from p. 262).

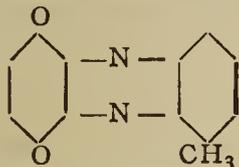
Quinone- $\alpha$ -methylphenazine.

IF mononitrotoluidoquinone be acted on under pressure with alcoholic ammonium sulphide, and the product be boiled with water, a bronze-coloured crystalline powder remains which has an exceedingly high melting-point. It dissolves in hot alcohol with a violet colour. The acetic acid solution is greenish blue, and on the addition of dilute sulphuric acid exhibits a red fluorescence.

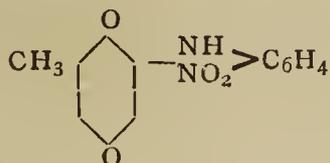
On analysis it gave the following results:—

	Found.	Theory.
C .. ..	69.2 p.c.	69.6 p.c.
H .. ..	4.2 ,,	3.6 ,,
N .. ..	12.8 ,,	12.5 ,,

The substance is quinone- $\alpha$ -methylphenazine—

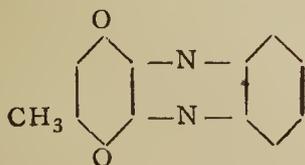


Toluquinone and *o*-nitraniline give in the same way nitranilidotoluquinone—



With alcoholic aminonium sulphide red crystals are obtained which dissolve in acetic acid with a green colour. On the addition of sulphuric acid the solution exhibits a red fluorescence.

This substance is probably quinonephenolazine—

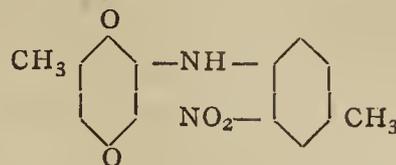


	Found.	Theory, C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub> .
C .. ..	69.2 p.c.	69.6 p.c.
H .. ..	4.4 ,,	3.6 ,,
N .. ..	12.9 ,,	12.5 ,,

By the action of toluquinone on metanitroparatoluidine in a solution of acetic acid and alcohol crystals are obtained of a brown colour in plates which are very insoluble, and the yield is very poor.

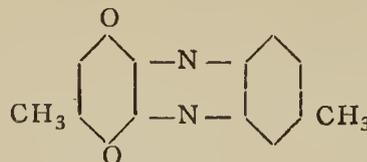
\* Ber. d. Deutsch. Chem. Gesell., xxiii., 2793; Chem. Soc Journ., Abstr., 1890, 1445.

The nitro-derivative is—



	Found.	Theory, C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> .
N .. ..	10.7 p.c.	10.3 p.c.

The reduction product can be obtained from alcohol in red shining crystals which dissolve with a green colour in glacial acetic acid and on the addition of sulphuric acid has a weak red fluorescence and is probably a quinone-tolazine—



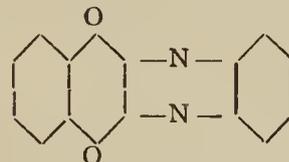
If orthonitraniline be treated with  $\alpha$ -naphthoquinone and glacial acetic acid for four hours at 120°C. and then alcohol added straw-coloured crystals are obtained. These dissolve with an orange colour in hot alcohol and decompose at a high temperature. They yield a brilliant red-coloured powder.

	Found.	Theory, C <sub>16</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> .
N .. ..	10.3 p.c.	9.5 p.c.

From this substance a reduction product of orthonitro-anilidonaphthoquinone has already been obtained which fluoresces and yields a green-coloured powder crystallising from alcohol in green-coloured plates.

The acetic acid and alcoholic solutions are brown and have a green fluorescence.

This substance is probably naphthoquinonephenazine—

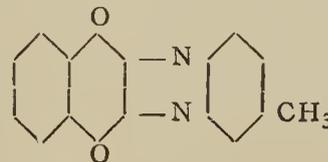


	Found.	Theory, C <sub>16</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub> .
C .. ..	74.4 p.c.	73.1 p.c.
H .. ..	3.9 ,,	3.1 ,,
N .. ..	11.1 ,,	10.7 ,,

Nitrotoluidonaphthoquinone can be prepared in the same way from metanitroparatoluidine and  $\alpha$ -naphthoquinone in a solution of glacial acetic acid. It forms silky orange-red coloured needles. The solution in alcohol is a brownish yellow colour.

	Found.	Theory, C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> .
N .. ..	9.7 p.c.	9.1 p.c.

The reduction product from this is  $\alpha$ -naphthoquinone-tolazine—



an olive-green coloured powder which crystallises from alcohol in steel-blue plates reflecting green light. The acetic acid and alcoholic solutions have a moss-green colour.

	Found.	Theory, C <sub>17</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> .
C .. ..	74.4 p.c.	74.45 p.c.
H .. ..	4.1 ,,	3.6 ,,
N .. ..	9.8 ,,	10.2 ,,

ON THE PHOTOGRAPHY OF THE  
LUMINOUS RAYS OF THE SHORTEST  
WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 263).

A LAYER of gelatin 0.00004 m.m. in thickness. Aluminium and tungsten sparks. Width of slit, 0.020 m.m. Time of exposure, 1, 2 sparks; 1, 2, 4, 8, 16, 32, 96 seconds; for tungsten, three minutes. The most refrangible ultra-violet is absorbed by this extremely thin film to an unexpected degree. Even the most refrangible zinc rays appear rather enfeebled, far more than those of aluminium, and the entire portion of the tungsten spectrum beyond No. 32 is totally absent, even on exposure of several minutes. Nothing can give a better idea of the resistance which the most refrangible rays encounter, even in so thin a stratum, than the behaviour of the line No. 32. Whilst without gelatin its earliest traces appear even after exposure of one second, with gelatin it does not become visible until after four seconds. The same intensity which it acquires in eight seconds requires, if gelatin is present, three or four times the length of exposure. After an exposure of thirty-two seconds, it is more intense than after ninety-six seconds with the use of gelatin.

If we collate these results, we see that gelatin absorbs the ultra-violet up to the cadmium line No. 18 very slightly, beyond this line more strongly, but beyond the line No. 24 to such an extent that here a film of gelatin not exceeding the tenth part of the thickness of the coating of an ordinary dry plate keeps back entirely all the rays, and that even the fiftieth part of this stratum weakens the most refrangible rays (185.2) down to one-third of their original photographic energy. At the same time, we must remember that this result was obtained with gelatin plates; consequently, under the repressing influence of the same absorbent, the transparency of which has to be ascertained, how much greater would not the absorption have appeared if plates free from gelatin could have come into use?

If we wish to procure a clear conception of the resistance which gelatin opposes to the most refrangible rays in the photographic plate, we must consider more closely the relation between the thickness of the coating of the plate, the particles of silver bromide, and the gelatin films employed.

The granular silver bromide which chiefly forms the sensitive constituent of all gelatin dry plates, consists of small globular granules which, *e.g.*, in my emulsions must, according to my measurements, continued for many years, have a diameter of 0.0012 to 0.0017. These granules are very uniformly distributed in the coating of the plates. If we suppose this coating resolved into strata of the thickness of such a granule running parallel with the surface of the plate, a single stratum suffices to absorb nearly all the rays which are more strongly deflected than the line No. 24. It is here assumed only that the granules of silver bromide are not more transparent than their connecting medium—the gelatin. This assumption is so far justified, as both the mode of origin of the silver bromide in the gelatin emulsion and its general behaviour have shown that the granule is not merely embedded in the gelatin, but pervaded by it. But it appears from this exposition that the purely photochemical effect is restricted to the upper strata of the coating of the plate, and that the number of the layers decreases also with the wave length of the rays concerned. If this is the case, the relations are exactly as with plates having a very thin coating of emulsion, which always gives inexpressive pale and mostly useless proofs.

All circumstances show that the want of intensity and

sensitiveness which the gelatin plate always shows in proofs of the most refrangible ultra-violet, and the sudden decrease of both beyond the cadmium line No. 24, depend to a considerable extent upon the insufficient permeability of the gelatin.

(To be continued).

THE PREPARATION OF PURE IODINE AND  
SOME OF ITS PROPERTIES.

By O. MEINECKE.

PERFECTLY pure iodine, in which foreign constituents can no longer be detected, may be obtained by precipitating a concentrated solution of iodine in potassium iodide with water, or by precipitation with sulphuric acid from a solution containing potassium iodide and iodine. For proceeding according to the first method, a solution of potassium iodide in two parts of water is saturated with powdered iodine, and water is then added until a small portion of the iodine is deposited. After twenty-four hours it is decanted, and water again added to the clear solution. The precipitates are thoroughly washed and dried over calcium nitrate.

For the second method, a solution containing 25 grms. potassium iodate and the same weight of potassium iodide was directly precipitated with dilute sulphuric acid; the precipitate is washed until the filtrate ceases to react with sulphuric acid, and dried over sulphuric acid.

The iodine obtained according to each method is sublimed twice with, and twice without, barium oxide.

The second method yields a pure product even in presence of bromine, chlorine, and cyanogen; whilst in the first method, to avoid contamination with cyanogen, it is advantageous to add a little hydrochloric or sulphuric acid.

For working up solutions containing iodine residues (including titration residues), the author acidifies and oxidises with potassium permanganate, until brown manganese peroxide is deposited, which is separated from the iodine by decantation. After washing, it is further purified as above directed.

Further experiments of the author's relate to the purification of impure iodine. The first method, sublimation with potassium iodide, yields a pure product at once if the impurities are small. If the quantities of foreign matter are larger, the sublimation must be repeated, and the purity of the iodine obtained must always be ascertained analytically. In any case the iodine must be finally sublimed without addition.

Musset's process consists in bringing the iodide to melt in a concentrated solution of potassium iodide, from which latter product it must be separated by repeated sublimation.

Instead of the solution of potassium, Meinecke uses a solution of calcium chloride of specific gravity 1.37, adding to this liquid a few grms. of potassium iodide and a little hydrochloric acid, so that the liquid has a brown colour. The mixture is heated to the melting-point of iodine, and kept at this heat for five minutes. The iodine is washed out and sublimed once alone and once with barium oxide, when it is nearly pure. The removal of cyanogen is complete, that of bromine and chlorine less so. The quantity of the latter is so slight that a single sublimation suffices for its entire removal.

The author has made careful experiments on the hygroscopic character of iodine. Freshly sublimed iodine was placed, whilst still hot, in tightly fitting glass jars, and preserved for use over sulphuric acid. This perfectly dry preparation served both for standardising by means of sodium thiosulphate and for experiments on the moisture of portions exposed to the air, or preserved in artificially moist atmospheres. During some hours no change from absorption of moisture was perceptible, and during five days the

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

proportion of water increased only by 0.06 per cent. Even pulverised iodine, under the most favourable circumstances, takes up at most 0.1 per cent. Specimens kept for four months over sulphuric acid, and opened once or twice every week, showed no change. The author therefore recommends this method of preservation. The author, with Topf, refers the smeary condition of iodine to contamination with dust.

For determining the moisture in iodine, the author superstratifies a weighed quantity of iodine in a glass tube (which is closed with a glass stopper) with a weighed quantity of silver powder, four to five times the weight of the iodine, and weighs again. If a rise of temperature occurs, owing to the reaction of the two elements, the weighing is deferred until complete cooling. The tube is then placed in a small beaker standing on an asbestos plate, which is heated moderately, so that the formation of silver iodide takes place gradually. The upper stratum of silver must remain unchanged.

During the absorption of the iodine, the water condenses in the upper part of the tube, whence it is driven off by a stronger heat. When the tube is perfectly cold it is weighed again, when the water is found as loss.—*Zeit. f. Analytische Chemie*, xxxii., p. 462.

### BORON BRONZE.

By H. N. WARREN, Research Analyst.

THIS alloy, or more correctly speaking, aluminium-boron bronze, is brought about by the introduction of aluminium containing boron, not as aluminium boride, but existing as graphite does in cast iron. Commercially, this part of the process is accomplished by heating in a specially constructed oxyhydrogen furnace an admixture of fluorspar and vitrified boric anhydride, until the dense fumes of boron fluoride commence to appear. At this stage, ingots of aluminium are introduced into the liquid mass; reduction at once takes place with the formation of free boron, which dissolves in the aluminium, rendering it crystalline and somewhat brittle. When this so-prepared aluminium is alloyed with copper to the extent of from 5 to 10 per cent, a bronze is obtained, denser and more durable than ordinary aluminium bronze, and free from brittleness; but the most peculiar property is the perfectness with which it casts and melts; whereas, in the manufacture of aluminium bronze, one of the greatest difficulties is to ensure an uniform mixture. Often a very difficultly fusible alloy of copper and aluminium is formed upon the surface of the already melted portion, and accompanied by superficial oxidation, thus obstinately refusing to alloy with the remainder. But in the case of the boron compound no such difficulties are met with, the alloy melting perfectly, and at lower temperature than when employing pure aluminium. Boron, in fact, seems to have been little studied, but it is evidently not so serious an enemy to cope with as its halogen silicon, which, when present in minute percentages only, determines the total ruin of the bronze with which it alloys; in other words, it stands almost entirely opposite to other elements, entering into the formation, and forming compounds with the more refractory metals with the greatest ease; for instance, borides of iron, manganese, nickel, cobalt, &c., may be readily formed by the reduction of their accompanying borates in the presence of carbon, whilst those of silver, copper, gold, &c., can only be formed by the introduction of elementary boron into the fused mass; borides of the alkali metals, and even calcium, barium, &c., have also been obtained, but boride of mercury still holds out.

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

**Sophistication of Wax.**—According to a consular report quoted in the *Chemiker Zeitung*, paraffin is extensively used in Morocco for the sophistication of bees' wax.

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

Ordinary Meeting, November 16th, 1893.

Dr. ARMSTRONG, President, in the Chair.

MESSRS. J. H. Coste, R. C. T. Evans, and C. A. Mitchell were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. David Anderson, 14, St. Julian's Road, Kilburn, N.W.; William Edward Bamber, Spring Lawn, Heaton, Bolton; William Rowland Bird, 73, Albion Street, New Swindon, Wilts; Chuni Lal Bose, 24, Mohendro Bose's Lane, Calcutta; John Cannell Cain, Stubbins Villa, Stubbins, near Manchester; F. D. Chattaway, St. Bartholomew's Hospital, E.C.; Samuel Henry Davies, Dalton Hall, Manchester; John Duncan, M.D., St. Petersburg, Russia; Frank Evershed, Kenley, Surrey; George Trench, Standard House, Faversham; Ernest William Gay, 14, St. Julian's Road, Kilburn, N.W.; Edward Frank Harrison, 17, Bloomsbury Square, W.C.; Edmond Herbert Hills, Darland House, Chatham; John Winder Holmes, 28, Crooms Hill, Greenwich; David Hamilton Jackson, M.A., B.Sc., Royal College of Science, South Kensington; George F. Gaubert, Ph.D., Anilin Fabrik, Ludwigshafen am Rh.; Robert Leonard Jenks, 68, Victoria Road, Clapham, S.W.; A. Lapworth, 13, Duchess Road, Birmingham; Godfrey Melland, Victoria Park, Manchester; J. M. Murray, B.Sc., Highfield, Holmes Chapel, Cheshire; Richard Paulusz, Colombo; William Henry Pearson, 5, Bryn Villas, Blaina, Monmouth; J. Holms Pollock, 37, Athole Gardens, Glasgow; Meredith Young, M.B., C.M., Brighouse, Yorks.

The following is the text of a letter addressed by the President to Professor Mendeleeff, the President of the Russian Chemical Society, St. Petersburg:—

"Learning that the Society over which you preside will celebrate its 25th Anniversary on the 18th of this month, I beg, on behalf of the Chemical Society of London, to tender our most hearty congratulations and our good wishes for the future.

"Notwithstanding the grave difficulties which your language imposes, your English colleagues learn from time to time of your labours, the name of your Society and a record of its work regularly appearing in our volume of abstracts of chemical papers. We are thus frequently brought face to face with researches of the greatest interest and importance, and the wish that we could enjoy less restricted intercourse with our Russian colleagues is often felt among us. We look forward to the time when this wish will be gratified, and trust that it may not be far distant.

"Our Society is proud to have enrolled your name on its lists of foreign members, and to have welcomed you as one of its Faraday Lecturers; and the roll also includes the name of Beilstein, which, however, is no longer the mere name of an individual, but a household word throughout the chemical world, and one which cannot be mentioned without the feeling of gratitude arising in the chemist's mind. There are many other names of Russian chemists indelibly associated in our memories with discoveries of fundamental importance."

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

\*76. "*The Normal Butylic, Heptylic, and Octylic Ethereal Salts of Active Glyceric Acid.*" By PERCY FRANKLAND, Ph.D., B.Sc., F.R.S., and JOHN MACGREGOR, M.A.

The authors have previously described the preparation and properties of the methylic, ethylic, propylic, isopropylic, normal, secondary, and isobutylic salts of both inactive and active glyceric acids, and have shown that in ascending the homologous series of salts of active glyceric

acid the rotatory power increases with the molecular weight, but that the rotation of the normal butylic compound is considerably less than this general relationship indicated it should be. In order to ascertain whether the increase in rotatory power continues indefinitely as the molecular weight increases, they have now prepared and examined the heptylic and octylic salts, and have also again prepared the normal butylic salt, which they had not before obtained in a state of purity. As will be seen from the subsequent Table, the results show that the rotatory power does not increase indefinitely as the homologous series is ascended, but that a maximum rotation is reached apparently at the butylic compound in the case of the normal series, the specific rotation of the heptylic being less, and that of the octylic still less than that of the normal butyl compound.

Such a maximum rotation in a homologous series has been predicted by Guye from a consideration of the successive values of the product of asymmetry, but the calculated maximum, as will be seen from the Table, falls on the propylic instead of on the butylic compound. In the case of the salts containing secondary radicles, of which, however, only the isopropylic and secondary butylic compounds have been examined, the maximum rotation is actually exhibited by the propylic compound as predicted by calculation.

Ethereal salt.	Density, 15°/15°.	Observed rotation in 198.4 m.m. tube. ( $\alpha$ ) <sub>D</sub> .	Specific rotation. [ $\alpha$ ] <sub>D</sub> .	Molecular rotation. [M] <sub>D</sub> .	Molecular deviation. [ $\delta$ ] <sub>D</sub> .	Product of asymmetry. (P × 10 <sup>6</sup> ).
Methylic..	1.2798	-12.2°	-4.80°	-5.76	-27.9	288.8
Ethylic ..	1.1921	21.7	9.18	12.30	52.8	344.8
Propylic ..	1.1448	29.4	12.94	19.15	74.9	358.2
Isopropylic	1.1303	26.5	11.82	17.49	67.8	358.2
Butylic						
(norm.)	1.1084	29.0	13.19	21.37	77.0	346.8
Isobutylic	1.1051	31.2	14.23	23.05	82.9	346.8
Butylic						
(sec.)	1.1052	23.2	10.58	17.14	61.7	346.8
Heptylic..	1.0390	23.3	11.30	23.05	68.3	268.7
Octylic ..	1.0263	20.8	10.22	22.28	62.6	241.8

\*77. "The Ethereal Salts of Diacetylgeric Acid in Relation to the Connection between Optical Activity and Chemical Constitution." By PERCY FRANKLAND, Ph.D., B.Sc., F.R.S., and JOHN MACGREGOR, M.A.

The methylic, ethylic, propylic, isopropylic, and isobutylic salts of active diacetylgeric acid were prepared by heating the corresponding salts of active glyceric acid with an excess of acetyl chloride, and then fractionally distilling *in vacuo*. These compounds are colourless, almost inodorous liquids, volatilising without decomposition even under ordinary atmospheric pressure at between 200° and 300°. The special interest attaching to them consists in the circumstance that, both in the methylic and ethylic compounds respectively, two of the groups attached to the asymmetric carbon atom are of equal mass, and, therefore, according to Guye's theory, these two compounds should be inactive, or nearly so, or at any rate some of the members of this series should exhibit a rotation of opposite sign to that exhibited by the glycerates. As will be seen from the Table, some of these anticipations are realised, the sign throughout being similar to that of the ethereal salts of glyceric acid, the increase in rotation on ascending the series of diacetylgerates proceeding on lines almost parallel to those followed in ascending the glycerate series, the diacetylgerates only starting from a higher level of rotation, so to speak. The authors consequently again urge the necessity of also taking into consideration the qualitative nature of the groups attached to the asymmetric carbon atom, and not their masses only.

	Density, 15°/15°.	Observed rotation at 15° C. in 198.4 m.m. tube. ( $\alpha$ ) <sub>D</sub> .	Specific rotation. [ $\alpha$ ] <sub>D</sub> .	Molecular rotation. [M] <sub>D</sub> .	Molecular deviation. [ $\delta$ ] <sub>D</sub> .	Products of asymmetry. (P × 10 <sup>6</sup> ).
Ethereal salt.						
Methylic..	1.1998	-28.65°	-12.04°	-24.56°	-80.0	0.0
Ethylic ..	1.1574	37.46	16.31	35.56	108.2	0.0
Propylic ..	1.1263	43.52	19.47	45.17	129.5	17.4
Isopropylic	1.1193	39.90	17.97	41.69	119.1	17.4
Isobutylic	1.0990	44.66	20.48	50.38	136.7	41.9

## DISCUSSION.

Mr. L. M. JONES observed that inasmuch as the product of dissymmetry employed presupposes the equality of the distances of the centres of gravity of the combined groups from the central carbon atom, it can only give an approximate indication of where the maximum "molecular deviations" will be found. In the case of the diacetylgerates, as the salts which have this product = 0 show marked activity, we should expect considerable divergence between the observed and predicted maxima.

Mr. RODGER drew special attention to the fact that the "molecular deviation,"—

$$\frac{\alpha}{l} \times \sqrt[3]{\frac{M}{d}},$$

employed by Guye in a recent communication, was probably the true value of the molecular rotatory power.  $\frac{\alpha}{l}$  is evidently the angle of rotation produced by unit length of substance.

$$\sqrt[3]{\frac{M}{d}}$$

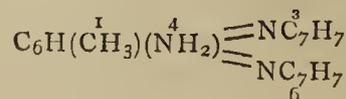
is the molecular length or a length which for different substances contains the same number of molecules, and the "molecular deviation" is, therefore, proportional to the angle of rotation produced by the same number of molecules or to the rotation per molecule. The dimensions of this quantity are those of an angle,—the physical magnitude actually measured,—whereas the ordinary measure of molecular rotation,—

$$\frac{\alpha}{l} \times \frac{M}{d},$$

is an angle multiplied by a surface. He also pointed out that the effect of temperature on rotatory power had been little studied. Such experiments as had been made indicated, however, that the temperature change varied with the chemical nature of the substance, and hence that relationships obtained at the same temperature, according to the usual custom, would no longer be the same if the temperature of comparison were altered. For these reasons the significant speculations of Guye could only be subjected to a fair test when "molecular deviations" had been measured at temperatures at which, as regards the property under consideration, the substances were in comparable states.

\*78. "The Oxidation of Paratoluidine." By ARTHUR G. GREEN.

The red crystalline substance obtained by Barsilowsky in 1873 by oxidising paratoluidine with potassium ferrocyanide has been variously considered as a polymeric paratoluene, as a tritoluylene-diamine, and a complex amidoazo-compound. The author has re-examined this remarkable substance. He arrives at the conclusion that the substance is a diparatolyimide represented by the formula—



derived from amidotoluquinone. This conclusion is deduced from the following facts. The base has the empirical composition  $C_7H_7N$ , and its molecular weight corresponds to the formula  $C_{21}H_{21}N_3$ . By treatment with chlorhydric acid it is readily decomposed, one paratoluidine residue being split off and a second being removed by further treatment of the intermediate product. On reduction, it takes up 2 atoms of hydrogen, affording a stable, colourless leuco-base. This latter is readily re-oxidised to the original substance, has very slight basic properties, and is not decomposed by acids or further reduced by boiling with stannous chloride. The leuco-base condenses readily with benzil, forming a coloured azonium compound; and it yields colourless, non-oxidisable anhydro-compounds with formic and acetic acids, thus showing all the characteristics of a mono-substituted orthodiamine. This result, taken in conjunction with the presence of two paratolyimide groups in the original substance, as shown by its decomposition by acids, proves that the leuco-base is a diparatolytriamidotoluene. Of the three possible formulæ for this compound the greatest probability attaches to that in which the two tolylamido-groups are relatively in the para-position. This formula would represent the leuco-base as an amido-derivative of diparatolyparatolylenediamine. The diparatolyparatolylenediamine was accordingly prepared by heating hydrotoluquinone with paratoluidine and zinc chloride and submitted to comparison with the leuco-base. A marked similarity in appearance and properties was observable, entirely in accordance with the view that the latter is the amido-derivative of the former. Moreover, the diparatolyparatolylenediamine was converted by oxidation into toluquinonediparatolyldiamine, and this substance showed a striking similarity in its appearance and in all its properties to Barsilowsky's base. There could, therefore, be little doubt that the tolylamido-groups in the leuco-base and the tolyl-imido-groups in the original compound occupy the para-position to each other, and that consequently the constitution of the Barsilowsky base is that given above, whilst its leuco-compound must be represented by the formula—



In agreement with this conclusion, the synthesis of Barsilowsky's base was effected by oxidation of a mixture of orthamidometaparaditolyamine and paratoluidine in acetic acid solution, whilst its lower homologue was prepared in a similar manner from orthamidometaparaditolyamine and aniline.

\*79. "The Action of Benzoic Chloride on Urine in presence of Alkali. Formation of Benzoic Derivatives of Urochrome." By J. L. W. THUDICHUM, M.D., F.R.C.P.

The author has examined the products of the action of benzoic chloride on urine in the presence of alkali. The urine rendered strongly alkaline with soda, and filtered from the precipitated phosphates, is mixed with benzoic chloride in the proportion of 50 c.c. for each litre of urine used. The mixture is kept cool and constantly agitated, care being taken to maintain a strong alkaline reaction. A yellowish white, semi-solid precipitate separates, which by extraction with alcohol may be separated into three parts: (1) an oily substance soluble in cold alcohol, (2) a solid soluble in hot alcohol, (3) a small quantity of a solid insoluble in boiling alcohol, which was not further examined. The oil and the solid substances are considered to be mixtures of various benzoic derivatives of urochrome, the normal colouring matter of urine, and of alcoholic compounds present in the urine. The mixed solid derivatives of urochrome contain between 58.9 and 63.2 per cent of carbon, 5 per cent of hydrogen, and between 3 and 1.5 per cent of nitrogen, from which the author concludes that they are mixtures of polybenzoic derivatives, as he found 12 per cent of nitrogen in urochrome.

The solid benzoic derivatives may be most readily crystallised by dissolving the original precipitate in boiling absolute alcohol, filtering the hot liquid, and eva-

porating until crystallisation begins. By fractionally crystallising the resulting mass from hot alcohol, the author separated it into three portions: (1) a crystalline solid not dissolved by boiling spirit ("insoluble ester"), (2) crystalline needles soluble in boiling spirit ("needle ester"), (3) laminæ resembling cholesterol in appearance soluble in cold spirit ("cholesteroid ester"). The mother-liquor contains for the most part the oily benzoic derivatives of urochrome.

By the action of benzoic chloride on an aqueous solution of urochrome (prepared by the ferric chloride method), solid benzoic derivatives were obtained containing 1.77 per cent of nitrogen. The same result may be secured by precipitating urine with phosphotungstic acid, regenerating by means of baryta, and extracting the residue with alcohol. The alcoholic solution, when mixed with mercuric chloride, furnishes a precipitate containing the urochrome and other bases. If this precipitate be decomposed with hydrogen sulphide, an acid liquid is obtained which, when acted on with benzoic chloride and soda, affords a precipitate of the benzoic derivatives of urochrome. Similarly, if the precipitate obtained by adding phosphotungstic or phosphomolybdic acid to acidified urine be dissolved in soda and the solution be mixed with benzoic chloride, the same derivatives of urochrome are precipitated. From this behaviour the author concludes that urochrome is at once an alcohol and a base.

The benzoic derivatives of urochrome are hydrolysed by strong alkali, but the liberated urochrome is, to some extent, decomposed, especially if the liquid be heated. Some, however, may be recovered by acidulating the strong alkaline solution with dilute sulphuric acid and precipitating with phosphotungstic acid and decomposing the precipitate with barium carbonate in the usual manner. When the derivatives are hydrolysed by heating with dilute sulphuric acid, much of the liberated urochrome suffers decomposition, producing the substance called by the author *uropittin*, as well as other urochrome "resins" (*uromelanin* and *omicholin*). Neither urochrome nor its black decomposition product, uromelanin, are carbohydrates. Both contain nitrogen.

The "cholesteroid" benzoic derivative obtained from urine furnished on combustion results agreeing with the formula  $C_{13}H_{12}O_8$ . When hydrolysed with dilute sulphuric acid, it yields about 50 per cent of benzoic acid, together with a resinous substance. It contained only a trace of nitrogen, and is probably the derivative of an alcohol. The author obtained no benzoic derivative of any substance in the nature of a sugar (*cf.* Wedenski, *Zeit. physiol. Chem.*, xiii., 122).

80. "The Combination of Hydrocarbons with Picric Acid and other Nitro-compounds." By WILLIAM A. TILDEN and MARTIN O. FORSTER.

The authors have instituted a compound described by Lextrait in 1886, which is formed by heating picric acid with pinene. It contains the elements of picric acid and a terpene, but differs from the picrates of other hydrocarbons in forming a peculiar potassium salt, in yielding picramide and borneol when submitted to the action of alcoholic ammonia, and in forming borneol and not simply a hydrocarbon under the influence of aqueous alkalis.

The authors have also instituted experiments on the behaviour of other hydrocarbons with nitro-compounds generally, from which it appears that, in order that a compound may be formed, at least two nitro-groups must be present in the nitro-derivative concerned. They conclude that the oxygen of the nitro-groups affords the link which, in ordinary cases, binds the hydrocarbon to the nitro-compound, while in the case of the pinene derivative the oxygen of the hydroxyl is probably also involved.

81. "The Formation of Pyrrol Derivatives from Aconitic Acid." By S. RUHEMANN, Ph.D., M.A., and F. E. ALLHUSEN, B.A.

The authors find that when the ethereal salt of dibromotricarballylic acid (which they prepared by exposure of a

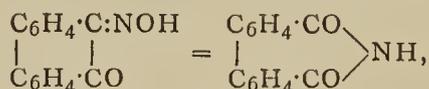
mixture of ethylic aconitate and bromine to direct sunlight) and aniline interact, besides a compound melting at 87—88°, which they regard as ethylic anhydroanilaconitate, an oil is formed which, on heating at 250—260°, yields an isomeric, ethylic phenylpyrrolonedicarboxylate, melting at 181°.

82. "The Conversion of  $\alpha$ -Hydrindonoxime into Hydrocarbostyryl." By F. STANLEY KIPPING, Ph.D., D.Sc.

The peculiar intramolecular change first observed by Beckmann in the case of diphenylacetoxime has been carefully studied by V. Meyer, Hantsch, and others during the last few years, and it has been shown that a great many open-chain hydroximes may be converted into substituted amides in accordance with the equation—



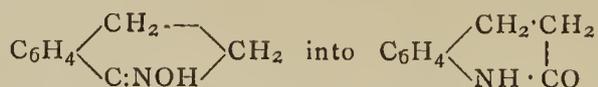
The behaviour of hydroximes of cycloid ketones, however, has been but little investigated. Camphoroxime has been shown to yield campholenonitrile,  $\text{C}_{10}\text{H}_{15}\text{N}$ , and not a substituted amide, as was to be expected from the behaviour of isonitrosocamphor, which yields camphorimide (Angelo, *Ber.*, xxvi., 59; Manasse, *ibid.*, 241), and the only case, in fact, in which the desired change has hitherto been accomplished with the hydroxime of a cycloid ketone of known constitution appears to be that of phenanthraquinonemonoxime, which as Wegerhoff has shown (*Ber.*, 1888, 2355), is readily transformed into diphenimide—



the closed chain of 6 carbon atoms being converted into a closed chain of 7 atoms by the introduction of an imido-group.

These considerations led the author to study the behaviour of hydrindonoxime. On subjecting this to the action of phosphorus pentachloride and water successively, it yielded a small quantity of a crystalline substance melting at 163°, represented by the formula  $\text{C}_9\text{H}_9\text{NO}$  (found C = 73.26; H = 6.32; required C = 73.47; H = 6.12 per cent). As far as could be ascertained without direct comparison, this substance is identical with hydrocarbostyryl.

This change from—



is, to some extent, analogous to the conversion of pyrroline into chloro- or bromo-pyridine, which appears to be one of the few cases on record of the conversion of a ring with 5 into one containing 6 elements, although the reverse operation, namely, the transformation of a ring containing 6 into one containing 5 elements is known, from Zincke's work, to be easily accomplished.

The publication of this note is desirable owing to the appearance of a paper by Wallach in the last number of the *Annalen* (cclxxvii., 154), in which he describes preliminary experiments on the behaviour of hydroximes of cycloid ketones.

83. "The Constitution of Lapachol and its Derivatives. II. The Azines of the Lapachol Group." By SAMUEL C. HOOKER.

The author gives an account of azines of the lapachol group prepared from orthotolylenediamine, and fully discusses the relations existing between lapachol and  $\alpha$ - and  $\beta$ -lapachone and the changes occurring in the quinone group in the course of the transformation of these compounds into each other. The constitution of several of the compounds is discussed in relation to their colour. The compounds described are methyllapazine, methylbromolapazine, methyl-lapeurhodone, methylhydroxy-lapeurhodone, methyl- $\alpha$ -naphtheurhodol, and methyl-chloronaphtheurhodone.

## PHYSICAL SOCIETY.

Ordinary Meeting, November 24th, 1893.

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

COL. MAITLAND, C.B., was elected a member of the Society.

Prof. S. P. Thompson then occupied the chair,

Whilst the PRESIDENT read a paper "On the Magnetic Shielding of Concentric Spherical Shells."

In this mathematical investigation the author considers cases in which the equipotential surfaces are surfaces of revolution about a line through the centre of the shells, and the permeability ( $\mu$ ) of each shell is constant. Taking the common centre as origin, the potential within any shell is expanded in terms of zonal spherical harmonics, and the ratio of the shielded to the unshielded field determined. The following important result is arrived at, viz., if the permeabilities of the enclosed and external space be the same, then the ratios of the shielded to the unshielded fields are the same for each harmonic term, whether the part shielded be external or internal. It is also shown that the shielding effect on external space when a small magnet is placed at the centre of the shell is the same as the shielding effect on the enclosed space when the shells are placed in a uniform magnetic field.

The case of a single shell with a small magnet at the centre is next considered, where the permeabilities of the internal and external spaces are taken as unity. Here the shielding depends on the ratio of the outer to the inner radius ( $a_1/a_0$ ). When the thickness of the shell is 1/100 of  $a$ , the ratio of shielded to unshielded field ( $\Psi/\psi_0$ ) is 3/13 when  $\mu=500$ , and 3/23 when  $\mu=1000$ .

For  $\mu=1000$ , increasing the thickness from  $a_1/10$  to  $a_1/2$  changes the shielding from 1/60 to 1/194, thus showing that after the shell is moderately thick, further increasing the thickness is not very effective. When the small magnet is displaced from the centre of the shell with its axis along a radius, then the shielding effect of the shell is greater on the side towards which the magnet is moved, and less on the opposite side. Thickening a single shell being inefficient, the effect of using two or three shells separated by air gaps is investigated. Here, as in the case of a single shell, the shielding is improved by adding permeable material either within the inner or without the outer shell. If the inner and outer diameters are given then, when the difference in these diameters is small one continuous shell gives the best result. For a larger difference two shells separated by an air gap are much more efficient than a single one, and filling up the air gap would appreciably diminish the screening effect. When the permeability of the substance is high, the best shielding is obtained when the radii of the bounding surfaces of the shells are in geometrical progression. The great value of lamination is shown in the following Table, where the volume of the permeable material is expressed in terms of that of the enclosed space, and the shielding in each case being the best:—

	Volume of material used.	External field.
Single shell.. ..	1.0	0.018
Two shells .. ..	5.0	0.0006
Three ,, .. ..	4.8	0.00016
Single shell.. ..	7.0	0.0102

The conditions for the best arrangement in each of the following cases are fully worked out in the paper, viz.:— Two shells when the largest and smallest radii and the volume of the material used are given; two contiguous shells of different permeabilities; and three shells of different permeabilities.

The main results of the investigation are that with thin

shells lamination is useless, whilst with thick shells it is essential if the best effect is desired. Experiments made on actual shells had fully confirmed the theoretical conclusions.

Prof. MINCHIN said the mathematical results were very simply expressed. Although the work was apparently restricted to zonal spherical harmonics, some of the important formulæ apply equally to general spherical harmonics. Referring to the difficulty of shielding by single thick shells, he pointed out that the equation giving the relation between the shielded and the unshielded fields with different thicknesses of shell represented a hyperbola with its asymptotes parallel to the axes; hence the shielding tended to a definite limit as the thickness increased indefinitely.

Mr. EVERSLED said he had been engaged for the last two years on the subject of magnetic shielding with a view to screening measuring instruments from external fields. In such cases it was not possible to use closed shells, and this introduced trouble. The best result he had yet obtained was to reduce the disturbance to about one-fifth. Another difficulty was introduced by the fact of the shield being magnetised by the current passing through the coil, and owing to hysteresis, the permeability was different according as the magnetisation increased or decreased. By using an outer iron shell a great improvement had been effected. To obtain the best results it was important to have no joints in the shields. A coil frame with two shields of bent iron was exhibited.

Mr. J. SWINBURNE remarked that the subject divided itself into two: shielding instruments and shielding sources. If a dynamo itself be shielded, this did not prevent the currents in the leads producing magnetic disturbances. This was very important in ships. By using an alternator with revolving fields all disturbances could be avoided.

Dr. C. B. BURTON enquired whether by considering the hydro-dynamical analogue of a porous material the case of perforated shells could be elucidated?

Mr. A. P. TROTTER wished to know if the homogeneity of the shield was of much consequence? At Oxford it had been found that a screen of four inches of scrap iron was better than boiler plate.

Mr. BLAKESLEY asked if the effect of moving a magnet sideways in a sphere had been observed? He thought the mathematics developed in the paper would be useful in working out the magnetic theory of the earth.

Prof. S. P. THOMPSON thought that taking the permeability as constant would not be quite correct, for  $\mu$  was a function of the magnetisation. Hence in the cases considered the outer shell would be the more permeable.

In his reply the PRESIDENT said scrap iron in contact was not like clear space, for there were comparatively free paths for the induction at the points of contact. As regards the shielding of the dynamo at Greenwich, Mr. Christie had written to say that the credit was due to the makers of the machine and shields, Messrs. Johnson and Phillips.

Prof. G. M. MINCHIN, M.A., read a paper on "*The Action of Electromagnetic Radiation on Films containing Metallic Powders.*"

After noticing the resemblance of the phenomena exhibited by tubes containing metallic filings shown by Mr. Croft on October 27 to those of photoelectric impulsion cells, he repeated some of the experiments with filings, and found the effects when the filings were of ordinary fineness. He also noticed that the experiments did not succeed either when the filings were very coarse or very fine. Coarse ones always conducted, whilst very fine filings or powders acted as insulators, except when strongly compressed. To establish a closer connection with the impulsion cells, he tried films of gelatin or collodion containing metallic powders. Directions for preparing the films are given in the paper. On inserting such a film in circuit with a battery, key, and galvanometer, it acts as

an insulator. To render a small portion conducting, the electrodes on the surface of the film are brought very close together, and one of the wires touched with an electrified body (an electric gas lighter was often used). This caused a current to pass. The electrodes may then be separated a little further, and the process repeated until any desired portion is rendered conducting. The peculiarity of such a film is that if the circuit be broken at the film, the film becomes an insulator; whereas, breaking the circuit at any other point leaves the film conducting. The action of the spark or charges on the conductivity of the films is attributed to the influence of electric surgings produced in the wires by the electric discharges.

The PRESIDENT read a written communication from Prof. O. J. Lodge, in which the writer suggested that the phenomena of the films, and also of Lord Rayleigh's water-jet experiment (in which water drops are caused to coalesce by the presence of an electrified body), were due to the range of molecular attraction being increased by electric polarisation.

Mr. BLAKESLEY said he had tried Mr. Croft's experiments, and found that conductivity could be established in a tube of filings whilst the circuit was inclosed. Breaking the circuit of a transformer or electromagnet would produce conductivity; hence he concluded that electric surgings were not essential. Another curious experiment was to put the discharging knobs of an electric machine on a photographic plate at a distance of a few inches. On turning the machine a small spark travels slowly along the plate from the negative to the positive knob. On reversing the polarity of the machine, the spark travels back along the same path, but if the polarity remains unchanged, a second spark usually travels along a different path.

Prof. C. V. BOYS asked Prof. Minchin whether the films themselves, or the contacts between the electrode and film, is made conducting by the sparks?

Prof. S. P. THOMPSON wished to know if ordinary photographic dry plates would serve the purpose?

Mr. EVERSLED enquired whether the metal used as electrode made any difference?

Prof. MINCHIN, in his reply, maintained that the phenomena were due to electric impulses. He had not tried photographic plates, and had always used platinum for his electrodes.

#### THE ROYAL SOCIETY.

Anniversary Meeting, November 30th, 1893.

Address of the President, LORD KELVIN, D.C.L., LL.D.

SINCE our last Anniversary Meeting, the Royal Society has lost eleven Fellows on the Home List, and two Foreign Members.

- Henry Tibbats Stainton, December 2, 1892, aged 70.
  - Sir Richard Owen, December 18, 1892, aged 89.
  - Dr. James Jago, January 18, 1893, aged 77.
  - Henry Francis Blanford, January 23, 1893, aged 58.
  - Thomas William Fletcher, February 1, 1893, aged 84.
  - Edward Walker, March 2, 1893, aged 73.
  - Alphonse de Candolle, March 28, 1893, aged 87.
  - Henry Edward Stanley, Earl of Derby, April 21, 1893, aged 67.
  - Ernest Edward Kummer, May 14, 1893, aged 84.
  - Rev. Charles Pritchard, May 28, 1893, aged 85.
  - Dr. John Rae, July 22, 1893, aged 80.
  - Thomas Hawksley, September 23, 1893, aged 86.
  - Sir Andrew Clark, Bart., November 6, 1893, aged 67.
- Biographical notices will be found in the *Proceedings*.

During the past session our standing committees have been as active as ever. The Library Committee have again had before them the question of finding accommodation to meet the rapid growth of our Library. One

measure which, with the consent of the Council, they have adopted to this end has been to part with a number of the literary and philosophical series of transactions published by those societies which are not, like our own, purely scientific. In some cases these series are being returned to the institutions who gave them; in others, where this is not desired, they are presented to libraries in which they will be of greater use than in our own.

The House and Soirée Committee have held more than their usual number of meetings; and, acting upon their advice, the Council appointed a Special Committee to arrange for the better accommodation of the Fellows at their ordinary meetings and of their visitors at the Annual Soirées. Upon the first floor a new doorway has been provided, which, it is hoped, will help to a freer circulation on the crowded nights of our Soirées, and on the ground floor, besides the arrangement of the meeting-room and the provision of a lecture table, and additional accommodation for diagrams, a preparation room is being fitted with suitable appliances for the use of those who are willing to illustrate their papers by experiment.

The generous gift of £2000 presented by our Fellow Mr. Ludwig Mond, in the early part of the session, to aid the work of the "Catalogue of Scientific Papers," has enabled the Catalogue Committee not only to carry on the current work of the Catalogue, which want of funds threatened to cripple, but also to take into consideration wider schemes than it was possible to contemplate before. The Committee have met several times during the past session, and it is hoped that the long-desired Subject Index may yet become an accomplished fact.

The Water Research Committee have continued their labours, and a Second Report on the vitality of microscopic pathogenic organisms in large bodies of water, dealing with the vitality and virulence of *Bacillus anthracis* and its spores, the result of Messrs. Percy Frankland and Marshall Ward's researches, has been completed during the past session and published in our *Proceedings*.

Except that additional assistants have been employed in the Catalogue Department, our staff remains unchanged.

During the past year, in the Mathematical and Physical Section of the *Philosophical Transactions*, twenty-one papers have been published, and in the Biological Section, ten; the two sections together containing a total of 1775 pages of letter-press, and 70 plates. Of the *Proceedings*, twelve numbers have been issued, containing 1282 pages and 19 plates.

Not the least important of the scientific events of the year is the publication, in the original German and in an English translation by Professor D. E. Jones, of a collection of Hertz's papers describing the researches by which he was led up to the experimental demonstration of magnetic waves. For this work the Rumford Medal of the Royal Society was delivered to Professor Hertz three years ago by my predecessor, Sir George Stokes. To fully appreciate the book now given to the world, we must carry our minds back to the early days of the Royal Society, when Newton's ideas regarding the forces which he saw to be implied in Kepler's laws of the motions of the Planets and of the Moon were frequent subjects of discussion at its regular meetings and at perhaps even more important non-official conferences among its Fellows.

In 1684 the Senior Secretary of the Royal Society, Dr. Halley, went to Cambridge to consult Mr. Newton on the subject of the production of the elliptic motion of the Planets by a central force,\* and on the 10th of December of that year he announced to the Royal Society that he "had seen Mr. Newton's book, 'De Motu Corporum.'" Some time later, Halley was requested to "remind Mr. Newton of his promise to enter an account of his discoveries in the register of the Society," with the result that the great work "*Philosophiæ Naturalis Principia*

*Mathematica*" was dedicated to the Royal Society, was actually presented in manuscript, and was communicated at an ordinary meeting of the Society on the 28th of April, 1686, by Dr. Vincent. In acknowledgment, it was ordered "that a letter of thanks be written to Mr. Newton, and that the printing of his book be referred to the consideration of the Council; and that in the meantime the book be put into the hands of Mr. Halley, to make a report thereof to the Council." On the 19th of May following, the Society resolved that "Mr. Newton's '*Philosophiæ Naturalis Principia Mathematica*' be printed forthwith in quarto, in a fair letter; and that a letter be written to him to signify the Society's resolution, and to desire his opinion as to the volume, cuts, &c." An exceedingly interesting letter was accordingly written to Newton by Halley, dated London, May 22, 1686, which we find printed in full in Weld's "*History of the Royal Society*" (vol. i., pp. 308—309). But the Council knew more than the Royal Society at large of its power to do what it wished to do. Biology was much to the front then, as now, and the publication of Willughby's book, "*De Historia Piscium*," had exhausted the Society's finances to such an extent that the salaries even of its officers were in arrears. Accordingly, at the Council meeting of the 2nd of June, it was ordered that "Mr. Newton's book be printed, and that Mr. Halley undertake the business of looking after it, and printing it at his own charge, which he engaged to do."

It seems that at that time the office of Treasurer must have been in abeyance; but with such a Senior Secretary as Dr. Halley there was no need for a Treasurer.

Halley, having accepted copies of Willughby's book, which had been offered to him in lieu of payment of arrears of salary\* due to him, cheerfully undertook the printing of the "*Principia*" at his own expense, and entered instantly on the duty of editing it with admirable zeal and energy, involving, as it did, expostulations, arguments, and entreaties to Newton not to cut out large parts of the work which he wished to suppress† as being too slight and popular, and as being possibly liable to provoke questions of priority. It was well said by Rigaud, in his "*Essay on the first publication of the Principia*," that "under the circumstances, it is hardly possible to form a sufficient estimate of the immense obligation which the world owes in this respect to Halley, without whose great zeal, able management, unwearied perseverance, scientific attainments, and disinterested generosity the '*Principia*' might never have been published."‡ Those who know how much worse than "law's delays" are the troubles, cares, and labour involved in bringing through the press a book on any scientific subject at the present day will admire Halley's success in getting the "*Principia*" published within about a year after the task was committed to him by the Royal Society, two hundred years ago.

\* It is recorded in the Minutes of Council that the arrears of salary due to Hooke and Halley were resolved to be paid by copies of Willughby's work. Halley appears to have assented to this unusual proposition, but Hooke wisely "desired six months' time to consider of the acceptance of such payment."

† The publication of the "*Historia Piscium*," in an edition of 500 copies, cost the Society £400. It is worthy of remark, as illustrative of the small sale which scientific books met with in England at this period, that, a considerable time after the publication of Willughby's work, Halley was ordered by the Council to endeavour to effect a sale of several copies with a bookseller at Amsterdam, as appears in a letter from Halley requesting Boyle, then at Rotterdam, to do all in his power to give publicity to the book. When the Society resolved on Halley's undertaking to measure a degree of the Earth, it was voted that "he be given £50 or fifty '*Books of Fishes*'" (Weld's "*History of the Royal Society*," vol. i., p. 310).

‡ "The third [book] I now design to suppress. Philosophy is such an impertinently litigious lady that a man had as good be engaged in lawsuits as have to do with her. I found it so formerly, and now I am no sooner come near her again but she gives me warning. The first two books without the third will not so well bear the title of '*Philosophiæ Naturalis Principia Mathematica*,' and therefore I have altered it to this, '*De Motu Corporum Libri duo*'; but, upon second thoughts, I retain the former title. 'Twill help the sale of the book, which I ought not to diminish now 'tis yours'" (*Ibid.*, p. 311).

§ *Ibid.*, p. 310.

\* Whewell's "*History of the Inductive Sciences*," vol. ii., p. 77.

When Newton's theory of universal gravitation was thus made known to the world Descartes's *Vortices*, an invention supposed to be a considerable improvement on the older invention of crystal cycles and epi-cycles from which it was evolved, was generally accepted, and seems to have been regarded as quite satisfactory by nearly all the philosophers of the day.

The idea that the Sun pulls Jupiter, and Jupiter pulls back against the Sun with equal force, and that the Sun, Earth, Moon, and Planets all act on one another with mutual attractions, seemed to violate the supposed philosophic principle that matter cannot act where it is not. Descartes's doctrine died hard among the mathematicians and philosophers of Continental Europe; and for the first quarter of last century belief in universal gravitation was an insularity of our countrymen.

Voltaire, during a visit which he made to England in 1727, wrote:—"A Frenchman who arrives in London finds a great alteration in philosophy, as in other things. He left the world full; he finds it empty. At Paris you see the universe composed of vortices of subtle matter; at London we see nothing of the kind. With you it is the pressure of the Moon which causes the tides of the sea; in England it is the sea which gravitates towards the Moon. . . . You will observe also that the Sun, which in France has nothing to do with the business, here comes in for a quarter of it. Among you Cartesians all is done by impulsion: with the Newtonians it is done by an attraction of which we know the cause no better."\* Indeed, the Newtonian opinions had scarcely any disciples in France till Voltaire asserted their claims on his return from England in 1728. Till then, as he himself says, there were not twenty Newtonians out of England.†

In the second quarter of the century sentiment and opinion in France, Germany, Switzerland, and Italy experienced a great change. The mathematical prize questions proposed by the French Academy naturally brought the two sets of opinions into conflict. A Cartesian memoir of John Bernoulli was the one which gained the prize in 1730. It not unfrequently happened that the Academy, as if desirous to show its impartiality, divided the prize between Cartesians and Newtonians. Thus, in 1734, the question being the cause of the inclination of the orbits of the planets, the prize was shared between John Bernoulli, whose memoir was founded on the system of vortices, and his son Daniel, who was a Newtonian. The last act of homage of this kind to the Cartesian system was performed in 1740, when the prize on the question of the tides was distributed between Daniel Bernoulli, Euler, Maclaurin, and Cavallieri; the last of whom had tried to amend and patch up the Cartesian hypothesis on this subject.‡

On the 4th of February, 1744, Daniel Bernoulli wrote as follows to Euler:—"Uebrigens glaube ich, dass der Aether sowohl *gravis versus solem*, als die Luft versus terram sey, und kann Ihnen nicht bergen, dass ich über diese Punkte ein völliger Newtonianer bin, vnd verwundere ich mich, dass sie den Principiis Cartesianis so lang adhären; es möchte wohl einige Passion vielleicht mit unterlaufen. Hatt Gott können eine *animam*, deren Natur uns unbegreiflich ist, erschaffen, so hat er auch können eine attractionem universalem materiae imprimiren, wen gleich solche attractio *supra captum* ist, da hingegen die Principia Cartesiana allzeit *contra captum* etwas involviren."

Here the writer expressing wonder that Euler had so long adhered to the Cartesian principles, declares himself a thorough-going Newtonian, not merely in respect to gravitation *versus* vortices, but in believing that matter may have been created simply with the law of universal attraction without the aid of any gravific medium or

mechanism. But in this he was more Newtonian than Newton himself.

Indeed Newton was not a Newtonian, according to Daniel Bernoulli's idea of Newtonianism, for in his letter to Bentley of date 25th February, 1692,\* he wrote:—"That gravity should be innate, inherent, and essential to matter, so that one body may act upon another at a distance through a vacuum without the mediation of anything else, by and through which their action and force may be conveyed from one to another, is to me so great an absurdity that I believe no man who has in philosophical matters a competent faculty of thinking can ever fall into it." Thus Newton, in giving out his great law, did not abandon the idea that matter cannot act where it is not. In respect, however, merely of philosophic thought, we must feel that Daniel Bernoulli was right; we can conceive the Sun attracting Jupiter, and Jupiter attracting the Sun, without any intermediate medium, if they are ordered to do so. But the question remains—Are they so ordered? Nevertheless, I believe all, or nearly all, his scientific contemporaries agreed with Daniel Bernoulli in answering this question affirmatively. Very soon after the middle of the Eighteenth Century, Father Boscovich† gave his brilliant doctrine (if infinitely improbable theory) that elastic rigidity of solids, the elasticity of compressible liquids and gases, the attractions of chemical affinity and cohesion, the forces of electricity and magnetism—in short, all the properties of matter except heat, which he attributed to a sulphureous fermenting essence—are to be explained by mutual attractions and repulsions, varying solely with distances, between mathematical points endowed also, each of them, with inertia. Before the end of the Eighteenth Century the idea of action-at-a-distance through absolute vacuum had become so firmly established, and Boscovich's theory so unqualifiedly accepted as a reality, that the idea of gravitational force or electric force or magnetic force being propagated through and by a medium seemed as wild to the naturalists and mathematicians of one hundred years ago as action-at-a-distance had seemed to Newton and his contemporaries one hundred years earlier. But a retrogression from the Eighteenth Century school of science set in early in the Nineteenth Century.

(To be continued).

**Determination of the Acid Hydrazides.**—II. Strache and S. Tritzer (*Monatshefte für Chemie*).—The authors have experimented on compounds of the general formula  $RNH-NHC_6H_5$ , where R signifies a univalent acid radicle. The authors prove that the acid hydrazides are oxidised by boiling Fehling's solution in the same manner as phenylhydrazine, with liberation of the total nitrogen.

**Examination of Tartaric Acid and Citric Acid for Metallic Lead and Compounds of Lead.**—M. Bucket (*Repert. Pharm. and Chemiker Zeitung*).—The author dissolves 200 grms. of the acids in three times their weight of water and adds ammonia in slight excess in order to effect the complete solution of any crystalline lead sulphate which may be present. After the lapse of twenty-four hours the liquid is decanted, the sediment collected upon a filter, washed, and dissolved upon the filter in nitric acid. From this solution the lead is separated as sulphate by sulphuric acid and alcohol in the well-known manner and weighed. Such lead must have been originally present in the metallic state. The solution of ammonium citrate or tartrate serves for the determination of lead compounds. It is acidified with hydrochloric acid, precipitated with sulphuretted hydrogen water, and the lead compounds are converted into lead sulphate as above directed.

\* "The Correspondence of Richard Bentley, D.D.," vol. i., p. 70.

† "Theoria Philosophiæ Naturalis reduceta ad unicum legem virium in natura existentium auctore P. Rogerio Josepho Boscovich, Societatis Jesu," 1st edition, Vienna, 1758; 2nd edition, amended and extended by the author, Venice, 1763.

\* Whewell's "History of the Inductive Sciences," vol. ii., pp. 202—203.

† *Ibid.*, vol. ii., p. 201.

‡ *Ibid.*, vol. ii., pp. 198, 199

## OBITUARY.

## THE LATE PROFESSOR TYNDALL.

On the evening of Monday, December 4th, British Science lost one of its most conspicuous representatives in the person of Dr. John Tyndall. The deceased had been suffering for some years from insomnia, and an overdose of chloral hydrate administered accidentally hastened his end. Tyndall was born in 1820, at Leighlin Bridge, in county Carlow. He appears to have been connected with William Tyndale, the martyred translator of the Bible into English.

Young Tyndall received his education at an Irish National School, and early showed an unusual aptitude and predilection for mathematical studies. In his nineteenth year he joined a division of the Ordnance Survey then stationed in the district. In this capacity he earned the good will of his superior, Lieut. Geo. Wynne, R.E. On quitting the Ordnance Survey, in 1843, he was engaged in the surveys necessitated by the Railway Mania. Here he encountered severe physical obstacles, but his resolution triumphed over all, and his plans and sections could always be deposited in time. It is recorded that he rejected all opportunities for private emolument.

In 1847, he accepted the appointment of teacher of physics at New Harmony, a college founded at Queenswood, Hants, by the socialistic apostle, Robert Owen. Here he became intimate with Dr. E. Frankland, who was in charge of the chemical laboratory. After the collapse of New Harmony, Tyndall and Frankland went to continue their studies at Marburg, under Bunsen. At the same time he was reading mathematics zealously, and making himself acquainted with the writings of Pichte and Goethe. These literary studies drew him in after life into a friendship with Carlyle.

His study of the phenomena of diamagnetism, undertaken at the suggestion of Knoblauch, brought him under the notice of Faraday. In 1851 he became acquainted with Ehrenberg, with whom he had frequent conversations on microscopic organisms. Among his other friends were Magnus, Du Bois Reymond, Clausius, Humboldt, and Helmholtz.

In 1853 he was elected Professor of Natural Philosophy at the Royal Institution. In 1855 he became Examiner under the Council for Military Education. Here he advocated a more liberal recognition of Science in the studies of Artillery officers and Engineers. On this subject he expressed himself with such freedom as to risk dismissal, which, however, did not take place.

In 1857 and 1858 Tyndall continued his studies on glaciation, which became his holiday subject.

In 1859 he took up the question of the absorption of radiant heat by gases and vapours, upon which he threw a new and a satisfactory light. For these researches he received, in 1864, the Rumford Medal of the Royal Society.

In 1863 he wrote his celebrated work "Heat considered as a Mode of Motion." In 1867 appeared the companion volume on "Sound," and in 1869-74 he published his lectures on Light. In these volumes he showed a wonderful skill in expounding physical phenomena and laws without a scaffolding of the higher mathematics.

In 1868 he took up the question of abiogenesis, and of the part played by microbia in the dissemination of epidemics. These results he expounded in his famous lecture on "Dust and Disease," delivered at the Royal Institution on January 21, 1870. His conclusions were supported on thousands of experiments, and though at first ridiculed by many medical and other scientific men, they are now universally accepted. It must be understood that Tyndall did not pose as the pioneer of the microbial theory of disease. But he did not blindly accept the teachings of Pasteur, Schröder, and others. He appears here as—save the case of Helmholtz—the only

mathematician who has done good service in any branch of biology.

Passing over Tyndall's valuable respirator, and his course of lectures in America, we must notice his Presidency of the British Association, at the Belfast Meeting (1874), and his celebrated Address. This oration excited the ire, firstly of the orthodox, and then—like the writings of Darwin—of the heterodox.

In 1876 Tyndall married Lady Louise Charlotte, eldest daughter of Lord and Lady Claude Hamilton.

A noteworthy phenomenon in Tyndall's life was his friendship for Carlyle. Of "the sage of Chelsea" he formed a more favourable estimate than is usually done. He defends Carlyle against the charge of being, like Socrates, an enemy of Science. His defence, however, can scarcely avail against certain well-known passages in Carlyle's own writings.

We cannot, in conclusion, proclaim Tyndall as an epoch maker in Science, but we must pronounce him the author of an abundance of most valuable research. He has at the same time made Science both more acceptable to, and more accepted by, the great bulk of the nation, by the masses as well as the classes.

We perceive that the German press speaks in terms of warm praise of John Tyndall, and of the services he has rendered to Science.

## 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. cxvii., No. 21, November 20, 1893.

**A New Model of a Reverberatory Electric Furnace with Movable Electrodes.**—Henri Moissan.—The construction of this furnace requires the accompanying illustration. The furnace has a horizontal tube of coke. If this tube is inclined by 30° the furnace is converted at once into a continuous apparatus for the production of the refractory metals, into which the mixture of oxides to be reduced is allowed to slide, whilst the liquid metal flows off easily on this inclined plane. In this continuous electric furnace the thermic phenomena of the arc are completely separated from the electrolytic phenomena. With a current of 600 ampères and 60 volts it is easy to obtain in an hour a regulus of fused metallic chrome of about 2 kilos. The metal is received in a crucible of chromium sesquioxide, where it remains liquid long enough to become refined. It is then perfectly liquid, and after solidification it yields a white, very hard metal of a fine grain and taking a brilliant polish. The author indicates as a specimen of the experiments which he has in progress the preparation of carbon and vanadium silicides. If we place silicon in a boat of carbon in the midst of the tube heated with a current of 1000 ampères and 60 volts, we obtain on the upper surface prismatic needles of carbon silicide which reach the length of several m.m.

**Action Exerted by some Metals in the Acid Solutions of their Chlorides.**—A. Ditte and R. Metzner.—This paper will be inserted at considerable extent.

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

**New Process for the Rapid Determination of Sulphur in Commercial Irons.**—H. A. Hooper.—From the  
CHEMICAL NEWS.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. viii., No. 92.

This issue contains no chemical matter.

*Zeitschrift für Analytische Chemie.*  
Vol. xxxii., Part 4.

**Detection of Higher Alcohols in Ethyl Alcohol.**—Bardy (*Amer. Apotheker Zeitung*).—The author mixes the spirit in question with four and a half volumes of a saturated solution of sodium chloride and half a volume of water, and shakes out repeatedly with carbon disulphide. The latter, when separated from the brine, is mixed with some concentrated sulphuric acid. This is again separated from the carbon disulphide. The latter is entirely removed by forcing air into it. There is now added to the sulphuric acid an equal volume of glacial acetic acid, and the whole is boiled for fifteen minutes in a reflux condenser. If a quantity of saturated brine equal to the original volume of spirit is now added, the acetic ethers of the butylic and amylic alcohols present separate out in the state of oily drops. If we measure the volume in a narrow graduated tube and multiply by 0.8, we find the quantity of the higher alcohols originally present.

**Detection of Acetone.**—A. Schwicker (*Chemiker Zeitung*).—The author proposes its conversion into iodoform by iodine in presence of ammonia. Under these conditions no iodoform is obtained from ethylic alcohol.

**Determination of Sulphur in Organic Substances.**—Walter Hempel (*Zeit. Angew. Chemie*).—The author utilises Berthelot's proposal to effect the combustion in an atmosphere of oxygen. He finds that the process may be effected at the ordinary pressure, so that the use of the calorimetric bomb may be dispensed with.

**The Gunning-Kjeldahl Method of Determining Nitrogen.**—A. L. Winton, jun.—From the CHEMICAL NEWS.

**Determination of Malic Acid.**—C. Micko (*Zeit. d. Allgem. Oestern. Apotheker Vereins*).—Will be inserted in full.

**Determination of Succinic Acid.**—Alfred Rau (*Archiv. f. Hygiene*).—This memoir will be inserted in full.

**Studies on the Determination of Glycerin.**—E. Suhr (*Archiv. f. Hygiene*).

**An Improved Process for the Rapid and Certain Detection of Cholera Bacilli.**—R. Koch (*Zeit. f. Hygiene*).—Already inserted.

**Examination of Mace.**—Th. Waage (*Pharm. Centralhalle*).—For this paper we must refer to the original.

**Examination of Essential Oils.**—A series of extracts from a trade circular issued by Schimmel and Co., April, 1893.

**Execution of the Iodine Addition Method.**—P. Welmans (*Pharm. Zeitung*).—The author proposes as a solvent for mercuric chloride and iodine a mixture of equal volumes of pure acetic acid and acetic ether or ethylic ether. The solution is adjusted with sodium thiosulphate, the value of which has been ascertained by means of a standard solution of potassium dichromate. The temperature has a decisive influence on the determination of the iodine number. In every experiment the initial and final temperature must agree with that of standardising. A temperature of between 17° and 20° is most suitable. All operations must be effected only in bottles or flasks with ground glass stoppers.

**Examination of Lanoline.**—Liebreich and Berend (*Pharm. Zeitung*) contest the opinion of Mente that the anhydrous lanoline of Jaffé and Darmstädter contains ethyl alcohol.

**Analysis of Irons.**—A very extensive series of extracts from *Stahl und Eisen*, the CHEMICAL NEWS, *Bull. de la*

*Soc. de l'Ind. Minérale, Chem. Centralblatt, Trans. of American Institute of Mining Engineers, Journal of Chemical Society; Berg und Hüttenm.-Zeitung, Journal of Society of Chemical Industry, Comptes Rendus, &c.*, forming a total too bulky for abstraction.

**The Centrifugal in the Service of the Examination of Urine.**—MM. Blix and Jolles.—Both authors admit that by means of a centrifugal apparatus small quantities of urinary deposits can be caused to subside rapidly, and thus rendered fit for microscopical and chemical examination. However, Jolles shows that the method is not suitable for quantitative determinations (*Vienna Med. Presse*).

**Determination of Acetone in Urine.**—R. Supino (*Revista Generale Italiana*).—The author adds to the distillate of the urine soda-lye and then solution of potassium iodide until the colour becomes blue, and then again alkali until the liquid is decolourised. The iodoform produced is shaken out with ether, the ether expelled by evaporation, the residue dissolved in strong alcohol and boiled with concentrated soda-lye (free from chlorine) for twenty minutes in a reflux refrigerator in order to convert the iodine into sodium iodide. After expelling the alcohol and acidifying the quantity of iodine, it is determined volumetrically with solution of silver. 1 c.c. of decinormal solution of silver indicates 1.93 m.grm. acetone.

**Detection of Biliary Pigment in Urine.**—O. Rosenbach (*Deutsche Med. Wochenschrift*) tests for bile pigment by the cautious addition of a few drops of a 5 per cent solution of chromic acid. The urine turns green. Excess is to be avoided, as otherwise the colour is a brownish red. H. Rosin gives another test in the *Berlin Klin. Wochenschrift*.

**Detection of Hæmatoporphyrine in Urine.**—A. Garrod.—From the *Journal of Physiology*.

**Uroroseine.**—Dr. Rosin (*Deutsch. Med. Wochenschrift*).—This substance may be obtained from normal urine, but in large proportion from pathological specimens. Its properties have been accurately described by Nencki and Sieber in *Zeit. Anal. Chemie*, xxii., 300.

**Detection of Albumen in Urine.**—B. Vas (*Ungar. Archiv. f. Medicin*) finds the reaction with sulpho-salicylic acid especially trustworthy. He adds a 20 per cent solution of sulpho-salicylic acid to eight drops, when 0.003 per cent may be recognised. The disturbing influence of urinary mucus may be avoided by precipitation with magnesium sulphate and testing for serum albumen in the filtrate ("Hygeia," April, 1892).

**Arsenical Poisoning.**—F. Strassmann (*Apotheker Zeitung*).—One of the pleas raised for the defence in case of the detection of arsenic in a corpse is that the arsenic may have been introduced after death (!). Strassmann shows that in cases of arsenical poisoning there is a uniform distribution of the poison in all the organs, whilst if arsenic is introduced after death it accumulates especially in the left kidney, the right kidney containing either mere traces or none at all.

**Career of Arsenious Acid in the Animal Organism.**—D. Vitali (*Bolletino Chémico-Farmacéutico*).—According to the author, arsenious acid in the organism is chiefly oxidised to arsenic acid and is then eliminated by way of the urine. Arsenic acid in the organism forms complicated compounds, in which it plays a part analogous to that of phosphorus in lecithine.

**Toxicological Importance of Copper.**—K. B. Lehmann and others.—From the *Eilfte Versamm. Bayer. Chemiker*.

**Atomic Weight of Boron.**—W. Ramsay and Emily Aston (from the CHEMICAL NEWS), also J. L. Hoskyns Abrahall (*Journal of the Chemical Society*) and E. Rimbach (*Berichte*).—These researches give the weight sought for respectively as:—10.966 (Ramsay and Aston), 10.825 (Abrahall), and 10.945 (Rimbach).

**Determination of Mon-acid and Di-acid Phosphate in Urine.**—E. Freund (*Centralblatt für Medic. Wissenschaften*) first titrates total phosphoric acid with solution of uranium, precipitates the mon-acid phosphates with barium chloride, and titrates afresh the filtrate. The difference referred to equal quantities of urine show the proportion of mon-acid phosphate.

**Detection of Carbamic Acid in Urine.**—J. J. Abel and E. Drechsel (*Archiv. f. Physiologie*) stir up the recent urine with much thick freshly-prepared milk of lime, shake well for from five to ten minutes, and filter. The filtrate (which must not give a precipitate with lime-water) is shaken up for fifteen minutes with calcium chloride and some crystallised calcium carbonate in a stoppered vessel. After a brief subsidence in an ice-closet, the liquid is filtered into three times its volume of alcohol cooled down to 0°; after subsidence for several hours the flocculent precipitate is filtered by means of a Sprengel pump, washed with alcohol and ether, and dried in a vacuum. The precipitate contains any carbaminic acid as a salt of calcium.

**Conditions of Solubility of Uric Acid.**—G. Rüdell (*Archiv. Exp. Pathologie*).—The presence of urea renders uric acid incapable of precipitation, except in presence of excess of acid.

## MISCELLANEOUS.

The Municipal Chemical Office of the City of Breslau.—The *Chemiker Zeitung* announces that during the last year the following poisons have been detected in human bodies sent in for examination:—Arsenic, in three cases; alcohol, chloroform, and hydrocyanic acid each in one case; and carbon monoxide in three cases.

The Association of German Naturalists and Physicians.—According to the *Chemiker Zeitung*, the sixty-sixth meeting of this body will be held next year in Vienna, beginning on September 24. It will be remembered that "Naturalist" (*Naturforscher*) in the German language includes the followers of any of the natural and physical sciences.

The Antiseptic Action of Cresol.—Lacroix-Hunkiabeyendian (*Journal de Pharmacie et de Chimie*).—A mixture of ortho-, meta-, and para-cresol is found to exert a stronger action upon microbia (*Staphylococcus pyogenes aureus*, *Tetragenus prodigiosus*, and the bacilli of cholera and typhus) than any of the pure compounds used singly. The solubility of the cresols in water is increased by the presence of a small quantity of cresol-sodium.

Royal Institution.—The following are the Lecture Arrangements before Easter:—Professor Dewar, Six Lectures (adapted to a Juvenile Auditory) on "Air—Gaseous and Liquid"; Professor Charles Stewart, Nine Lectures on "Locomotion and Fixation in Plants and Animals"; The Rev. Canon Ainger, Three Lectures on "The Life and Genius of Swift"; Mr. W. Martin Conway, Three Lectures on "The Past and Future of Mountain Exploration"; Professor Max Müller, Three Lectures on the "Vedânta Philosophy"; Professor W. H. Cummings, Three Lectures on "English Schools of Musical Composition" (with Musical Illustrations); The Right Hon. Lord Rayleigh, Six Lectures on "Light" (with special reference to the Optical Discoveries of Newton). The Friday Evening Meetings will begin on January 19th, when a Discourse will be given by Professor Dewar, on "Scientific Uses of Liquid Nitrogen and Air"; succeeding Discourses will probably be given by Mr. A. P. Graves, Mr. T. J. Cobden-Sanderson, Professor W. F. R. Weldon, Professor Silvanus P. Thompson, Professor John G. McKendrick, Dr. W. H. White, The Right Hon. Lord Rayleigh, and other gentlemen.

## MEETINGS FOR THE WEEK.

- MONDAY, 11th.—Society of Arts, 8. (Cantor Lectures). "The Art of Book and Newspaper Illustration," by Henry Blackburn.  
— Medical, 8.30  
TUESDAY, 12th.—Institute of Civil Engineers, 8.  
— Medical and Chirurgical, 8.30.  
— Photographic, 8.  
WEDNESDAY, 13th.—Society of Arts, 8. "Carriage-way Pavements for Large Cities," by Lewis H. Isaacs.  
— Pharmaceutical, 8.  
THURSDAY, 14th.—Royal, 4.30.  
— Mathematical, 8.  
— Institute of Electrical Engineers, 8.  
FRIDAY, 15th.—Quekett Club, 8.

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THE CHEMICAL NEWS.

Vol. LXVIII., No. 1777.

PROCESSES FOR MANUFACTURING GAS FROM OIL,  
WITH SPECIAL REFERENCE TO THE PEBBLES PROCESS.\*

By W. IVISON MACADAM, F.R.S.E., F.I.C., F.C.S., &c.

THAT a rich illuminating gas could be obtained by the destructive distillation of oils has been known for many years. In the earlier experiments the ordinary greasy or fatty oils were employed, but the cost of material was so great that the works erected were rapidly closed. The oils used were principally colza or rape oil and train or whale oil. The amount of gas obtained was from 70 to 90 cubic feet per gallon of oil; whilst the illuminating power ranged from 30 to 70 candles. The cost was rarely below twenty-five to thirty shillings per thousand cubic feet. These fatty or greasy oils are combinations of the triatomic alcohol, glycerin ( $C_3H_5(OH)_3$ ), with fatty acids, principally palmitic ( $C_{16}H_{31}HO$ ), stearic ( $C_{18}H_{35}HO$ ), and oleic ( $C_{18}H_{33}HO$ ). When destructively distilled the glycerin passes, to a large extent, into the aldehyd acrolein ( $C_3H_3O,H$ ); whilst the fatty acids yield a series of compounds of which the olefines form the greater part. The gas is therefore very rich in carbon, and burns with a smoky flame, requiring special burners for its consumption.

Next in time comes "coal oil." This substance is a very complex mixture of carbon and hydrogen compounds. It contains members of the benzol, paraffin, olefine, acetylene, and other series. It is obtained during the purification of ordinary coal-tar, and is sometimes used as an illuminating oil. The specific gravity runs from 840 to 850 (water 1000). It contains proportions of the lower members of the benzol, olefine, and paraffin series, which give it a low flashing-point ( $65^\circ$  to  $70^\circ$  F.), and low burning point ( $70^\circ$  to  $80^\circ$  F.). The yield of gas is, however, high, averaging over 100 cubic feet per gallon of oil, with an illuminating value equal to about 70 standard candles. The gas is rich in members of the olefine series, of which it contains over 45 per cent. It also contains some members of the paraffin series, but only small quantities of the acetylenes. By the newer processes this substance should give valuable results.

The most important classes of carbon and hydrogen compounds from which gas may be distilled are the petroleums and paraffins. The first of these terms is more strictly applied to certain naturally formed hydrocarbons found widely distributed over the surface of the globe. The term paraffin has been adopted for the materials derived from shales, &c., when these are destructively distilled in closed retorts with or without the admission of steam, and with or without the presence of air.

The natural hydrocarbons, whilst widely distributed, not only geographically but geologically, are found in large quantities only in a few localities. In Russia, the Baku deposits have been long known; in Burmah the substance has been worked for centuries; in Japan and China; in Egypt, &c. With the exception of the Russian deposits, all other localities fall into insignificance beside the enormous underground reservoirs discovered in America. The vastness of these American deposits of natural oil may, perhaps, be better understood when I state the area already proved, by boring and other means, is over 200,000 square

miles, and that the production in the year 1882 reached a total of 30,460,000 barrels, or over 1,279,320,000 gallons, of which Pennsylvania alone sent out 1,174,757,220 gallons. Since then the output has decreased somewhat. In the case of Russia the export is gradually increasing. In 1882 the total number of gallons manufactured was only 200,000,000; in 1884 the amount had risen to 429,400,000 gallons.

The American petroleums consist, chemically, principally of true paraffins ( $C_nH_{n+2}$ ), with an admixture of the olefines ( $C_nH_{n+2}$ ), and traces of the benzols ( $C_nH_{n+6}$ ). The Russian naphthas, on the other hand, are, to a large extent, made up of olefines, with some benzenes, paraffins, and acetylenes. They contain little or no solid paraffin.

In America especially the lighter and more volatile members of the paraffin series (methane and ethane) are found in great quantities as natural gas, and are in admixture with hydrogen and small proportions of carbonic anhydride ( $CO_2$ ). This natural gas is of high heating value, and is of the greatest importance in those works requiring a heat of great intensity, such as in the manufacture of steel.

Paraffin oils are obtained by the destructive distillation of shales in closed retorts. The total volatile matter in these shales varies greatly, but may be stated at from 16 to 28 per cent, with a probable average of 23 per cent. When heated in the retorts the yield of crude oil is about 12 to 13 per cent. The specific gravity is from about 860 to 880 (water 1000). The total production of crude oil, in Scotland, is equal to 60,000,000 to 62,000,000 gallons per annum. There is also produced during the shale distillation 4 to 6 per cent permanent gas. One sample of this gas gave, on analysis, the following results:—

Carbonic anhydride .. .. .	15'40
Hydrogen .. .. .	34'53
Carbonic oxide .. .. .	10'72
Methane .. .. .	4'02
Nitrogen .. .. .	35'33
	100'00

The gas burns with a pale almost non-luminous flame, and is employed for heating the retorts, &c. It gives a hot flame, and is well suited for firing purposes. It is also used for lighting the crude retort benches, but for this purpose requires to be carburetted by passage through light naphthas. When the science of oil distilling was less perfectly understood, this gas was purified by means similar to those employed for coal-gas, and used for domestic lighting. Now the illuminating agents are almost perfectly separated, and the flame has become practically non-luminous.

Crude paraffin oil is made up chemically to a large extent of members of the olefine series, with less proportions of the paraffins and traces of benzols and some acetylenes. It differs, therefore, from the natural petroleum, which is more largely composed of true paraffins. The names, in fact, would be more descriptive if the term paraffin were confined to the American natural oil.

The American petroleum is not so readily broken up into a permanent gas. In some experiments I made with a sample of burning oil of 799 specific gravity I obtained 86 cubic feet of a  $66\frac{1}{2}$ -candle gas per gallon of oil. The decomposition, moreover, was not so complete as with other oils, and consequently when stored the gas lost a greater proportion of its luminosity by condensation.

Crude shale oil may be distilled into permanent gas with good results, but as the material is either solid or semi-solid, it is very difficult to work, as even when heated it is liable to "set" in the small pipes leading to the retorts. In some tests made with an oil of 850 gravity, we obtained from the gallon  $98\frac{1}{2}$  cubic feet of permanent gas of 50 candle power. The crude oil contains impurities, from which it may be separated by distillation in a current of steam; and the resulting oil gives much better results when made into gas. During the oil

\* Report of Lecture delivered before the North of Ireland Association of Gas Managers, August, 1893.

distillation the gravity is reduced to close on 800, and the gallon of oil will then yield over 100 cubic feet of a 70-candle gas.

Such oils, however, are not well suited for gas making, with the older forms of apparatus, as, containing the light volatile hydrocarbons, they are highly inflammable, and are dangerous to store. At the same time they contain the valuable "burning" oils, the solid paraffins, and heavy lubricating oils. These bodies are generally extracted from the shale oil before the residue is employed for gas making. The process varies in different works, but generally consists first in a distillation with steam, then in a treatment with sulphuric acid, and afterwards with soda to remove certain nitrogenous-alkaloidal bodies belonging to the pyridine series, &c., and tar acids of the carbolic and other series. The oil is then again distilled, but the distillate is "cut" into two portions; (a) a light oil, containing naphtha, burning oil, and intermediate oils, with some of the softer solid paraffins; and (b) a heavy oil, from which is extracted intermediate and lubricating oils, and solid paraffins of the higher fusing-points. These various fractions are extracted after repeated treatments with sulphuric acid and soda, followed by distillation, this latter aided by a current of steam. The products then are:—

1. Light oils or naphthas (750 gravity).
2. Burning oils (805 to 830 gravity).
3. Intermediate oils (840 to 870 gravity).
4. Lubricating oils (870 to 890 gravity).
5. Solid paraffin.

The light oils or naphthas may be distilled into permanent gas, but are more usefully employed as solvents for india-rubber, as turpentine substitute for paints, for carburetting (mechanically) water-gas, &c.

The burning oils give a good yield of illuminating gas. An oil of 815 gravity gave us 100 cubic feet per gallon of a gas of 63-candle power, and a second oil of 830 gravity yielded over 100 cubic feet of a 50-candle power gas for the gallon of oil.

The solid paraffins are too valuable to be economically distilled, even were the mechanical difficulty of their solid condition overcome.

The oil from which the solid paraffins of higher fusing-points have been extracted is "green" oil, and may be readily converted into gas. A sample of 884 oil gave 102 cubic feet of gas, having an illuminating value of 53-candle power. This oil, however, still contains some of the softer solid paraffins, which can be removed by freezing when the liquid becomes "blue" oil. This class of oil is also used for gas making, with good results. The average result obtained by us may be stated at 128 cubic feet of gas of 54-candle power per gallon of oil. After further purification and distillation this oil becomes "lubricating" oil of various gravities and "body." A lubricating oil of 873 gravity readily gave 102 cubic feet of a gas 61-candle power; whilst a heavy lubricating oil, of 894 gravity, gave 94 cubic feet of a 57-candle gas per gallon of oil distilled.

It is, however, with the intermediate oils that the present, as well as the future, of oil-gas making will remain. These oils, after the most careful fractionation and treatment, are too heavy to burn in ordinary lamps, as their viscosity is too high to admit of their ascending the wick by their own capillarity. They may, however, be burned to advantage in specially-constructed lamps. They are also too light in body for use as lubricants, and were, therefore, almost waste substances. Before the days of oil-gas these oils were submitted to the process of "cracking," and in America this is still carried out. The method simply depends upon the fact that the higher members of the olefine series, when subjected to a prolonged application of radiant heat at or near their distillation point, are converted partly into lower members of the same series, and partly into marsh-gas (methane). The paraffins present are almost entirely converted into lower

members of the olefine series. By this means the gravity is lowered and the viscosity destroyed. After a treatment with acid and soda and a distillation, they may be used for burning in ordinary paraffin lamps. They, however, never give satisfaction, as, being so largely composed of olefines, they form combinations with the vitriol used in the treatment, and on being burned the wicks become loaded with sulphur compounds, and are charred. The products of combustion also contain much sulphurous anhydride (SO<sub>2</sub>). Since the demand for gas-oil has increased, cracking, in this country at least, has entirely disappeared, and the intermediate oils have now a distinct value in themselves. The flashing-point of the intermediate oils runs from 230° F. to 250° F., and the firing-point over 280° F. There is, therefore, no danger from volatile inflammable vapours lodging in the store tanks. The yield of gas per gallon of oil is about 94 cubic feet, and the quality close on 60 candles. The gas consists of about 35 to 37 per cent of olefines—with methane, hydrogen, and some benzenes and acetylenes.

Until within the last few years oil known as "gas oil" was on the market. This product was obtained by distilling the mixed tars formed by the addition of the acid and soda during the various stages of refining the paraffin oils. The gas-oil was an amber-co'oured liquid; contained leucolines and pyridines from the soda-tar and hydrocarbons especially rich in carbon. It burned with a very smoky, sooty flame, and gave a gas rich in acetylenes. The manufacturers now find that it is more economical to burn the tars as fuel below the boilers and stills. It is injected by a current of steam, and is a valuable fuel.

The gas made from oil is used either directly as an illuminant or to enrich other gas of a poorer quality. In the processes I propose to describe I have purposely left out those forms of apparatus which enrich poor illuminating gas by passing it directly through highly volatile hydrocarbons. Such processes are purely mechanical, and result simply in the suspension of the highly volatile liquid in a large body of a permanent gas. The Patentees of oil-gas apparatus have invariably attempted to distil the oil by one operation into gas, and their processes require a considerable heat on the retorts. As by-products they obtain a condensable tar of benzolnaphthalene character and more or less carbon (*not coke*). The Peebles process, as I propose to show, makes no such claim, and the only by-product is a hard and valuable coke.

Of the first class I will describe the processes of (a) Pintsch, (b) Keith, (c) Alexander and Paterson (Kirkintilloch), (d) Brooks, and latterly I will take up the Peebles process and show how it differs from the other methods.

Pintsch's apparatus is especially constructed to work burning and lubricating oils, or oils of the class intermediate between burning and lubricating. It is not adapted for crude oils or other oils which set to solid or semi-solid masses at ordinary temperatures. The retorts are  $\square$ -shaped, and are worked in pairs. The higher retort has a tray placed in it, on which is received the oil to be distilled. The intention of the tray is to keep the cold oil from falling on the hot retort surface and probably damaging it. Besides this, however, it acts as a vapouriser and as a collector of much of the carbon deposited from the oil, and thus aids in cleaning the retort. The oil, having become vapourised and partially broken up or decomposed in this upper retort, passes by a neck-piece, situated at the back of the higher retort, downwards to the lower retort, where, meeting with a higher temperature, the decomposition into permanent gas is fully accomplished. The gas then passes to the tar pit, where some dark liquid is deposited, and thence to condensers where it is cooled, and to a washer and purifier, from which it goes to the gas-holder. The condensers have nothing very novel about them, but the washer deserves description. It consists of a cylindrical column, in which is suspended an iron tray with a corrugated under surface, so constructed as to spread the gas and compel it to come

in contact with the water. The gas passes by perforations in the side of the tray to the upper gas chamber, and thence by a pipe to the purifier. This latter is of the usual pattern, except that the iron tray gives place to a basket-work square, on which is placed the mixture of oxide of iron and sawdust intended to remove any sulphur compounds that may be in the gas.

The quantity of gas produced by this apparatus may run as high as 90 cubic feet per gallon of oil, but in ordinary working from 80 to 85 cubic feet is looked upon as a fair return. For each 1000 cubic feet of gas made about 4 gallons of tar is obtained. This tar has not been very fully investigated, but in some experiments I made I was successful in isolating several members of the benzene series, some olefines and acetylenes, and a considerable proportion of naphthalene. It is said to find a market on the Continent, but, so far as my own experience goes, it is generally consumed as a fuel below the steam-boiler employed to compress the gas. It yields a good heat, and is well suited for the purpose. At the same time it appears to be a great pity that so much valuable material should be lost. Generally, the Pintsch gas is employed for the lighting of railway carriages, floating buoys, light-houses, lightships, &c. In such cases the gas is compressed by powerful pumps into steel cylinders under a pressure of about 13 atmospheres. These store cylinders then supply the smaller portable cylinders, which, in the case of railway carriages, are generally fixed below the flooring. On the Thames and Clyde, as well as several other home rivers, Messrs. Pintsch have supplied floating buoys. These are generally spherical in form, with the lower part removed and an inverted saucer-shaped bottom rivetted on. This form of bottom is found the best to overcome the force of a current. The sphere is surmounted by an iron superstructure holding the lamp and lenses. In the newer form the gas receiver is an independent receptacle placed inside the outer sphere. By this means the risk of damage by collision is, to a great extent, overcome. These gas buoys are usually charged at a pressure of from 5 to 10 atmospheres; have a consumption of 0.75 cubic foot per hour; a flame with a candle power equal to about 5 standard candles, but which, by means of lenses, is increased to an apparent 17 to 20 candles; and burn night and day without recharging for fully 100 days. The buoys are recharged as nearly as possible each two months, but, having a much larger storage power, can be safely left for a much longer period. At first some difficulty was found in keeping the lights burning, but by a very simple form of concussion box this difficulty has been completely overcome, and I am informed by the inspector of the Clyde Navigation Trust that such a thing as a light becoming extinguished is unknown.

Besides these buoys, the Clyde Navigation Trust have several light towers, lighthouses, &c., working with the gas.

As showing the ease of working and saving of cost, I may instance the Garmoyle lightship, which previously required the regular attendance of a man and his wife, with an outlay for wages, oil, &c., of nearly £150 per annum. Now there is no attendant on board, and the gas is charged to two steel cylinders once each two months. The supply of gas is much in excess of the two months' requirements, and on one occasion the gas did not require replenishing till after fully three months, and then it was not exhausted. The cost for gas is about £12 to £16 per annum. The light burns continuously, and requires little or no attention.

All of the Clyde installations are fed from one gas-works, situated at Port Glasgow, the gas being carried to the various points by a specially-constructed screw steamer, the "Torch." This beautiful little vessel carries two steel cylinders, which are kept fully charged; and the boat is always ready to go to any point should an accident occur. So far only one instance has taken place in which her services have been necessary.

The Pintsch gas is also used for gas engines, at Toward

Point and Little Cumbrae. The apparatus at Toward Point is of one horse-power and works a fog bell; the Little Cumbrae gas-engine is of six horse-power, and is used to blow the siren.

During the compression of the gas a certain amount of loss is sustained by the condensation of part of the luminants. This condensation is equal to about one gallon of hydrocarbon per 1000 cubic feet of gas, and the loss of illuminating power is nearly 20 per cent. The initial candle power of the gas is equal to about 50 standard candles for each 5 cubic feet burned.

The products under this system may shortly be said to be, for 12½ gallons of oil, 1000 cubic feet of gas, 4 gallons of tar, and 1 gallon of hydrocarbon. The hydrocarbon consists largely of benzenes.

Many statistics have been published by the various companies using this apparatus as to the cost of the gas. Two of the largest railway companies put the cost, after deducting residuals, but exclusive of distribution or interest on plant, at 6s. per thousand cubic feet, and their make at from 78 to 80 cubic feet per gallon of oil.

(To be continued).

## THE ORGANIC ELEMENTS.

By W. PREYER.

THE fourteen organic elements of the first order take a prominent position in the genetic system. They all belong to the first and second generation, consequently to the oldest elements. Thirteen of them are placed on the first, the second, and the third stage of condensation, iron alone is found on the fourth, and their distribution among the seven branches is characteristic. To Branch I. belong Na and K; to II., Mg, Ca, and Fe; to IV., C and Si; to V., N and P; to VI., O and S; to VII., F and Cl; whilst H precedes all the others. Group III. contains no organic element of the first order. The differences between the atomic weights are:—

Na } 16.08	Mg } 15.76	C } 16.33.
K } 16.08	Ca } 15.92	Si } 16.33.
N } 16.98	O } 16.06	F } 16.4.
P } 16.98	S } 16.06	Cd } 16.4.

The elements of terrestrial protoplasm, as it now exists, display more manifold relations than to all the other elements, and agree with the assumption that the organic elements, before being so condensed as they are now on the earth's surface, formed protoplasms capable of persisting at higher temperatures, and being possibly biophores—vehicles of life in other places.

In order to obtain a nearer insight into the properties of the elements of protoplasm which enable it to form living bodies, I have for many years collected facts on the occurrence of the organic elements of the second order in the protoplasm of plants and animals. The following are the elements in question:—L, Bo, Al, Ti, Cr, Mn, Cu, Zn, As, Br, Rb, Sr, I, Cs, Ba, whilst the remainder seem to occur in living plants and animals only if their compounds have been artificially introduced.

The question in how far the organic elements of the second order may, at least, temporarily replace or substitute those of the first order has, in spite of its profound interest, been as little thoroughly examined as the other on which it depends, that the compounds of the majority of all the elements, those especially with higher atomic weights and low specific heats, are not capable of being assimilated by the animals and plants living at present upon the surface of the earth.

Too little has also been ascertained with certainty on the occurrence of the organic elements in the sun, and in

other fixed stars, to allow us to conclude with certainty as to the composition of the protoplasms of remote worlds capable of living at high temperatures. But, as I have shown elsewhere, it can no longer be doubted that prior to the present telluric protoplasm and zoöplasm, there lived another ultimately derived from the sun.

In this respect it is noteworthy that of the fourteen elements of our organism eight have been certainly recognised in the sun (H, Na, K, Mg, Ca, Fe, Si), three do not seem present in the solar atmosphere (N, P, S), three (O, Cl, F) are doubtful.—*Das Genetische System der Chemischen Elemente.*

### DETERMINATION OF MALIC ACID.

By C. MICKO.

As the extractive substances and inorganic acids present in wine are partially precipitated on throwing down the malic acid with lead acetate, the author's method is so contrived that phosphoric and sulphuric acids, as also much of the organic substances, are partly thrown down and partly destroyed. This is especially the case with tannin and the colouring-matter of wine, so that at last the filtrates are either faintly coloured or, as in ciders, almost colourless. The extractive matters which remain in solution, if acidulated with acetic acid and treated with lead acetate and an excess of alcohol at from 80 to 85 per cent, give no precipitates.

The determination, in which it must be remembered that any chlorides present may occasion a separation of lead chloride, is arranged as follows:—

100 c.c. of wine are evaporated down to a few c.c. on the water-bath, the residue is put in a flask, and allowed to stand for an hour at the common temperature with the addition of 4 to 5 c.c. bi-normal sulphuric acid. It is then gradually mixed, with constant agitation, with 50 c.c. of strong alcohol and 50 c.c. of ether and allowed to stand for from six to ten hours. During this time, the constituents insoluble in ether-alcohol have been deposited. We filter, wash the precipitate with ether-alcohol, add 100 c.c. water to the filtrate in order to prevent the etherification of the acids, distil off the greater part of the ether-alcohol on the water-bath, and lastly expel the last traces of the alcohol by distillation in a vacuum. After refrigeration to from 50° to 60°, the chlorine is precipitated with a fresh preparation of silver sulphate, using the smallest possible excess. At this temperature, in presence of free sulphuric acid, there occurs only a slight reduction of the silver.

After the silver chloride is deposited, the filtrate is neutralised with potassium carbonate, and evaporated down to a small volume. The solution is then further treated exactly as directed in *Zeit. Anal. Chemie* (xxx., 465) for separating malic acid from succinic, citric, and tartaric acid. In case of ciders, the portion taken for analysis should not exceed 50 c.c.—*Oester. Apotheker Vereine.*

### THE TOXICOLOGICAL SIGNIFICATION OF COPPER.

THIS much-contested question, with especial reference to preserved vegetables (peas, &c.),—which are obtained of a fine green colour by an addition of copper salts—has been closely examined by Prof. K. B. Lehmann (*Elfte Versammlung der freien Vereinigung Bayerischer Vertreter der Angewandten Chemie*, p. 16) and others. It is known that Galippa found in grain, per kilo., from 5 to 10 m.grms.; flour, 8 m.grms.; bread, from 1 to 4 m.grms.; potatoes, 2 m.grms.; green beans, 2.2 m.grms.; lentils, 6.8 m.grms.; beans, from Soissons, 11 m.grms.; cocoa, 11 to 29 m.grms.; chocolate, 5.20 m.grms. copper. In 1

kilo. of beef there is found 1 m.grm. copper; in 1 kilo. of human liver, from 3 to 15 m.grms. Sheep's liver, according to Lehmann's analysis, contains, per kilo., 18 m.grms.; calf liver, 48 m.grms.; ox liver, 51 m.grms.; dogs, and cats' liver, 10 to 12 m.grms.; ox, sheep, and rabbit kidney, 3.8 to 8 m.grms. of copper. On the regular consumption of small quantities of copper, the proportion of copper in the urine is not increased, as it seems to be retained by the liver. The results in the last experiments remained the same, whether the Bunsen burners used in the necessary chemical operations were of brass—a material containing copper—or of iron.

In a kilo. of fruit coloured, according to the rules of art, with copper salts, Mayrhofer found only 151–76 m.grms.; in vegetables, from 25 to 45 m.grms. copper. He is of opinion that 25 m.grms. of copper is perfectly sufficient for the purpose of the green staining, the fixation of the chlorophyll, according to Tschirch, as copper phyllocyanate. The proportion of copper in vegetables carelessly stained with copper may reach 270 m.grms. per kilo. without being especially recognised by the taste.

According to Lehmann's own experiments, which agree with numerous other scientific observations, small doses of copper, even on prolonged ingestion, are endured without any inconvenience. Doses of copper salts which introduce into the system, along with the food, about 100 m.grms. of copper, occasion light disturbances of health, a bad after-taste, vomiting, &c., but nothing further.

Small doses of copper have proved so harmless that Mayrhofer's notion—"On the basis of present experience, a proportion of 25 m.grms. copper in 1 kilo. of preserved vegetables cannot be regarded as injurious to health,"—was unanimously adopted at the Congress of Bavarian Chemists.

### FOGS, CLOUDS, AND LIGHTNING.\*

By SHELFORD BIDWELL, M.A., LL.B., F.R.S.

THE air, as every one knows, is composed almost entirely of the two gases, oxygen and nitrogen. It also contains small quantities of other substances, of which the chief are carbonic acid gas and water vapour, and it is the latter of these constituents, water vapour, or "steam," as it is sometimes called, that will principally concern us this evening.

The quantity of invisible water vapour which the air can at any time take up depends upon the temperature; the higher the temperature of the air the more water it can contain. The proportion, however, never exceeds a few grains' weight of water to a cubic foot of air. Air at any temperature, containing as much water as it can possibly hold, is said to be "saturated," while the temperature at which air containing a certain proportion of water becomes saturated is called the "dew point."

The water vapour contained in the atmosphere plays a very important part in many natural phenomena. Among other things, it is the origin of clouds and of fogs. If a body of air containing water in the form of invisible vapour is quickly cooled to a temperature below its dew point, a portion of the vapour becomes condensed into a number of minute liquid particles of water, forming a visible mist, which, when it is suspended in the upper regions of the air, is called a cloud, and when it rests upon the surface of the earth is only too familiarly known as a fog.

The cooling of water-laden air may be brought about in various ways, resulting in the formation of clouds of several distinct characters. [Photographic examples of cumulus, stratus, and cirrus clouds were exhibited upon the screen.] For experimental purposes a small body of

\* A Lecture delivered at the Royal Institution of Great Britain, May 5, 1893.

air may be most conveniently cooled by allowing it to expand. I have here a flask of air which can be connected with the partially exhausted receiver of an air-pump. Inside the flask is an electrical thermometer or thermo-junction, the indications of which can be rendered evident to all present by the movement of a spot of light upon a scale attached to the wall. A deflection of the spot of light to the left indicates cold, to the right heat. When the stop-cock is opened, so that a portion of the air escapes from the flask into the air-pump receiver, you see at once a violent movement of the spot of light to the left, showing that the expansion of the air is accompanied by a fall of temperature. If more air from the room is allowed to enter the flask, the spot moves in the opposite direction.

The large glass globe, upon which the beam from the electric lantern is now directed, contains ordinary air kept in a state of saturation, or nearly so, by the presence of a little water. You will observe that although heavily laden with water vapour the air is perfectly transparent. If, now, we turn a tap and so connect the globe with the exhausted receiver, the air expands and becomes colder; the space inside the globe is no longer able to hold the same quantity of water as before in the form of vapour, and the excess is precipitated as very finely-divided liquid water,—water dust it may be called,—which fills the globe and is perfectly visible as a cloud or mist. In a few minutes the cloud disappears, partly, no doubt, because some of the particles of water have fallen to the bottom of the vessel, but chiefly because the air becomes in time warmed up to its original temperature (that of the room), and the suspended water is converted back again into invisible vapour.

Now let us repeat the experiment, and before the cloud has time to disperse let us admit some fresh air from outside. The cloud, as you see, vanishes in an instant. The compression of the air raises the temperature above the dew point, and the small floating particles of water are transformed into invisible vapour.

I once more rarefy the air, and admit a fresh supply while holding the flame of a spirit lamp near the orifice of the inlet pipe, so that some of the burnt air is carried into the interior of the globe. When the air is again expanded a cloud is formed, which is, as you observe, far more dense than the others were. It appears on examination that the increased density of this cloud is not due to the condensation of a greater quantity of water. Little, if any, more water is precipitated than before. But the water particles are now much more numerous, their increased number being compensated for by diminished size. Within certain limits the greater the number of particles into which a given quantity of water is condensed the greater will be the apparent thickness of the mist produced. A few large drops will not impede and scatter light to the same extent as a great number of small ones, though the actual quantity of condensed water may be the same in each case.

Then comes the question, why should the burnt air from the flame so greatly increase the number of the condensed drops? An answer, though perhaps not quite a complete one, is furnished by some remarkable experiments made by M. Coulier, a French professor, nearly twenty years ago. He believed his experiments pointed to the conclusion that water vapour would not condense at all, even at temperatures far below the dew point, unless there were present in the air a number of material particles to serve as nuclei, around which the condensation could take place. All air, he says, contains dust; by which term he does not mean such dust as is rendered evident in this room by the light scattered along the track of the beam issuing from the electric lantern, which consists of comparatively gross lumps of matter, but particles of ultra-microscopical dimensions, "more tenuous than the motes seen in a sunbeam." It is upon such minute specks of matter that water vapour is condensed. Anything that increased the number of dust particles in the

air increased the density of the condensation by affording a greater number of nuclei. Air in which a flame had been burnt he supposed to be very highly charged with finely-divided matter, the products of combustion, and thus rendered extraordinarily "active" in bringing about condensation. And that, according to Coulier's view, is the reason why such a dense fog was formed when air which had been contaminated by the spirit flame was admitted to our globe.

On the other hand, air, even burnt air, which has been filtered through tightly-packed cotton-wool, is found to be perfectly inactive. No cloud or mist will form in it, however highly it may be super-saturated. Coulier explained this fact by supposing that the process of filtration completely removed all dust particles from the air.

On the table before you is a globe containing air which has been thus treated, and which is kept saturated by a little water. When this globe is connected with the exhausted receiver, no trace of any mist is produced: the air remains perfectly clear. We will now admit a little of the ordinary air from outside, and again cool it by expansion. Quite a respectable cloud is thereupon formed in the globe.

The experiments of Coulier were repeated and confirmed by Mascart. The latter also made one additional observation, which may very probably turn out to be of great importance. He found that ozone, or rather strongly ozonised air, was a very active mist producer, and that, unlike ordinary air, it was not deprived of its activity by filtration.

Four or five years later, all the facts which had been noticed by Coulier, and others of an allied nature, were independently discovered by Mr. Aitken, who has devoted much time and study to them and made them the foundation of an entirely new branch of meteorology.

Later, perhaps, we may see reason to doubt whether all the conclusions of Coulier and Aitken are quite accurate, especially as regards the action of so-called products of combustion.

What has been said so far applies equally to the generation of clouds and of country fog, for a pure unadulterated fog, such as occurs in rural districts, consists simply of a cloud resting upon the surface of the earth. The fogs, however, which afflict many large towns, and London in a marked degree, appear to possess a character peculiar to themselves. They are distinguished by a well-known colour, which has sometimes been likened to that of pease soup: their density is abnormal, so is their persistence; and they often occur when the temperature of the air is considerably above the dew point. But what renders them especially objectionable is their acrid and corrosive quality, in virtue of which they exert a highly deleterious action upon animal and vegetable life.

The uncleanness of a town fog is of course due to the sooty and tarry matters with which it is charged, and which are derived from the smoke of innumerable fires. Its other and more mischievous specialities are mainly attributable to certain products of the combustion of sulphur, a substance which exists in relatively large proportions (from half to one per cent) in nearly all varieties of coal.

We may make a sample of London fog in the glass globe by burning a little sulphur near the orifice of the inlet pipe while air is being admitted; and in order to prevent the entrance of any solid particles of sublimed sulphur, we will filter the air through a little cotton-wool. The fog formed when the air is expanded far exceeds in density any we have yet seen. The globe appears almost as if it were filled with something that could be cut with a knife.

This is hardly the time or the place to discuss the possible methods by which town fogs might be abolished as such, or rendered as innocuous as those of the country. It is impossible to doubt that year by year they are increasing in virulence, and when the burden of the evil becomes too grievous to be borne, as is likely to be the

case before many more winters are passed, the remedy will perhaps be found in the compulsory substitution of gas for coal as the ordinary domestic fuel.

Everyone has noticed how dense and dark a thunder-cloud is. It shuts out daylight almost as if it were a solid substance, and the glimmer that penetrates it is often imbued with a lurid or copper-coloured tint.

I had always found it rather difficult to believe that these peculiarities were due simply to the unusual extent and thickness of the clouds, as is commonly supposed to be the case, and it occurred to me about three years ago that perhaps some clue to the explanation might be afforded by the electrification of a jet of steam. On making the experiment I found that the density and opacity of the jet were greatly increased when an electrical discharge was directed upon it, while its shadow, if cast upon a white screen by a sufficiently strong light, was of a decidedly reddish brown tint.

As a possible explanation of the effect, I suggested that there might occur some action among the little particles of water of a similar nature to that observed by Lord Rayleigh in his experiments upon water jets. Perhaps you will allow me to show his fundamental experiment before further discussing the steam jet.

A jet of water two or three feet long is made to issue in a nearly vertical direction from a small nozzle. At a certain distance above the nozzle the continuous stream is found to break up into separate drops, which collide with one another, and again rebounding become scattered over a considerable space. But when the jet is exposed to the influence of an electrified substance, such as a rubbed stick of sealing-wax, the drops no longer rebound after collision, but coalesce, and the entire stream of water, both ascending and descending, becomes nearly continuous. Look at the shadow of the jet upon the screen, and notice what a magical effect the electrified sealing-wax produces.

There is one other point to which I wish to direct your particular attention. If the sealing-wax, or better, the knob of a charged Leyden jar, is held very close to the jet, so that the electrical influence is stronger, the separate drops do not coalesce as before, but become scattered even more widely than when no electrical influence was operating. They become similarly electrified and, in accordance with the well-known law, repel one another.

We will now remove the water jet, and in its place put a little apparatus for producing a jet of steam. It consists of a half-pint tin bottle, through the cork of which passes a glass tube terminating in a nozzle. When the water in the bottle is made to boil a jet of steam issues from the nozzle, and if we observe the shadow of the steam jet upon the screen we shall see that it is of feeble intensity and of a neutral tint, unaccompanied by any trace of decided colour. A bundle of needles connected by a wire with the electrical machine is placed near the base of the jet, and when the machine is worked electricity is discharged into the steam. A very striking effect instantly follows. The cloud of condensed steam is rendered dense and dark, its shadow at the same time assuming the suggestive yellowish brown colour.

I at first believed that we had here a repetition, upon a smaller scale, of the phenomenon which occurs in the water jet. The little particles of condensed water must frequently come into collision with one another, and it seemed natural to suppose that, like Lord Rayleigh's larger particles, they rebounded under ordinary circumstances, and coalesced when under the influence of electricity. The great majority of the small particles ordinarily formed consisted, I thought, of perhaps only a few molecules, which were dispersed in the air and again converted into vapour without ever having become visible, while the larger particles formed by their coalescence under electrical action were of such dimensions as to impede the more refrangible waves of light. Hence the brownish yellow colour.

Other explanations have been proposed. There is the

molecular shock theory of the late R. Helmholtz (who, as it turned out, had studied electrified steam jets before I made my own experiments); I shall refer to his speculation later. And there is the dust-nucleus theory, which no doubt appears a very obvious one.

Though I knew that my own hypothesis was not quite free from objection, neither of these alternative ones commended itself to me as preferable; and so the matter rested until a few months ago, when the steam jet phenomenon was discussed anew in a paper communicated to the Royal Society by Mr. Aitken. Mr. Aitken said that he did not agree with my conjecture as to the nature of the effect. This led me to investigate the matter again, and to make some further experiments, the results of which have convinced me that I was clearly in error. At the same time it seems to me that the explanation which Mr. Aitken puts forward is little less controllable than my own. Mr. Aitken's explanation of the phenomenon is, like mine, based upon Lord Rayleigh's work in connection with water jets, but, unlike mine, it depends upon the experiment which shows that water particles when strongly electrified are scattered even more widely than when unelectrified. He believes, in short, that electrification produces the effect, not by promoting coalescence of small water particles, but by preventing such coalescence as would naturally occur in the absence of electrical influence. In the electrified jet, he says, the particles are smaller but at the same time more numerous; thus its apparent density is increased.

The chief flaw in my hypothesis lies in the fact that the mere presence of an electrified body like a rubbed stick of sealing wax, which is quite sufficient to cause coalescence of the drops in the water jet, has no action whatever upon the condensation of the steam jet. There must be an actual discharge of electricity. But it is by no means essential, as Mr. Aitken assumes, that this discharge should be of such a nature as to electrify, positively or negatively, the particles of water in the jet. If, instead of using a single electrode, we employ two, one positive and the other negative, and let them spark into each other across the jet, dense condensation at once occurs. [Experiment.] So it does if the two discharging points are removed quite outside the jet. [Experiment.] A small induction coil giving sparks an eighth of an inch in length causes dense condensation when the electrodes are more than an inch distant from the nozzle and on the same level. [Experiment.] In one experiment a brass tube two feet long was fixed in an inclined position with its upper end near the steam jet, and its lower end above the electrodes of the induction coil. In about three seconds after the spark was started dense condensation ensued, and it ceased about three seconds after the sparking was stopped. No test was needed, though in point of fact one was made, to show that the steam was not electrified to a potential of a single volt by this operation. And the time required for the influence to take effect showed that whatever this influence might be it was not induction.

The inference clearly is that in some way or other the action is brought about by the air in which an electrical discharge has taken place, and not directly by the electricity itself. The idea has no doubt already occurred to many of you that it is a dust effect. Minute particles of matter may be torn off the electrodes by the discharge, and form nuclei upon which the steam may condense. The experiments of Liveing and Dewar have indeed shown that small particles are certainly thrown off by electrical discharge, and the idea that such particles promote condensation appears to be supported by the fact that if a piece of burning material, such as touch-paper, is held near the jet so that the products of combustion can pass into it, thick condensation is produced. [Experiment.]

From a recent paper by Prof. Barus, published in the *American Meteorological Journal* for March, it appears that he also is of opinion that such condensation is in all cases due to the action of minute dust particles. Yet it

is remarkable that Mr. Aitken, the high priest and chief apostle of the philosophy of dust, gives no countenance to the nucleus theory. He does not even advert to its possibility. I imagine that his experiments have led him, as mine have led me, to the conclusion that it is untenable. And this not only in the case of electrical discharge, but also in the case of burning matter.

If we cause an electrical discharge to take place for some minutes inside a suitably arranged glass bottle, and then, ten or fifteen seconds after the discharge has ceased, blow the air from the bottle into the steam jet, the condensation is not in any way effected. Yet the dust could not have subsided in that time. And again, if we fill another large bottle with dense clouds of smoke by holding a bundle of burning touch-paper inside it, and almost immediately after the touch-paper is withdrawn, force out the smoke-laden air through a nozzle, upon the jet—you can all see the black shadow of the smoke upon the screen—nothing whatever happens to the jet. Yet a mere scrap of the paper which is actually burning, though the ignited portion may not be larger than a pin's head, at once darkens the jet. Dead smoke (if I may use the term) exerts little or no influence by itself: there must be incandescent matter behind it. The question naturally arises, whether incandescent matter may not be sufficient of itself, without any smoke at all? We can test this by making a piece of platinum wire red hot and then holding it near the jet. It is seen to be quite as effective as the burning touch-paper. Yet here there can be no nuclei formed of products of combustion, for there is no combustion; there is simply ignition or incandescence.

One other point I may mention. It is stated by Barus in the paper above referred to that the fumes given off by a piece of phosphorus constitute a most efficient cause of dense condensation. This is true if they come directly from a piece of phosphorus; but if phosphorus fumes are collected in a bottle and then directed upon the jet, all traces of unoxidised phosphorus being first carefully removed, they are found to be absolutely inoperative. Phosphorus in air can hardly be said to be incandescent, though it is luminous in the dark; but it appears to act in the same manner as if its temperature were high.

All these facts seem to indicate that the several causes mentioned—electrical, chemical, and thermal—confer upon the air in which they act some temporary property—certainly not due to mere inert dust—in virtue of which it acquires an abnormal power of promoting aqueous condensation.

I thought that possibly some clue as to the nature of this property might be obtained by observing how some other gases and vapours behaved; but though the experiments I made perhaps tend to narrow the dimensions of the mystery, I cannot say that they have completely solved it. Indeed some of the results only introduce additional perplexities.

One of the most natural things to try is hydrochloric acid, which is known to have a strong affinity for water. If we heat a little of the acid solution in a test-tube, closed with a cork, through which a glass tube is passed, and direct the issuing stream of gas upon the jet, the densest condensation results. [Experiment.] The vapours of sulphuric and nitric acids also cause dense condensation, and I suppose both of these have an affinity for water. But so also, and in an equally powerful degree, does the vapour of acetic acid; yet the affinity of this acid for water, as indicated by the heat evolved when the two are mixed, is very small.

(To be continued).

Variations of the Electric Conditions of High Regions of the Atmosphere.—Ch. André.—The observations made showed that in fine weather the electric field does not necessarily increase with the altitude; it is the same at the same instant along the same vertical line.—*Comptes Rendus*, cxvii., No. 22.

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 272).

C. In Silver Bromide.—If we expose silver bromide to the luminous rays it soon takes a blue greyish violet colour. This circumstance could not be overlooked in the investigation of its transparency. I have taken it so far into account as to reduce the exposure to a minimum in taking proofs. The very energetic sparks required were yielded by the above-named influence machine in connection with the Riess battery, but an inductorium was also employed. That my silver bromide screen must have assumed a colour is involved in the nature of the case, though the appearance was invariably contrary. Whether and in how far this colouration has been manifested in the absorption spectra it did not appear with certainty. But from one circumstance it may be inferred that it cannot have any great importance: the first and the last proof of the same screen did not essentially differ from each other.

The silver bromide for the screens, like that of the dry gelatin plate, was prepared with an excess of alkaline bromide, then washed, and the quartz plate used for the gelatin experiments coated therewith in a wedge-shaped layer and dried. As with the gelatin the coating of the plate was here also scraped away for a short extent, but only in three plates of increasing thickness. In this manner there were obtained three screens of different thickness for the rays. The thickness of these screens I have not been able to ascertain. The micrometer used for gelatin was quite useless on account of the liability of the coating of the plate to suffer injury, and the microscope was not certain enough. The use of the screen-plate in taking photographs was here as with gelatin. The proofs this time extended, not as in the former cases merely to the most refrangible ultra-violet, but they comprise the entire region from the Fraunhofer line D to the most refrangible rays of the aluminium.

I selected a wider spectral region than in the former proofs in order to acquire a better insight into the absorption relations of the silver bromide. The plates for this purpose contained erythrosine silver, which is well known to confer on bromine silver gelatin a remarkable sensitiveness to the yellow. For electrodes of the influence machine there were used two brass balls, which yielded a very efficient light. With a slit of 0.020 m.m. in width a single spark showed the spectrum in an almost uninterrupted succession of its lines from D to the wave length 200  $\mu\mu$ . For the most refrangible rays there were again used aluminium electrodes and the inductorium.

The total result of these proofs may be briefly summed up by saying that the silver bromide employed absorbs energetically all the rays of the region in question, even the cyanic blue, the green, and the yellow. Even the thinnest of the three layers, although to the eye strongly translucent, almost totally kept back the light of a single spark. The thicker layers did the same even on a rather more prolonged exposure. If we compare the spectra photographed with the same time of exposure we find that the absorption in silver bromide extends almost uniformly over the entire spectrum, but that the most refrangible rays from about the wave-length 210  $\mu\mu$  are rather less affected. This part of the spectrum is everywhere relatively rather more powerful than the other spectrum. Hence if the degree of the absorption afforded a certain standard for sensitiveness, the sensitiveness of silver bromide must decrease somewhat towards the more refrangible side. But I cannot ascribe too high a value to this

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II April, 1893).

conclusion, since it is sufficiently known from the foregoing that the lines of this region are in general paler than the others. In consequence the contrast of intensity between parallel proofs varies within such narrow limits that its estimation is always involved in considerable uncertainty.

According to these proofs we may assume that silver bromide is sufficiently sensitive for photographing the unknown ultra-violet, and that the want of intensity from which my proofs suffered must be referred to the presence of gelatin.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### THE ROYAL SOCIETY.

Anniversary Meeting, November 30th, 1893.

Address of the President, LORD KELVIN, D.C.L., LL.D.

(Concluded from p. 279).

FARADAY, with his curved lines of electric force, and his dielectric efficiency of air and of liquid and solid insulators, resuscitated the idea of a medium through which, and not only through which but *by* which, forces of attraction or repulsion, seemingly acting at a distance, are transmitted. The long struggle of the first half of the Eighteenth Century was not merely on the question of a medium to serve for gravific mechanism, but on the correctness of the Newtonian law of gravitation as a matter of fact however explained. The corresponding controversy in the Nineteenth Century was very short, and it soon became obvious that Faraday's idea of the transmission of electric force by a medium not only did not violate Coulomb's law of relation between force and distance, but that, if real, it must give a thorough explanation of that law.\* Nevertheless, after Faraday's discovery† of the different specific inductive capacities of different insulators, twenty years passed before it was generally accepted in Continental Europe. But before his death, in 1867, he had succeeded in inspiring the rising generation of the scientific world with something approaching to faith that electric force is transmitted by a medium called ether, of which, as had been believed by the whole scientific world for forty years, light and radiant heat are transverse vibrations. Faraday himself did not rest with this theory for electricity alone. The very last time I saw him at work in the Royal Institution was in an underground cellar, which he had chosen for freedom from disturbance; and he was arranging experiments to test the time of propagation of magnetic force from an electro-magnet through a distance of many yards of air to a fine steel needle polished to reflect light; but no result came from those experiments. About the same time, or soon after, certainly not long before the end of his working time, he was engaged (I believe at the shot-tower near Waterloo Bridge on the Surrey side) in efforts to discover relations between gravity and magnetism, which also led to no result.

Absolutely nothing has hitherto been done for gravity either by experiment or observation towards deciding between Newton and Bernoulli, as to the question of its propagation through a medium, and up to the present time we have no light, even so much as to point a way for investigation, in that direction. But for electricity and magnetism, Faraday's anticipations and Clerk-Maxwell's splendidly developed theory have been established on the sure basis of experiment by Hertz's work, of which his own most interesting account is this year presented to

the world in the German and English volumes to which I have referred. It is interesting to know, as Hertz explains in his introduction, and it is very important in respect to the experimental demonstration of magnetic waves to which he was led that he began his electric researches in a problem happily put before him thirteen years ago by Professor von Helmholtz, of which the object was to find by experiment some relation between electromagnetic forces and dielectric polarisation of insulators, without, in the first place, any idea of discovering a progressive propagation of those forces through space.

It was by sheer perseverance in philosophical experimenting that Hertz was led to discover a finite velocity of propagation of electromagnetic action, and then to pass on to electromagnetic waves in air and their reflection, and to be able to say, as he says in a short reviewing sentence at the end of his eighth paper: "Certainly it is a fascinating idea that the processes in air which we have been investigating, represent to us on a million-fold larger scale the same processes which go on in the neighbourhood of a Fresnel mirror, or between the glass plates used for exhibiting Newton's rings."

Professor Oliver Lodge has done well, in connection with Hertz's work, to call attention\* to old experiments, and ideas taken from them, by Joseph Henry, which came more nearly to an experimental demonstration of electromagnetic waves than anything that had been done previously. Indeed Henry, after describing experiments showing powerful enough induction due to a single spark from the prime conductor of an electric machine to magnetise steel needles at a distance of 30 feet in a cellar beneath with two floors and ceilings intervening, says that he is "disposed to adopt the hypothesis of an electrical plenum," and concludes with a short reviewing sentence: "It may be further inferred that the diffusion of motion in this case is almost comparable with that of a spark from a flint and steel in the case of light."

Professor Oliver Lodge himself did admirable work in his investigations with reference to lightning-rods,† coming very near to experimental demonstrations of electromagnetic waves; and he drew important lessons regarding "electrical surgings" in an insulated bar of metal "induced by Maxwell's and Heaviside's electromagnetic waves," and many other corresponding phenomena manifested both in ingenious and excellent experiments devised by himself and in natural effects of lightning.

Of electrical surgings or waves in a short insulated wire, and of interference between ordinary and reflected waves, and of positive electricity appearing where negative might have been expected, we hear first, it seems, in Herr von Bezold's "Researches on the Electric Discharge" (1870), which Hertz gives as the third paper of his collection, with interesting and ample recognition of its importance in relation to his own work.

In connection with the practical development of magnetic waves, you will, I am sure, be pleased if I call your attention to two papers by Professor G. F. Fitzgerald, which I heard myself at the meeting of the British Association at Southport, in 1883. One of them is entitled "On a Method of Producing Electromagnetic Disturbances of comparatively Short Wave-lengths." The paper itself is not long, and I shall read it to you in full, from the "Report of the British Association," 1883:—"This is by utilising the alternating currents produced when an accumulator is discharged through a small resistance. It is possible to produce waves of as little as 2 metres wave length, or even less." This was a brilliant and useful suggestion. Hertz, not knowing of it, used the method; and, making as little as possible of the "accumulator," got waves of as little as 10 c.m. wave-length in many of his fundamental experiments. The title alone of Fitzgerald's other paper, "On the Energy Lost by

\* "Electrostatics and Magnetism," Sir W. Thomson, Articles I. (1842) and II. (1845), particularly § 25 of Art. II.  
† 1837, "Experimental Researches," 1161—1306.

\* "Modern Views of Electricity," pp. 369—372.

† "Lightning Conductors and Lightning Guards," Oliver J. Lodge, D.Sc., F.R.S. Whittaker and Co.

Radiation from Alternating Currents," is in itself a valuable lesson in the electromagnetic theory of light, or the undulatory theory of magnetic disturbance. It is interesting to compare it with the title of Hertz's eleventh paper, "Electric Radiation"; but I cannot refer to this paper without expressing the admiration and delight with which I see the words "rectilinear propagation," "polarisation," "reflection," "refraction," appearing in it as sub-titles.

During the fifty-six years which have passed since Faraday first offended physical mathematicians with his curved lines of force, many workers and many thinkers have helped to build up the Nineteenth Century school of *plenum*; one ether for light, heat, electricity, magnetism; and the German and English volumes containing Hertz's electrical papers, given to the world in the last decade of the century, will be a permanent monument of the splendid consummation now realised.

But, splendid as this consummation is, we must not fold our hands and think or say there are no more worlds to conquer for electrical science. We do know something now of magnetic waves. We know that they exist in nature and that they are in perfect accord with Maxwell's beautiful theory. But this theory teaches us nothing of the actual motions of matter constituting a magnetic wave. Some definite motion of matter perpendicular to the lines of alternating magnetic force in the waves and to the direction of propagation of the action through space, there must be; and it seems almost satisfactory as a hypothesis to suppose that it is chiefly a motion of ether with a comparatively small but not inconsiderable loading by fringes of ponderable molecules carried with it. This makes Maxwell's "electric displacement" simply a to-and-fro motion of ether across the line of propagation; that is to say, precisely the vibrations in the undulatory theory of light according to Fresnel. But we have as yet absolutely no guidance towards any understanding or imagining of the relation between this simple and definite alternating motion, or any other motion or displacement of the ether, and the earliest known phenomena of electricity and magnetism—the electrification of matter, and the attractions and repulsions of electrified bodies; the permanent magnetism of loadstone and steel, and the attractions and repulsions due to it: and certainly we are quite as far from the clue to explaining, by ether or otherwise, the enormously greater forces of attraction and repulsion now so well known after the modern discovery of electromagnetism.

Fifty years ago it became strongly impressed on my mind that the difference of quality between vitreous and resinous electricity, conventionally called positive and negative, essentially ignored as it is in the mathematical theories of electricity and magnetism with which I was then much occupied (and in the whole science of magnetic waves as we have it now), must be studied if we are to learn anything of the nature of electricity and its place among the properties of matter. This distinction, essential and fundamental as it is in frictional electricity, electro-chemistry, thermo-electricity, pyro-electricity of crystals, and piezo-electricity of crystals, had been long observed in the old-known beautiful appearances of electric glow and brushes and sparks from points and corners on the conductors of ordinary electric machines and in exhausted receivers of air-pumps with electricity passed through them. It was also known, probably as many as fifty years ago, in the vast difference of behaviour of the positive and negative electrodes of the electric arc lamp. Faraday gave great attention to it ("Experimental Researches," Series 12 and 13, Jan. and Feb., 1838) in experiments and observations regarding electric sparks, glows, and brushes, and particularly in his "dark discharge" and "dark space" in the neighbourhood of the negative electrode in partial vacuum. In [1523] of his 12th series he says, "The results connected with the different conditions of positive and negative discharge will have a far greater influence on the philosophy of

electrical science than we at present imagine." His "dark discharge" ([1544—1554]) through space around or in front of the negative electrode was a first instalment of modern knowledge in that splendid field of experimental research which, fifteen years later, and up to the present time, has been so fruitfully cultivated by many of the ablest scientific experimenters of all countries.

The Royal Society's *Transactions* and *Proceedings* of the last forty years contain, in the communications of Gassiot (*Roy. Soc. Proc.*, x., 1860, 36, 269, 274, 432), Andrews and Tait (*Ibid.*, x., 1860, 274; *Phil. Trans.*, 1860, 118), Cromwell Varley (*Roy. Soc. Proc.*, xix, 1871, 236), De la Rue and Müller (*Ibid.*, xxiii., 1875, 356; xxvi., 1877, 519; xxvii., 1878, 374; xxix., 1879, 281; xxxv., 1883, 292; xxxvi., 1884, 151, 206; *Phil. Trans.*, 1878, 55, 155; 1880, 65; 1883, 477), Spottiswoode (*Roy. Soc. Proc.*, xxiii., 1875, 356, 455; xxv., 1875, 73, 547; xxvi., 1877, 90, 323; xxvii., 1878, 60; xxix., 1879, 21; xxx., 1880, 302; xxxii., 1881, 385, 388; xxxiii., 1882, 423; *Phil. Trans.*, 1878, 163, 210; 1879, 165; 1880, 561), Moulton (*Roy. Soc. Proc.*, xxix., 1879, 21; xxx., 1880, 302; xxxii., 1881, 385, 388; xxxiii., 1882, 453; *Phil. Trans.*, 1879, 165; 1880, 561), Plücker (*Roy. Soc. Proc.*, x., 1860, 256); Crookes (*Ibid.*, xxviii., 1879, 347, 477; *Phil. Trans.*, 1879, 641; 1880, 135; 1881, 387), Grove (*Roy. Soc. Proc.*, xxviii., 1878, 181), Robinson (*Ibid.*, xii., 1862, 202), Schuster (*Ibid.*, xxxvii., 1884, 78, 317; xlii., 1887, 371; xlvii., 1890, 300, 506), J. J. Thomson (*Ibid.*, xlii., 1887, 343; xlix., 1891, 84), and Fleming (*Ibid.*, xlvii., 1890, 118), almost a complete history of the new province of electrical science which has grown up, largely in virtue of the great modern improvements in practical methods for exhausting air from glass vessels, by which we now have "vacuum tubes" and bulbs containing less than 1-190,000th of the air which would be left in them by all that could be done in the way of exhausting (supposed to be down to 1 m.m. of mercury) by the best air-pump of fifty years ago. A large part of the fresh discoveries in this province have been made by the authors of these communications, and their references to the discoveries of other workers very nearly complete the history of all that has been done in the way of investigating the transmission of electricity through highly rarefied air and gases since the time of Faraday.

Varley's short paper of 1871, which, strange to say, has lain almost or quite unperceived in the *Proceedings* during the twenty-two years since its publication, contains an important first instalment of discovery in a new field—the molecular torrent from the "negative pole," the control of its course by a magnet, its pressure against either end of a pivoted vane of mica according as it is directed by a magnet to one end or the other, the shadow produced by its interception by a mica screen. Quite independently of Varley, and not knowing what he had done, Crookes was led to the same primary discovery, not by accident, and not merely by experimental skill and acuteness of observation. He was led to it by carefully designed investigation, starting with an examination of the cause of irregularities which had troubled\* him in his weighing of thallium; and, going on to trials for improving Cavendish's gravitational measurement, in the course of which he discovered that the seeming attraction by heat is only found in air of greater than 1-1000 (Crookes, "On the Viscosity of Gases at High Exhaustions," § 655, *Phil. Trans.*, Feb., 1881, 403) of ordinary density; and that there is repulsion increasing to a maximum when the density is decreased from 1-1000 to 36-1,000,000, and thence diminishing towards zero as the rarefaction is farther extended to density 1-20,000,000. From this discovery Crookes came to his radiometer, first without and then with electrification, powerfully aided by Sir George Stokes (*Phil. Trans.*, clxxii., 1881, 387, 435); and he brought all his work more and more into touch with the

\* Tribulation, not undisturbed progress, gives life and soul, and leads to success when success can be reached, in the struggle for natural knowledge.

kinetic theory of gases; so much so that when he discovered the molecular torrent he immediately gave it its true explanation—molecules of residual air, or gas, or vapour projected at great velocities\* by electric repulsion from the negative electrode. This explanation has been repeatedly and strenuously attacked by many other able investigators, but Crookes has defended it ("Address to the Institute of Telegraphic Engineers," 189), and thoroughly established it by what I believe is irrefragable evidence of experiment. Skilful investigation perseveringly continued brought out more and more of wonderful and valuable results:—the non-importance of the position of the positive electrode; the projection of the torrent *perpendicularly* from the surface of the negative electrode; its convergence to a focus and divergence thenceforward when the surface is slightly concave; the slight but perceptible repulsion between two parallel torrents due, according to Crookes, to negative electrifications of their constituent molecules; the change of direction of the molecular torrent by a neighbouring magnet; the tremendous heating effect of the torrent from a concave electrode when glass, metal, or any ponderable substance is placed in the focus; the phosphorescence produced on a plate coated with sensitive paint by a molecular torrent skirting along it; the brilliant colours—turquoise-blue, emerald, orange, ruby-red—with which grey colourless objects and clear colourless crystals glow on their struck faces when lying separately or piled up in a heap in the course of a molecular torrent; "electrical evaporation" of negatively electrified liquids and solids (*Roy. Soc. Proc.*, June 11, 1891); the seemingly red-hot glow, but with no heat conducted inwards from the surface, of cool solid silver kept negatively electrified in a vacuum of 1-1,000,000 of an atmosphere, and thereby caused to rapidly evaporate. This last-mentioned result is almost more surprising than the phosphorescent glow excited by molecular impacts in bodies not rendered perceptibly phosphorescent by light. Both phenomena will surely be found very telling in respect to the molecular constitution of matter and the origination of thermal radiation, whether visible as light or not. In the whole train of Crookes's investigations on the radiometer, the viscosity of gases at high exhaustions, and the electric phenomena of high vacuums, ether seems to have nothing to do except the humble function of showing to our eyes something of what the atoms and molecules are doing. The same confession of ignorance must be made with reference to the subject dealt with in the important researches of Schuster and J. J. Thomson on the passage of electricity through gases. Even in Thomson's beautiful experiments showing currents produced by circuital electromagnetic induction in complete poleless circuits, the presence of molecules of residual gas or vapour seems to be *the essential*. It seems certainly true that without the molecules there could be no current, and that without the molecules electricity has no meaning. But in obedience to logic I must withdraw one expression I have used. We must not imagine that "presence of molecules is *the essential*." It is certainly *an essential*. Ether also is certainly *an essential*, and certainly has more to do than merely to telegraph to our eyes to tell us of what the molecules and atoms are about. If a first step towards understanding the relations between ether and ponderable matter is to be made, it seems to me that the most hopeful foundation for it is knowledge derived from experiment on electricity in high vacuum; and if, as I believe is true, there is good reason for hoping to see this step made, we owe a debt of gratitude to the able and persevering workers of the last forty years who have given us the knowledge we have; and we may hope for more and more from some of themselves and from others encouraged by the fruitfulness of their labours to persevere in the work.

\* Probably, I believe, not greater in any case than 2 or 3 kilometres per second.

## NOTICES OF BOOKS.

*The Magic Lantern, its Construction and Use.* By A FELLOW OF THE CHEMICAL SOCIETY. London: Perkin, Son, and Rayment. Small 8vo., pp. 140. Second Edition.

THE magic lantern has now become a most valuable aid to the lecturer and the teacher. It gives far clearer and more intelligible illustrations than can be produced by means of the chalk and black-board, or even by ready-made diagrams. The microscope and the spectroscope are, of course, still as necessary as ever, or rather more necessary; but for placing our results before an audience, or even a numerous class, we must have the lantern.

The work before us gives a very full and practical description of the instrument and its manipulation. With one passage we take the liberty of disagreeing. Says the author: "The earnest worker, in whatever branch he may be engaged, likes to be self-dependent as far as possible." But the earnest worker likes to economise time, and does not want to be detained from actual investigation by preparing his requisites. We should, on this principle, recommend the lanternist, whenever possible, to buy compressed oxygen in cylinders.

Where manganese peroxide is used for the production of oxygen care should be taken that it is not contaminated with native antimony sulphide, a powder very similar in appearance. This impurity, which is sometimes present not from fraudulent intention, but from carelessness, has occasioned serious explosions.

In fine, we must pronounce this little book a most useful guide for lecturers, or for men of science who have to read papers before a Society.

*Foundations of the Molecular Theory*: comprising Papers and Extracts by John Dalton, Joseph Louis Gay-Lussac, and Amadeo Avogadro (1808–1811). Edinburgh: W. F. Clay. London: Simpkin, Marshall, and Co. (Ltd.). 1893.

THIS little work is one of the "Alembic Club Reprints." It gives, in order of time, the papers which exhibit the development of the idea of a connection between the number of particles in different gases and their volume.

Dalton, it will be seen, doubts the accuracy of Gay-Lussac's results. Avogadro accepts at once Dalton's theory and Gay-Lussac's facts, and reconciles them by drawing a distinction between the atom and the molecule of an elementary gas. Ampère's letter to Berthollet (1814) has not been here inserted, as it leaves the question exactly as it had been already done by Avogadro, who had drawn identical conclusions from identical premises.

*Agricultural Journal published by the Department of Agriculture of the Cape Colony.* Vol. vi., No. 20.

THIS paper continues to show great energy. We find that the steel-coloured ladybird, *Orcus chalybeus*, a native of Australia, is now being successfully employed to make war upon the scale insects on the orange and lemon trees. It is to be hoped that this species has not the cannibal propensity of some of the English ladybirds, the larvæ of which greedily devour the pupæ.

The necessity of tree-planting in South Africa is ably insisted upon. The introduction of goats into the Colony was a capital error.

There are complaints of "wireworm" attacking and injuring sheep. The insect (?) in question surely cannot be the *Elater* larva which is so destructive to root-crops.

It is a curious and most unpleasant fact that, if sheep have been exposed to a period of insufficient food, there

occurs in their wool a weak spot which is almost fatal to its utility for manufacturing purposes.

It is not edifying to learn that, as far as fruits are concerned, colonial produce is placed on the same footing as that from alien countries!

*Spirits and the Manufacture of Cognac.* ("Les Eaux-de-Vie et la Fabrication du Cognac"). With Thirty-nine Figures inserted in the Text. By A. BAUDOIN, Director of the Public Laboratory of Agricultural and Industrial Chemistry at Cognac. Paris: J. B. Baillière et Fils. 1893.

M. BAUDOIN, whose official position and wide experience give him an exceptional opportunity to do justice to his subject, has produced a most valuable work on ardent spirits, with especial attention to the brandies of Cognac.

He gives a general account of spirituous liquors, the production of which he traces back to the most remote antiquity. He distinguishes grain-spirits, the spirits obtained from stone-fruits, the rums and tafias, the spirits distilled from cider and those from wine. He is evidently aware of root-spirits,—les eaux-de-mort, as they might fairly be called,—distilled from potatoes and beet-root, but he does not honour them with a special chapter.

Concerning the celebrity of Cognac, the author gives an amusing anecdote. Mgr. Cousseau, a former bishop of Angoulême, used to tell that, dining one day at Rome with some cardinals, he was questioned as to the locality of his see. "I am bishop of Angoulême and the Charente," said he. But as no one seemed to understand he added "I am also bishop of Cognac." At this name all the guests exclaimed, Cognac! Cognac! Cognac! Oh, what a superb bishopric!

The distillation, the composition, and the adulterations of brandies are fully described. It is remarkable that the finest Cognacs are produced by small cultivators who use a very simple plant. But we hear a very similar statement concerning Irish whiskies. The product of the small stills, "potheen," is often found superior to that produced with the most elaborate and costly plant.

Several German recipes are here given for counterfeiting Cognac. But a totally spurious Cognac is even manufactured in the Vaterland, distilled—would it have been imagined?—from the wines of Gruenberg, in Silesia!

M. Baudoin, we suspect, scarcely sees the full absurdity of manufacturing a superior brandy from a wine which in Germany has been proverbial for its unparalleled vileness. There are several grades of Gruenberg, the worst of which is so harsh that if a glass of it is poured over a man's neck he dies of strangulation!

Our author, though not ignoring the evils of alcoholism, maintains that under certain conditions a small dose of "veritable Cognac" is a valuable medicine. Hence, according to the pundits of "Teetotalism," there can be for him and his book no salvation.

To analysts who are called upon to examine spirits and to spirit merchants M. Baudoin's work will prove of great value.

**Anilide of Gallic Acid: its Ethers and its Salts.**—P. Cazeneuve.—A substance, first obtained by Schiff, has received the industrial name of gallanol. The author shows that gallanol is identical with the anilide of gallic acid, and that gallic blue has a constitution analogous to that of gallocyanine. He describes a number of the compounds of this substance. With zinc acetate gallanilide forms the three compounds which are theoretically possible. Gallanilide also forms insoluble compounds with many alkaloids. Quinine and strychnine in an aqueous saline solution give with gallanilide precipitates comparable to the tannates.—*Bull. de la Soc. Chim. de Paris*, ix.—x., No. 22.

## CORRESPONDENCE.

### EASY RULES FOR CONVERTING THERMOMETRICAL DEGREES.

To the Editor of the Chemical News.

SIR,—Regarding the rules for converting thermometrical degrees from Centigrade to Fahrenheit and from Fahrenheit to Centigrade in Mr. G. Watmough Webster's letter of Nov. 10th (*CHEM. NEWS*, lxxviii., 234).

After carefully comparing them with other simple rules for the same purpose by doing examples for both high and low temperatures mentally, I can see very little in them to make them preferable. The following formulæ are very simple, and they, as well, need no "expert reckoner," and can be used "without even needing pencil and paper." I include formula for Reaumur scale.

$$\frac{F-32}{9} = \frac{C}{5} = \frac{R}{4}$$

These formulæ are easily remembered, since everyone knows 9 degrees of F. equal 5 of C. or 4 of R. The rule would be—

F. to C.—Add 32, divide by 9, and multiply by 5.

C. to F.—Divide by 5, multiply by 9, and add 32.

R. to C.—Divide by 4 and multiply by 5.  
&c., &c.

However, I prefer to picture the formulæ I have given in my mind and work out mentally.—I am, &c.,

MILTON L. HERSEY.

Canadian Pacific Rly. Testing Laboratory,  
Montreal, November 27, 1893.

## 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. cxvii., No. 22, November 27, 1893.

The mayor of Angers invited the Academy to be represented at the inauguration of the statue of Chevreul, which took place on December 3.

**Preparation of Metallic Lithium.**—M. Gantz.—This paper will be inserted in full.

**Improvement of Dietetic and Lubricating Oils by an Electric Treatment.**—L. A. Levat.—Having placed a column of olive oil of rancid taste and dark colour at the negative electrode of a voltameter impelled by a small Siemens machine (magnetic type of feeble voltage), the author put the voltameter in tension until the column of water situate under the column of oil was completely electrolysed. The oil was much lighter in colour. It had become rather turbid, probably from a mechanical mixture of water. The flavour was completely modified, having become almost mild, with a slight remnant of a very agreeable piquancy. He submitted to hydrogenation a score of ill flavoured samples of various sources, and had constantly succeeded in purifying their taste and their colour. With care the oil does not become turbid, but remains limpid. In the second place he made a series of experiments on lubricating oils of bad quality, containing at least 5 per cent of free acid. The acidity always decreased in the minimum proportion of 1/5. On submitting the same oil to electrolysis a second time, the acidity was diminished by 3/10.

**Chloralose.**—M. Hanriot and Ch. Richet.—In a former paper the author has indicated the physiological properties of the two isomers resulting from the union of glucose and chloral, chloralose and parachloralose. Chloralose,  $C_8H_{11}Cl_3O_6$  is slightly soluble in water and ether, soluble in alcohol, and melts at  $187^\circ$ . Parachloralose is insoluble in most solvents, and melts at  $227^\circ$ . Chloralose, parachloralose, and all their derivatives contain the three chlorine atoms of the chloral, and it is evident that the chloral unites with the glucose by its aldehyd group, and that chloralose must contain the group—



**A Ptomaine Extracted from the Urine in Influenza.**—Dr. A. B. Griffiths and R. S. Ladell.—The ptomaine extracted from the urine in cases of influenza is a white substance crystallising in prismatic needles, soluble in water, and of a slightly alkaline reaction. It forms a hydrochlorate, a chloroplatinate, and a chloraurate, all crystalline. It gives a brownish precipitate with phosphotungstic acid, a yellowish with phosphomolybdic acid, a yellow with picric acid, and a red with tannic acid. The composition of this base is  $C_9H_9NO_4$ . It is poisonous, inducing a strong fever and death in eight hours. It is not met with in normal urine.

*Bulletin de la Société Chimique de Paris.*  
Series 3, Vols. ix. and x., Nos. 20 and 21.

**Isoconicine.**—A. Ladenburg.—The author repeats here the theoretical views which, he considers, may explain the nature of isoconicine. He has endeavoured to split up hydroquinaleine, but has not succeeded in obtaining an active base.

**Acrylic Isomers of Borneol.**—Ph. Barbier.—The essential oils of licari, coriander, and roses consist almost exclusively of definite principles corresponding to the formula  $C_{10}H_{18}O$ . They are licareol, coriandrol, linalol, geraniol, and rhodinol. The author has examined licareol at great length.

**The Separation and the Volumetric Determination of Lead.**—MM. Zindemann and Motten.—This paper will be inserted in full.

## NOTES AND QUERIES.

\*\*\* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Brewing.**—Can any reader please inform me—(1) What is generally used in fining sour ale? (2) What is the composition generally used to give a froth to ale?—HYDROGEN.

## MEETINGS FOR THE WEEK.

TUESDAY, 19th.—Institute of Civil Engineers. 8.  
— Pathological, 8.30.

WEDNESDAY, 20th.—Society of Arts, 8.  
— Geological, 8.  
— Microscopical, 8.  
— Meteorological, 8.

THURSDAY, 21st.—Chemical, 8. "The Oxidation Products of Corydaline," by Prof. Dobbie and A. Lauder.

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THE CHEMICAL NEWS,

VOL. LXVIII., No. 1778.

ON THE ACTION OF REDUCING AGENTS  
ON NICKELO-POTASSIC CYANIDE.

By THOMAS MOORE.

IN Crookes's "Select Methods" there is mentioned a test for nickel, proposed by Pappasogli, which is performed by immersing a strip of zinc in a solution of nickelo-potassic cyanide containing ammoniac chloride and free ammonia, whereby a red colouration is produced. Being somewhat curious as to the cause of this colour, I consulted several works on chemistry, amongst others the Dictionaries of Chemistry by Watts, Wurtz, and Dammar, but finding no mention of the reaction, decided to go into the matter. The results of some of the initial experiments, embodied in this communication, may not be without interest.

It was early noticed that the red colour was very fugitive, and that this evanescence was due to the absorption of oxygen from the air. The presence, too, of a large quantity of zinc compounds in solution tended to complicate many of the reactions, so that I was compelled to cast about for a more suitable reducing agent, and conduct the reduction in an atmosphere of hydrogen. The only substances which gave a rapid colouration were a solution of stannous chloride in sodic hydrate and sodium amalgam, although for obvious reasons the latter is preferable. By acting on moderately strong solutions of the nickelo-potassic cyanide by sodium amalgam added in successive portions, an intensely deep red solution is readily obtained, which gives precipitates on the application of different reagents totally different from those obtained with the ordinary  $K_2NiCy_4$ . The following are the most characteristic:—

Argentific nitrate, dissolved either in water, potassic cyanide, or ammonia, gives a heavy black precipitate of metallic silver.

- Mercuric chloride, grey precipitate.
- Plumbic acetate, black precipitate, insol. in KHO or  $C_2H_4O_2$ ; decomposes on drying, leaving yellow PbO.
- Bismuth nitrate, black precipitate.
- Arsenic trioxide, deep brown precipitate.
- Gold chloride slowly reduced.

Judging from these reactions, it is evident the body exercises a strong reducing action, as indeed it might have been supposed to do from the manner of its production, and from the avidity with which it absorbs oxygen and becomes decolourised by such substances as permanganate or bichromate of potash, peroxide of hydrogen, &c. The solution, when acidified, separates out an orange-yellow flocculent precipitate, which, when rapidly filtered off, and washed once or twice with cold water, dissolves in alkalis, forming a red solution. The precipitate darkens rapidly when exposed to the air, changing to a dirty blue colour, and decomposes completely on drying, even in a current of hydrogen, into what appears to be a mixture of oxide and cyanide of nickel.

To obtain an insight into its composition, a certain quantity of the well-reduced liquid was run into an ammoniacal solution of argentic nitrate, the precipitate filtered off and well washed, first with ammonia, and then with sodic hyposulphite, and then weighed. In the filtrate the nickel was then separated out and determined, and the ratio of the oxygen of the silver to the metallic nickel then calculated. By this means it was found that:—

58.7 grms. Ni required..	..	6860 c.c. oxygen.
58.7 "	"	6405 "
58.7 "	"	6670 "
58.7 "	"	5988 "

The oxygen absorption was then estimated in another way, by introducing a quantity of the solution into a burette filled with oxygen, and thoroughly agitating until the colour vanished, then balancing the pressures, and calculating the observed absorption to the dry gas at normal temperature and pressure. The colourless solution was then run into a receptacle, and the nickel estimated.

Ni.	O found. C.c.	O calculated. C.c.	O in 58.7 grms. Ni. C.c.
0.08816	11.15	11.21	7425
0.0744	9.24	9.46	7290
0.0779	9.27	9.90	7539
0.0494	6.34	6.29	7533
0.0580	7.44	7.37	7353
0.0646	8.07	8.21	7333

It will be noticed that these numbers are very concordant considering the instability of the substance, but decidedly higher than those obtained by the silver method; this may perhaps be accounted for by the solvent action of the alkaline cyanide on the reduced silver; at the same time it is very evident that they agree very closely with two-thirds of a volume of oxygen to 58.7 parts (the atomic weight) of nickel; or, conversely, the red solution containing 3 atoms of nickel absorbs 2 atoms of oxygen in passing into the ordinary cyanide ( $NiCy_2$ ), which would seem to indicate a compound ( $Ni_3X_2$ ) where X is monatomic. Unfortunately, however, the excessive instability of the precipitate given by hydrochloric acid has up to the present excluded the possibility of an analysis, but I hope as the work proceeds to overcome this, and investigate the nature of some of the aforementioned precipitates, which latter, it may be mentioned, seem to be free from cyanogen.

Noumea, New Caledonia.

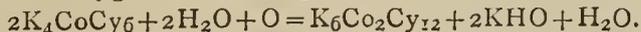
ON THE OXIDATION OF COBALTO-  
CYANIDE OF POTASSIUM.

By THOMAS MOORE.

THE formula given in text-books for the conversion of cobalto-cyanide of potassium into the corresponding cobalti-cyanide in presence of free hydrocyanic acid is usually expressed by two equations, the first representing the reaction without access of air,—



the second exhibiting the oxidising influence of atmospheric oxygen, and consequent formation of water,—



From the latter it is given to understand that the  $K_4CoCy_6$ , in passing into  $K_6Co_2Cy_{12}$ , takes up one volume of oxygen; but actual experiments seem to demonstrate that whatever may be the composition of the resultant cobalti-cyanide, it is certainly accompanied by an absorption of oxygen greater than that required by the equation, which can only be regarded as true under certain conditions of temperature, &c.

In the course of some experiments on this subject it was noticed that on adding a mixture of sodic hydrate and potassic cyanide to a solution of cobalt, and well agitating until no further absorption took place, the liquid became of a deep brown-red colour, and an amount of oxygen was taken up much in excess of that required by the above formula, the quantity varying from 8000 to 9600 c.c. for 59 grms. of cobalt, whereas theory demands only 5600 c.c. On applying the same process with this difference, that the sodic hydrate was omitted, and the cobalt solution rather strongly acidified before mixing, a marked change was observed,—the solution became uniformly yellow and the absorption less, though still much in excess of the required quantity, as will be observed

from the following figures taken at random from a considerable number of experiments:—

Co employed .. ..	0.0259	0.0614	0.0856	grms.
O absorbed at 0° and				
760 m.m .. ..	3.3	7.755	11.02	c.c.
O absorbed on 59				
grms. Co. .. ..	7503	7450	7516	c.c.

Here it will be noticed that the consumption of oxygen is very regular, and would seem to indicate either the formation of some compound differing in composition from the usually accepted  $K_6CO_2Cy_{12}$ , or that some side reaction takes place. A number of experiments were performed to detect the latter, but saving the production of an insignificant amount of ammonia no other by-products were found. It is probable, then, that at least two higher cobalti-cyanides exist; and this is supported by the fact that the above oxidised solutions, when boiled, evolve oxygen, and are then converted into the  $K_6CO_2Cy_{12}$ . Experiments are still being carried out to isolate these compounds in a pure state if possible, with the object of establishing their exact composition and properties.

Noumea, New Caledonia.

## PROCESSES FOR MANUFACTURING GAS FROM OIL,

WITH SPECIAL REFERENCE TO  
THE PEBBLES PROCESS.\*

By W. IVISON MACADAM, F.R.S.E., F.I.C., F.C.S., &c.

(Concluded from p. 285.)

KEITH'S apparatus differs in the form of retort from that previously described. It consists in a single through retort of  $\Delta$ -shape, but having in the centre, midway between the back and front, a depression. The oil is fed in at the front, and the gas passes out at the back of the retort. This class of apparatus has been adopted by the Northern Lights Commissioners for installations at Ailsa Craig and Langness, Isle of Man. In both cases the gas is used for gas-engines to blow sirens, and in the first case also for illumination.

I have no practical experience with this apparatus, but my father, Dr. Stevenson Macadam, under instructions from the Northern Lights Commissioners, went very fully into the merits of both Keith's and Pintsch's apparatus, and the following is a summary of his results:—

<i>Keith's apparatus.</i>	No. 1.	No. 2.
Gas per gallon of oil..	85.05 cub. ft.	84.82 cub. ft.
Illuminating value ..	63.25 candles.	59.52 candles.

<i>Pintsch's apparatus.</i>		
Gas per gallon of oil..	90.70 cub. ft.	103.36 cub. ft.
Illuminating value ..	62.50 candles.	59.15 candles.

I am not aware of the quantity of tar produced in Keith's apparatus, nor am I aware how far the gas may be compressed, nor of the loss of illuminating value during compression. Before employing the gas for gas-engines, Mr. Keith dilutes it with one-half its volume of atmospheric air. The apparatus used is novel and efficient. The cost of the gas is stated to be 5s. 9d. per thousand cubic feet; but this sum does not include carriage of oil and coal, wear and tear of retorts, apparatus, &c., nor the cost of labour or distribution.

The Alexander and Paterson apparatus was intended at first for the production of gas from burning oil (815 specific gravity). Worked with this class of oil it readily gives 100 cubic feet of a 63-candle gas per gallon. Later, however, I recommended the use of intermediate oils, as

gas can be produced from these at a much cheaper rate, owing to the smaller cost of material. In tests made with this apparatus, and intermediate oils of 864 gravity, 94 cubic feet of a 56-candle gas were easily obtained. The apparatus is simple, consisting of a retort, the door of which is perforated to allow of the introduction of tubes. The oil is passed by these tubes to the back of the retort, being largely vaporised *en route*; it then comes in contact with the heated sides of the retort, and is permanently broken up into a gas, which is drawn from the front of the retort. After condensation in upright pipes the gas is passed direct to the holder. Working with high-class intermediate oils well purified, the want of purifiers to remove sulphur compounds is not felt. The total amount of sulphur in the shale is not usually over  $1\frac{1}{2}$  per cent, and of this only 0.028 per cent can be traced to the crude oil: during the process of refining the most of this disappears. Where desired, however, the addition of a purifier is readily introduced. The apparatus is simple, easily worked, and especially suited for works or gentlemen's houses. It is working in several places, and is giving satisfaction. Where a pure oil-gas of high illuminating power is desired, and where such is not afterwards to be mixed with coal-gas, this apparatus is one of the best I know.

The Brooks's patent differs from all the foregoing, in so far as it is specially built for crude oils. The retort is most curiously shaped, in a zigzag fashion, and the special advantage of this form is said to lie in the greater contact of the oil with the heated sides of the retort. The process also differs from the others in so far as there is introduced a current of steam, which is broken up along with the oil, thus increasing the quantity of gas although lowering its lighting quality. The process is largely in use in America, and gives successful results. It is also patented in this country, but I am not aware of its being worked here. The peculiar form of retort is distinctly against its adoption, and I can see no reason for the form. Experience has clearly demonstrated that the process of gas-making from oil consists, chemically, in the degradation of higher carbon and hydrogen compounds to lower forms, accompanied by the production of bodies rich in carbon and free hydrogen, &c. These processes are best carried out by a heat radiated from a large surface, and not by direct contact with the metal. Direct contact leads to the production of much free hydrogen, and the deposition of free carbon in the retorts, with consequent loss of illuminating power. This has been fully brought out in experiments made by my father so long ago as 1872, with an apparatus packed with coke, and by myself in tests made with thin tubes. Further, the temperature required to break up oils into permanent gas of high illuminating value is an orange-red: whilst a white-heat increases greatly the gas produced, but practically destroys the illuminating power. With small tubes or zigzag apparatus it is almost impossible to regulate the temperature.

The Pebbles process essentially differs from any of the other processes mentioned; for, whilst these act by one direct heat action, the Pebbles process, by means of a lower heat and constant return circulation of the condensable products, only gives a partial breaking up at each circulation. In the newer forms of apparatus, as at Galashiels, the coal-gas and oil-gas retorts are back to back, and the waste heat of the former serves to heat the latter. The retorts need not, however, be so placed, for at Pebbles the coal-gas and oil-gas are made in the same oven, but for economical working the Galashiels setting should be best. The coal-gas retorts are of the usual  $\Delta$ -shape and size, and set in the ordinary way, whilst the best form of retort for the oil-gas is cylindrical. The Galashiels retorts are 9 feet long and 27 inches internal bore, and they are laid with a backward inclination. From the front of the retort there is an ordinary ascension, bridge, and dip-pipe to the hydraulic main. The condensers are nearly horizontal, with a slight upward

\* Report of Lecture delivered before the North of Ireland Association of Gas Managers, August, 1893.

tendency, and lead to a scrubber, on the principle adopted regularly in shale-oil works. The trays in the scrubber are fed with oil from a cistern attached to the upper part of the apparatus. From the scrubber the gas passes to the ordinary dry purifiers, where it meets with the coal-gas, and the mixed gases then go to the holder in the usual manner. The oil to the retort is obtained from what is called the compensating tank. In this tank the overflow from the hydraulic main, the liquids from the condensers, and the fresh oil are intermingled, with the result that a perfectly liquid substance is maintained throughout the whole working. Moreover, the apparatus, being of considerable size, acts as a settling tank, in which any solid carbonaceous matter is removed. The oil passes from the compensating tank by means of a pipe with regulating valve, to the ascension pipe, where the introduction of the liquid oil tends to wash the ascending gas, and remove any suspended carbonaceous particles. By this circulation method liquid residuals are avoided, and the residue left in the retort, when it is coked down, is a dense and very pure carbon with less than 0.5 per cent of ash, and readily burned. For this solid residue 20s. per ton has been regularly obtained at Peebles. It yields a smokeless flame of great heat intensity. The gas yield by this method runs, with "blue" oils, about 85 to 86 cubic feet per gallon, and the illuminating value when the gas is burned by itself is about 59-candle power. When burned in admixture with poorer illuminating gas the value is much greater. A month's actual working yielded—

Coal-gas ..	1,217,600	cubic feet of 18	candle power.
Oil-gas ..	253,400	" "	" "
Total gases ..	1,471,000	" "	30.51 "

	Cubic feet.		Candles.
Coal-gas ..	$1,217,600 \div 5 = 243,520$	$\times 18$	$= 4,383,360$
Total gas ..	$1,471,000 \div 5 = 294,200$	$\times 30.51$	$= 8,976,043$

Therefore candle power from 253,400 cubic feet of oil-gas = 4,592,682 candles, which, divided by the make (253,400 cubic feet) = 18.12 candles per cubic foot, and  $\times 5 = 90.60$  candle power as the true illuminating value of the oil-gas as an enricher. This gain in illuminating value by mixing is equal to 53.74 per cent. To explain this gain we need to consider several points. When any complex body is subjected to a sufficient amount of heat it is resolved into its elementary constituents, or into more simple bodies. If the heat applied be great enough, the ultimate particles will be driven so far apart that chemical union is rendered impossible. If, on the other hand, the heat is less, only partial decomposition results, and the substances produced are still compounds, although less complex than the original substances acted on. If the oil be subjected to the highly heated surface of a retort, the decomposition is almost complete—methane is formed, any oxygen goes into carbon monoxide or dioxide, hydrogen is set free, and all excess carbon is deposited as free carbon. If, on the other hand, the heat from the furnace is compelled to pass through the sides of the retort, and to be communicated to the atmosphere of the retort, which, in its turn, radiates the heat on the volatilised oil, the resulting decomposition will not be so complete, and the gases left will be more complex in nature, and more highly carbonaceous. To produce light from carbonaceous gases the carbon requires to be set free and then raised to a considerable temperature, so as to become incandescent. The incandescence may lead only to a glow, or, as the temperature rises, to a more decided light. If in the gas flame the heat, in this case derived from the burning of the hydrogen, carbonic monoxide, &c., is sufficient to produce a great enough temperature, the maximum of light will result. If these gases are too small in amount, then the flame becomes smoky and the light less. In oil-gas the last condition holds good, and the balance is brought about by the admixture with a poorly carbonaceous gas containing much hydrogen, and which on burning gives sufficient heat to

render the excess carbon of the oil-gas incandescent. In other words, the excess of carbon in the oil-gas is rendered incandescent by the excess of heat-producing bodies in the poorer gas, and the result is an excess of light over that obtained from either gas alone. The 18-candle splint gas becomes valuable as an enricher on account of the excessive heat of its combustion, and the 59-candle power oil-gas enriches on account of its excessive carbon. Both gases are required to give the desired result, and both therefore have a claim on the excess of light obtained from admixture.

I have seen the Peebles process on several occasions, and can testify to the ease of working and regularity of product, and I feel sure that the process has a great future.

#### DETECTION OF NITRONAPHTHALENE IN MINERAL OILS.

By NORMAN LEONARD, B.Sc.

NITRONAPHTHALENE, the  $\alpha$ -derivative, is frequently added to mineral oils for the purpose of removing the fluorescence, or "bloom." The following method for its detection depends upon the reduction of nitronaphthalene to naphthylamine.

A small quantity of the oil is gently warmed with zinc dust and dilute hydrochloric acid, and the mixture agitated from time to time. During this process the faecal odour characteristic of  $\alpha$ -naphthylamine will be perceived. After the reduction is complete, the acid aqueous liquid is drawn off by the aid of a separator. A portion of this liquid, when neutralised with ammonia, gives with ferric chloride a blue precipitate, which rapidly becomes purple. The remainder of the solution may be rendered alkaline with soda and extracted with ether. The latter is then evaporated and the residue dissolved in a little alcohol. On the addition of a drop of a solution of sodium nitrite, acidified with acetic acid, a yellow colour is produced which is changed to crimson by hydrochloric acid.

#### ON ENDOTHERMIC REACTIONS EFFECTED BY MECHANICAL FORCE.\*

PART I.

By M. CAREY LEA.

IN a preceding paper the effects of pressure on the silver haloids were described. These salts were readily blackened and so gave evidence of partial reduction. That investigation was undertaken with the object of bringing into complete harmony the effects upon these haloids of the different forms of energy. It had been previously shown with respect to all the other forms of energy that a slight impression made upon the haloids caused an effect not visible to the eye, but capable of indefinite increase by the application of a reducing agent. Also, it had been shown in the case of mechanical force that a slight application would cause an invisible effect which could be rendered evident by the application of a reducing agent. It seemed to follow almost necessarily that a powerful application of the same agent would bring about an effect visible to the eye. Experiment proved this to be the case.

It next appeared to be worth while to examine whether the same agent, mechanical force, would not be capable of bringing about analogous chemical changes in other compounds. For the nature of these changes was something quite different from anything that had been previously described. In Prof. Spring's well-known investigation, combination was brought about between substances whose tendency to combine was restrained by

\* From the *American Journal of Science*, vol. xlv., 1893.

their being in the solid form. This obstacle was removed by subjecting them to great pressure, and the same remark applies to some of the interesting experiments of Dr. Hallock. But the reduction of the silver haloids and other reactions presently to be described involve a quite different principle. The reactions produced are all endothermic; energy is consumed in accomplishing them, and this energy is supplied by mechanical force.

The combination of screw and lever affords the best means of applying pressure. A careful study as to the most suitable method of using these powers led to the selection of the vice form. It was found, however, that the manufacturers of heavy vices were unwilling to undertake to furnish vices with jaws that would sustain the force intended to be exerted on them, namely, that of a steel lever three feet long acting on a screw with six turns to the inch. I was therefore obliged to have them made under my own supervision. From a bar of tough rolled iron, 4 inches wide by  $1\frac{1}{2}$  thick, pieces about 18 inches long were cut and were forged into shape by a blacksmith; where the jaws met they were faced with steel, welded on. Suitable screws were easily obtained, but the nuts furnished with them having commonly only an inch in length would subject the thread to the danger of stripping. They were replaced with nuts 4 inches in length, thus distributing the strain over 24 turns of the thread. Two vices made in this way over a year ago have endured severe use without the least sign of strain.

With a lever having three feet in length between the centre of the screw head and the end at which the force is applied acting on a screw with six turns to the inch, the multiplication of force is 1357 times. As it is easy to apply a pull of a hundred pounds or even much more, a pressure of 135,000 pounds is easily obtained. As it was intended to keep the substances which were to be subjected to pressure from any contact that might affect them they were folded up in platinum foil and this was set in a V-shaped piece of soft sheet copper. The portion of material which received the pressure was about  $\frac{1}{2}$  inch long by  $\frac{1}{4}$  wide; it consequently had an area of about  $\frac{1}{8}$  of a square inch. This limited surface received a pressure in the proportion of over a million pounds to the square inch or about seventy thousand atmospheres. These of course are calculated pressures subject to deduction for friction. The amount lost in this way cannot be determined, but is known to be considerable.

By the aid of these means the following results were obtained. In all cases the material was wrapped in either platinum or silver, usually platinum, foil. There was no action in any case on the metal, which preserved its full brightness in the parts in contact with the material, so that the effects observed were due to pressure only.

*Silver sulphite* in platinum-foil was moderately darkened by two days pressure.

*Silver salicylate* was rendered very dark by two days pressure.

*Silver carbonate* was moderately darkened by a somewhat longer pressure.

*Silver tartrate* was not affected.

*Silver oxide* was thoroughly dried at  $150^{\circ}$ . A piece of platinum-foil was heated to redness and rapidly cooled, a portion of oxide was folded up in it and weighed. Weight found 0.7639. It was then subjected to very great pressure for four days. Weight found to be 0.7639, no change.

*Ferric oxide* recently precipitated and dried. No effect produced by pressure, no formation of ferrous oxide.

*Potassium Platinobromide*.—Where the pressure was greatest the brilliant red colour of this substance was blackened, not superficially only, but all through.

*Ammonium Platinochloride*.—Moderate but well-marked darkening.

*Potassium Chlorate*.—When this substance was subjected to pressure by itself no effect whatever was pro-

duced and not a trace of chloride was formed. But when it was mixed with silver nitrate, both in fine powder and subjected to pressure, there was an evident formation of silver chloride. The material was no longer completely soluble in water, but left an abundance of white flakes which darkened when exposed to light.

*Mercuric oxide* requires a very high pressure to produce an effect upon it. It then darkens slightly, but very distinctly, and this change seems to be accompanied by a slight loss of weight, requiring, however, very careful weighing to detect it.

The darkened part as well as the rest dissolves without difficulty in acetic acid, and consisted therefore probably of traces of mercurous oxide and not metallic mercury.

*Mercurous chloride* showed no change.

*Mercuric Chloride*.—Corrosive sublimate, perfectly free from calomel, which commercial sublimate is very apt to contain, was subjected to great pressure and then treated with ammonia. As no darkening took place there had evidently been no reduction.

*Mercuric Iodide*.—Red mercuric iodide when subjected to very great pressure darkened considerably, and at points where the pressure was greatest it became absolutely black. It did not appear, however, that any iodine was set free, none could be extracted with alcohol.

*Mercuric Oxychloride* ( $2\text{HgO}, \text{HgCl}_2$ ).—Heavy pressure caused much darkening.

*Sodium thiosulphate* with a moderate pressure compresses to a hard translucent cake, but does not undergo any decomposition.

To the foregoing cases are to be added those of the three silver haloids described in a previous paper; these blackened with a quite moderate pressure even in the case of the iodide.

Although in all these instances the darkening is well marked, still the actual proportion of material affected is small, so that in many cases it is difficult to apply tests to decide as to the precise nature of the substances formed. In some cases, however, this can be done, and we are justified in concluding that many of the salts of easily reducible metals, especially of silver, mercury, and platinum, undergo reduction by pressure. Such reactions are endothermic, and it therefore follows that mechanical force can bring about reactions which require expenditure of energy, which energy is supplied by mechanical force precisely in the same way that light, heat, and electricity supply energy in the endothermic changes which they bring about.

In the second part of this paper additional support will be adduced for these conclusions.

## THE DETERMINATION OF SUCCINIC ACID.

By ALFRED RAU.

The author studies the question in how far the quantity of succinic acid occurring during fermentation depends on the conditions in which the fermentation takes place. The methods hitherto employed seem to the author unsatisfactory. He finds that at  $15^{\circ}$  100 parts of anhydrous ether dissolve 1.193 parts of succinic acid, whilst the same volume of alcohol at 96 vol. per cent dissolve 9.986, alcohol of 90 per cent 11.984, methylic alcohol 15.730, acetone, 5.544 parts. In benzol succinic acid is insoluble.

In a 2 per cent solution of neutralised succinic acid, lime water and calcium chloride did not produce a precipitate until after the addition of alcohol. Barium chloride, after alcohol, gave complete precipitation. Tartaric acid and malic acid are also completely thrown down in an alcoholic solution. Strontium chloride gives no precipitate, even in the presence of alcohol. Magnesium sulphate and magnesia mixture give no precipitate, and the latter precipitates tartaric acid but not malic acid. Zinc, cadmium, and aluminium sulphates occasion

an imperfect precipitation, but not if malic and tartaric acid are present. Uranium acetate gives a precipitate, which is prevented by malic and tartaric acids. Stannous chloride and mercurous nitrate precipitate imperfectly (as also with tartaric and malic acid). Lead hydroxide and acetate precipitate imperfectly. Silver nitrate precipitates succinic acid perfectly, tartaric acid only in concentrated solutions, and malic acid only in such as are more concentrated than 1 : 800.

Nickel, manganese, glucinum, copper sulphate, and mercuric chloride produce no precipitate. Ferric chloride gives the well-known voluminous reddish-brown precipitate. Rau observed that the presence of sugar and glycerin did not interfere, whilst tartaric and malic acids hinder complete precipitation.

The author evaporates 100 c.c. of urine to a syrup, extracts repeatedly on the water-bath with boiling alcohol, and each time filters the alcoholic extract when cold. The extracts are mixed and distilled. The residue is dissolved in a little hot water; the solution, if it becomes turbid on cooling, is filtered, mixed with barium nitrate and 4 vols. of alcohol at 90 per cent, and well stirred. The precipitate, containing tartaric, malic, and succinic acid, after it has settled is filtered, washed with alcohol at 70 per cent, and heated for some time with a sufficient quantity of sodium carbonate.

The liquid is filtered, neutralised with nitric acid, evaporated down to a small volume, and, after neutralising with ammonia, treated with magnesia mixture. After subsiding for three to four hours the liquid is filtered from the precipitate which contains tartaric acid; the liquid is heated with potassa lye until all ammonia is expelled. The deposit is then filtered off, exactly neutralised with nitric acid, diluted to 100—150 c.c., and precipitated with solution of silver nitrate (1 : 20).

The precipitate is collected on a tared filter, washed, dried, and weighed. As a check it may be ignited in a porcelain crucible, and the metallic silver obtained is weighed. The results of the two weighings should correspond. If the liquid contains chlorine this element must be determined in 25 c.c., and the silver found as chloride must be deducted. — *Archiv. f. Hygiene and Zeitschr. f. Anal. Chem.*

## FOGS, CLOUDS, AND LIGHTNING.\*

By SHELFORD BIDWELL, M.A., LL.B., F.R.S.

(Concluded from p. 289).

AMMONIA-GAS, when dissolved in water, causes the evolution of much heat. Yet a stream of this gas directed upon the jet has no action. [Experiment.]

Ozonised air, which Mascart found so effective in his experiments with the closed vessel, is quite inoperative with the steam jet. Equally so is the vapour of boiling formic acid, which I believe is chemically a much more active acid than acetic, and has a lower electrical resistance. (See Table).

### Condensation of Steam Jet.

#### Active.

Air, oxygen or nitrogen, in which electrical discharge is occurring.

- Burning and incandescent substances.
- Fumes from phosphorus.
- Hydrochloric acid.
- Sulphuric acid vapour.
- Nitric acid vapour.
- Acetic acid vapour.

#### Inactive.

Air, &c., in which electrical discharge has ceased for about ten seconds.

- Smoke without fire.
- Bottled phosphorus fumes.
- Ammonia.
- Ozone.
- Steam.
- Alcohol vapour.
- Formic acid vapour.
- Sulphurous acid.

It seems that we have here a pretty little problem which might, perhaps, be solved without much difficulty by a competent chemist, but which quite baffles me.\* Is it possible that the condensing vapours may contain dissociated atoms?

To return to the electrical effect. There are only two kinds of chemical change that I know of which could be brought about in air by an electrical discharge. Either some of the oxygen might be converted into ozone, or the oxygen and nitrogen of the air might be caused to combine, forming nitric acid or some such compound. The former of these would not account for the action of the air upon the jet, because, as we have seen, ozone is inoperative; the latter might. But if the activity of the air is due to the presence in it of a compound of oxygen and nitrogen, then it is clear that an electrical discharge in either nitrogen or oxygen separately would fail to render those gases active.

I arranged a spark bottle, inside which an induction-coil discharge could be made to take place; two bent tubes were passed through the cork, one reaching nearly to the bottom for the ingress of the gas to be tested; the other, a shorter one, for its egress. The open end of the egress tube was fixed near the steam jet, and first common air, then oxygen, and then nitrogen were successively forced through the bottle while the coil discharge was going on. All produced dense condensation, but I thought that oxygen appeared to be a little more efficient than common air, and nitrogen a little less.

This last experiment points to a conclusion to which at present I see no alternative. It is that the action on the jet of an electrical discharge is due in some way or other to dissociated atoms of oxygen and nitrogen. There is nothing else left to which it can be due.

So far as Robert Helmholtz's explanation coincides with this conclusion I think it must be accepted as correct. As to the precise manner in which he supposed the dissociated atoms to act upon the jet, it is more difficult to agree with him. He thought that the abnormal condensation was a consequence of the molecular shock caused by the violent re-combination of the dissociated atoms in the supersaturated air of the jet, the action being analogous to that which occurs when a supersaturated solution of sulphate of soda, for example, is instantly crystallised by a mechanical shock.

To me this hypothesis, ingenious as it is, seems to be more fanciful than probable, but I can only hint very diffidently at an alternative one. To many chemical processes the presence of water is favourable, or even essential. Is it possible that the re-combination of free atoms may be assisted by water? And is it possible that dissociated atoms in an atmosphere of aqueous vapour may obtain the water needed for their union by condensing it from the vapour?

According to Helmholtz, flames and incandescent substances generally cause dissociation of the molecules of oxygen and nitrogen in the surrounding air. This, I believe, is generally admitted. I do not know whether slowly oxidising phosphorus has the same effect.

If it is conceded that the atmospheric gases are dissociated by electrical discharges, and that the presence of such dissociated gases somehow brings about the dense condensation of water vapour, we may still regard the electrified steam jet as affording an illustration of the abnormal darkness of thunder-clouds.

\* A Lecture delivered at the Royal Institution of Great Britain May 5, 1893.

\* Two chemists of the highest eminence have been good enough to consider the problem for me, but they are unable to throw any light upon it.

Perhaps another source of dissociated atoms is to be found in the ozone which is generated by lightning flashes. A molecule of ozone consists of three atoms of atomic oxygen, while one of ordinary oxygen contains only two. Ozone is an unstable kind of material and gradually relapses into ordinary oxygen, the process being that one atom is dropped from the three atom molecules of ozone, these detached atoms in course of time uniting with one another to form pairs. Thus two molecules of ozone are transformed into three of oxygen. A body of ozone is therefore always attended by a number of dissociated atoms which are looking for partners.

In the steam jet experiment there is not time for the disengagement of a sufficient number of isolated atoms from a blast of ozone to produce any sensible effect. But the case is otherwise when the vapour is confined in a closed vessel, as in Mascart's experiment, or when it occurs in the clouds, where the movement of air and vapour is comparatively slow.

Ozone, it will be remembered, was found by Mascart to produce dense condensation in a closed vessel even after being filtered through cotton-wool. Similar filtration seems to entirely deprive the so-called products of combustion of their active property, a fact which has been adduced as affording overwhelming evidence in favour of the dust nucleus theory. Coulier himself, however, detected a weak point in this argument. He produced a flame which could not possibly have contained any products of combustion except steam, by burning pure filtered hydrogen in filtered air; yet this product was found to be perfectly capable of causing dense condensation, and, as in his former experiments, filtration through cotton-wool deprived it of its activity.

These anomalies may, I think, be to a great extent cleared up if we assume that the effect of the cotton-wool depends, not upon the mere mechanical obstruction it offers to the passage of particles of matter, but upon the moisture which it certainly contains, and which may act by attracting and facilitating the reunion of dissociated atoms before they reach the air inside the vessel. According to this view ozone would remain an active condenser in spite of its filtration, because free atoms would continue to be given off by it after it had passed the cotton-wool. The filtration experiment should be tried with perfectly dry cotton-wool, which, however, will not be easily procured, and, if my suggestion is right, dry wool will be found not to deprive ordinary products of combustion of their condensing power.

To sum up. I think my recent experiments show conclusively that the dense condensation of the steam jet is not due directly either to electrical action or to dust nuclei. The immediate cause is probably to be found in dissociated atoms of atmospheric gases, though as to how those act we can only form a vague guess.

The discourse concluded with some remarks upon atmospheric electricity, and the exhibition of lantern photographs of lightning flashes.

### ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.\*

By VICTOR SCHUMANN, of Leipzig.

(Continued from p. 290).

**D. In Air.**—In my previous proofs of the most refrangible rays a reduction of the focal distance had reduced the resistance of the air to the desired degree. The present purpose required more energetic means. The air must be removed entirely, or at least so far that its resistance

did not permanently damage the photographic effect. The conditions were therefore again pressing, but this time for photographing in a vacuum to a heightened extent, which my former designs for a spectral apparatus translucent for the ultra-violet had already taken into consideration.

Still the same considerations as formerly stood in the way of the execution of an exhausted spectroscopy. And yet it was the sole remaining means that offered a prospect of success as long as I would not forsake the systematic examination of the obstacles.

The technical difficulties in the construction of such an apparatus were increased as soon as we wished to place in the vacuum not merely the prism and the lenses, but also the plate and the slit. If both remain outside the vacuum, not merely the construction of the apparatus but also its management will be much simplified. The adjustment of the slit, the care of its edges, the exchange of the plates, and the displacement of the case in series of proofs, as well as the arrangement of the case itself, can remain exactly as in an ordinary spectral apparatus.

The exhaustion may then be effected more simply. It does not need to take place at every change of the plates. The apparatus when once exhausted is available for a long time and for any desired number of proofs. At the same time such an instrument is relatively simple in its exhausted part, and the stratum of air between the slit and the plate can be brought without difficulty to the modest dimension of 1 centimetre in thickness.

According to the observations of others as well as to my own I considered a stratum of air of this thickness as quite unobjectionable for the present purpose. If the air had been at all an obstacle in my earlier proofs with a short focal distance the spectrum must decide when I reduced the thickness of the stratum to more than its thirtieth part, as was actually the case in a stratum of air of the thickness of a centimetre.

This idea was at the foundation of the apparatus with which I sought to decide on the absorption of the most refrangible rays in the air.

I introduced the prism and the lenses of the apparatus of a short focus, carefully observing their respective positions, into a brass case closed air-tight. It had behind the slit and in front of the photographic plate two apertures for light, which were closed with plane parallel plates of fluor-spar. Without the vacuum, at the distance of 2 m.m. vertically from the fluor-spar plate concerned, were the aperture of the slit and the photographic plate. When in use the apparatus was connected (by means of a glass ground junction) with a mercurial air-pump (Geissler, of Bonn), by which it was exhausted according to the manner of Geissler tubes.

This was, in broad outlines, my first exhaustible spectrum apparatus. I omit here a minute description of the movement of the object lens, the slide of the slit, and the track of the case, as I purpose mentioning them in full by the opportunity of certain important improvements which I devised afterwards. But for the better understanding of the following results I will describe the path of the rays between the spark and the photographic plate at the respective distance of 4 m.m. The rays traversed before reaching the vacuum a stratum of air of 6 m.m. in thickness and the first closing plate (3 m.m.), in the vacuum the lens of the collimator, the prism, and the lens of the camera, on leaving the vacuum at the angle of 20° the other closing plate of the same thickness, and lastly, still at the same angle, the stratum of air of 2 m.m. which separated the covering plate from the photographic plate. As the prism of the lenses were of fluor-spar no other absorbents came into consideration except air, which acted as a stratum of approximately 10 m.m. in thickness.

The spark was supplied by the smaller inductorium and a Leyden jar. The electrodes were of aluminium and tungsten. The photographic plates were by Schleussner. Their treatment was like that already described.

(To be continued).

\* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

ON THE ASSAY OF THE MANGANESE  
OXIDES BY MEANS OF HYDROGEN  
PEROXIDE.

By ADOLPHE CARNOT.

It is known that oxygenated water is decomposed with effervescence in contact with manganese peroxide, and that a small quantity of this oxide is sufficient to destroy an indefinite quantity of oxygenated water.

It is not the same when the peroxide and the oxygenated water are in contact with an acid, even if very dilute or feeble, capable of combining with manganese oxide. There is then a simultaneous decomposition of the two peroxides, and the quantity of oxygen evolved is exactly double of that found in manganese peroxide in excess of MnO.

This reaction is produced readily even in the cold with nitric acid. The author's method agrees in principle with that of Dr. Lunge, but the arrangement is different, no special apparatus being required. Carnot makes use of a small flask, holding about 150 c.c., closed with a caoutchouc stopper, having two perforations. In one of these passes a straight tube, drawn out at the lower end and fitted at the top with a funnel and a glass cock. The other admits the delivery-tube, bent in the shape of S, and terminating at the top of a graduated jar, containing 300 c.c., filled with water, and placed over a water trough.

We put into the flask 1 grm. of the oxide to be examined, then about 30 c.c. of water, and 20 c.c. of nitric acid, in order to decompose any nitrates which the ore may contain. When all carbonic acid has been expelled we insert the stopper, but without introducing the drawn-out tube as far as the liquid. We leave the cock open and introduce the delivery-tube under the graduated jar. The tube is then filled with water as far as its issue from the water trough.

The flask is fixed on a stand with clasps. The tube is immersed to the bottom of the flask, the glass cock is closed, and we pour into the funnel 20 c.c. of oxygenated water at 10 vols. Carefully turning the cock, we allow the reagent to flow gently into the flask, and we close the flask at the moment when the last portions of the liquid have passed through. With most manganese oxides the reaction takes place at once, without heating, and is completed in a few minutes if we take care to shake the flask from time to time. For some very compact oxides it is necessary to heat slightly to complete the reaction. It is then necessary to cool the flask, or give it time to return to the temperature of the external air, before proceeding to measure the gas.

It is sufficient to measure the increase of the total gaseous volume, taking care that the temperature and the pressure have remained the same as at the beginning of the experiment. For this purpose the graduated jar is grasped in wooden tongs or with a layer of paper to prevent the direct contact of the fingers, and it is lowered into the water trough until the level of the water is exactly the same within and without. The branch of the S-tube which had been inserted in the graduated jar is withdrawn. The jar is immersed into the water to give the gas which it contains the temperature shown by the thermometer inserted in the water trough, and we determine the volume of the gas after having brought it to the atmospheric pressure.

Let  $V$  be the volume thus found. In order to have the total gaseous volume, it is necessary to add to  $V$  the small volume,  $v$ , of gas which has filled the extremity of the delivery-tube, originally full of water, a volume which is easily measured once for all. On the other hand, we must deduct the volume of oxygenated water which has been introduced into the flask, and which has displaced an equal volume of gas. This volume equals 20 c.c. We represent the total increase of the gaseous volume by  $Vt$ ; that is to say,  $V + v = 20$  c.c. The valuation has been

made at the temperature,  $t$ , and the atmospheric pressure,  $H$ , observed in the experiment. The gas is saturated with moisture, the tension of which is known, according to the temperature. As this increase is due to the oxygen yielded, half by the manganese oxide, and half by the oxygenated water, we must only take the half to calculate the gas yielded by 1 grm. of the ore.—*Bull. de la Soc. Chim. de Paris.*

METHOD FOR THE BACTERIOLOGICAL  
EXAMINATION OF WATER.

By Dr. G. P. DROSSBACH.

THE present universally received method for the bacteriological examination of water, which consists essentially in the distillation of a measured quantity of water in nutrient gelatin and the enumeration of the colonies visible with the lens which have grown up in two or three days, has scarcely more than a relative value, which falls more into the rear if the investigation is made, not for technical, but for dietetic purposes. According to our present knowledge of the vital conditions of pathogenous microbia it cannot be expected that they can be brought to development in the above-mentioned manner. Even such pathogenic species as flourish relatively well on our artificial nutrient media at a moderate temperature do not reach this characteristic development in less than three or four days. But in the same time the saprophytes and hyphomycetes, which are always present in water rapidly liquefy and overgrow the plate. In this manner we therefore detect merely the saprophytes and hyphomycetes as the pathogenic species are not developed during the short time of the experiment.

If the too rapid growth of the colonies is checked by spotting with solution of mercuric chloride, there often appear in from three to five days, mostly in the depth of the gelatin, a great number of colonies belonging to almost all the species which are able to grow at the temperature of the blood, and which consequently fulfil one condition for developing a pathogenic activity. This customary plate method should only be used for technical purposes or for checking water-filters. For determining the absolute values of a drinking water it is worthless. For such purposes the determination of the germs capable of development at blood-heat, especially those of the optionally anaerobic species, is exclusively suitable. That the casting of agar plates requires rather more skill should scarcely be a reason why the last-named process has not been universally introduced. Probably the decisive point has been that to many persons the evacuation of the air and working with Gruber tubes appears too tedious, whilst working with pyrogallol is unpleasant and often unsuccessful.

In order to overcome these difficulties, I examined the properties of other chemicals which absorb oxygen. Ferrous oxide proved to be very useful. Though not capable of giving vital conditions suitable for the most rigidly anaerobic species, it suffices for the development of many, and prevents them from being overpowered by the aerobic species. Ferrous oxide is best used in a box-exsiccator, the bottom of which is covered with a layer of concentrated soda lye of 1 to 2 c.m. in depth. This is cautiously superstratified with the concentrated solution of an equivalent quantity of ferrous chloride so that the two liquids do not mix. The lid is put on, and luted with a melted mixture of two parts wax and one part oil of almonds. The liquids are then mixed by means of a rather vigorous circular movement, when the ferrous oxide is set free with a strong production of heat, and coats the interior surface of the exsiccator in the state of a thick paste. If on use the box is not opened longer than it is absolutely necessary, and if a sufficient quantity of oxide is present, the box may be used repeatedly.

Chromous oxide absorbs oxygen much more energetically than ferrous oxide. Chromous oxide, indeed, cannot be used as such, since it decomposes water, and the liberation of oxygen raises the lid of the exsiccator. Chromous acetate may be conveniently used. A concentrated solution of crude chromium sesquioxide is reduced by means of zinc and a little hydrochloric acid until the solution appears of a pure blue. It is poured (without filtration) upon the stratum of soda-lye in the exsiccator, proceeding exactly as directed above. The red acetate liberated absorbs oxygen with extreme energy, the heat liberated reaching even to redness. If the lower part of the exsiccator is of a sufficient size, and from 100 to 200 grms. of chromous chloride have been employed, the box may be used many times in succession.

The most strictly anærobic species are thus developed on the nutrient medium cast in Petri capsules.

It is advantageous not to cover the capsules, and to place them upon each other supported on wire triangles.—*Chemiker Zeitung*.

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INTERNATIONAL CONGRESS OF APPLIED  
CHEMISTRY.  
UNDER THE PATRONAGE OF THE BELGIAN  
GOVERNMENT.

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THIS Congress, which is to be held at Brussels on the 4th of August, 1894, and will last a week, is promoted by the Belgian Association of Chemists, and will have for Honorary President M. de Bruyer, Minister of Agriculture, Industry, and Public Works.

The science and practice of chemical analysis plays such an important part in the commercial side of industrial and agricultural chemistry, both in the control of manufactures themselves and in the solution of hygienic problems, &c., that it becomes more and more important that there should be greater agreement, and accord, between the various methods of analysis now in vogue among analytical chemists. That there should be so much disagreement between the results obtained from different laboratories is greatly to be regretted; but these disagreements (when they occur) are more often caused by the employment of different methods than by any want of skill or care on the part of the operators. To remedy this state of things the Organising Committee of the Congress considers that it is indispensable that there should be a unification of methods of analysis, not only in each country, but universally, and that the standard processes to be adopted should be decided by international agreement. It is in the endeavour to solve the inevitable difficulties of such a scheme that the proposed Congress has been convened.

The Congress will be very much on the lines of the British Association, even to the organisation of excursions to various industrial and agricultural establishments.

The Congress will be divided into four sections:—

- A. *Sugar Industries*: subdivided into ten heads, comprising the estimation of water in sugar, the estimation of the commercial value of molasses, the estimation and comparison of colour in sugars, &c.
- B. *Agricultural Chemistry*: subdivided into nine heads, comprising the estimation of nitrogen in manures, the complete analysis of Chili saltpetre, the estimation of phosphoric acid, the analysis of milk, &c.
- C. *Food Products and Public Health*: subdivided into five heads, comprising the estimation of the purity of butter, distilled liquors, the bacteriological examination of potable waters, the micrographic examination of pepper, &c.
- D. *Chemical Biology*: subdivided into seven heads, comprising various problems in brewing, the manufacture of vinegar, the analyses of molasses with regard to distilling, &c.

It is proposed to start eventually a "Review of Reviews of Applied Biological Chemistry," published in several languages, and containing a *résumé* of chemical work of this description from all parts of the world.

We may add that the date of this Congress has been fixed so as to coincide with several *fêtes*, in connection with the universal exhibition to be held at Anvers, so that profit and pleasure may be combined.

Further information with regard to rules, regulations, subscriptions, &c., can be obtained from the Secretary-General, M. Sachs, 68, Rue d'Allemagne, Brussels; or from M. H. van Laer, 15, Rue de Hollande, Brussels.

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PROCEEDINGS OF SOCIETIES.

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CHEMICAL SOCIETY.

*Ordinary Meeting, December 7th, 1893.*

Dr. ARMSTRONG, President, in the Chair.

MESSRS. E. A. Hancock and E. A. Warmington were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Henry Purefoy Fitz-Gerald, Wellington College, Berks; Alfred Hutchinson, The Leys, Cambridge; Frank Hughes, 27, Fairfield Rd., Chelmsford; Norman Leonard, 2a, Lorne Road, Brixton, S.W.; Arthur Luty, 30, Bryn-y-Mor Terrace, Swansea; A. H. Macdonald, The Green, Marlborough, Wilts; David Paterson, Lea Bank, Roslin, N.B.; J. Cardwell Quinn, Woodcroft, Gateacre, near Liverpool; Arthur Ross, 1, Glengall Rd., Old Kent Rd., S.E.; Walter Smithson Rowntree, 53, Grosvenor Road, London, S.W.; Richard A. Rouillard, 5, Dundonald Rd., Wimbledon, and Mauritius; Charles Henry Smith, Re Bungalow, Nassau, Bahamas, W.I.; Alfred E. Tanner, 2, Bruce Grove, Tottenham; Hamilton Marc Wingate, 3, Buckingham Street, Glasgow, W.

The following were duly elected Fellows of the Society:—Frederic Edmund Bowman; Harry Fielden Briggs; Frank Browne; John Dixon Brunton; C. M. Caines; Thomas Petson Carswell; Harry J. Chaney; Allan Thomas Cocking; John A. Craw; Charles Sordes Ellis; Alexander M. Forrester; Henry Garnett; W. H. Grieve; Harry Edwin Hadley; Henry Ormsby Hale; Harold Harris; Wm. Hesketh; H. B. Holthouse; Bertram Hunt; W. F. Mawer; J. R. Morgan; F. Morton; George F. Payne; G. P. Rees; Thomas Anderson Reid; Philip Schidrowitz; W. Edgar Sims; Frederick Shapley; Robert Curley Styles; Jocelyn Field Thorpe; William Herbert Walden; Frank Ernest Welchman; William Gilchrist White; Edward Humphreys Winder; Stanley Wyndham.

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

\*84. "An Apparatus for the Extraction and Estimation of the Gases Dissolved in Water." By E. B. TRUMAN, M.D.

The apparatus described is so constructed that the air having been removed chiefly by means of a water pump and ultimately by a Sprengel mercury pump, a measured bulk of the water can then be introduced, if desirable without allowing it to come into contact with the air. The dissolved gases which spontaneously escape from the water can be pumped off, and the water can be subsequently heated so as to drive off any gas remaining dissolved and also the carbon dioxide fixed by carbonates.

\*85. "The Magnetic Rotation of Hydrogen Chloride in Different Solvents, and also of Sodium Chloride and of Chlorine." By W. H. PERKIN, Ph.D., F.R.S.

Experiments are described which have afforded results confirmatory of those previously published by the author. It is shown that when isoamylic oxide is nearly saturated

with hydrogen chloride at temperatures between 0° and 25°, no appreciable interaction takes place, the values obtained by direct weighing agreeing with those afforded by titration with alkali; action takes place only very slowly between the two substances at ordinary temperatures. Hydrogen bromide acts far more rapidly on isoamylic oxide. It is further shown that hydrogen chloride acts extremely slowly on ethylic and isoamylic alcohols at ordinary temperatures. Hydrogen chloride when dissolved in these alcohols has a higher molecular rotation than when dissolved in isoamylic oxide, the value being, however, than that afforded by aqueous solutions, thus:—

In aqueous solution .. .. .	4.300
In alcoholic solution .. .. .	3.324
In isoamylic oxide .. .. .	2.245

The molecular magnetic rotation of sodium chloride was found to be 4.080 in the solid state and 5.068 in aqueous solution.

The value obtained for chlorine, using a solution in carbon tetrachloride, was 2.188, which is considerably higher than the value calculated from compounds such as propyl chloride (1.733).

\*86. "Analysis of Water from the Zem-Zem Well in Mecca." By C. A. MITCHELL, B.A. (Oxon.), King's College, London.

Through the kindness of Lady Burton I have been enabled to make an analysis of water from the Zem-Zem well in Mecca, which was obtained from the well by the late Sir Richard Burton, disguised as a pilgrim dervish, in 1853.

The Zem-Zem well, according to tradition, is the well of Hagar, and is used for no other purpose than for drinking and religious ablution. Each pilgrim to Mecca is anxious to drink and bathe in the water, but as there is not sufficient for all the following device is adopted:—An Arab standing on the wall of the well draws the water up and pours it over the pilgrims as, stripped to the waist, they advance in turn. As it pours over him each drinks what he can, and the remainder runs down, soaking through the loin cloth, back into the well to be used again on succeeding pilgrims. If this practice has been continued day after day and year after year, it is not surprising to find that the water is very rich in chlorine and albumenoid ammonia, and that the solid residue is large in amount.

The sample examined was contained in two small hermetically sealed tin bottles, which had remained untouched since Sir Richard Burton brought them from Mecca. Each held about 200 c.c. On opening them there was a slight evolution of gas. In each case there were minute silky crystals in suspension, and a few earthy particles settled at the bottom. These crystals, on examination, proved to be a tin compound, probably stannic hydrate, as they were unaltered on evaporating with strong nitric acid, and, after fusing them with pure sodium carbonate, no trace of chloride or sulphate could be detected in the solution. These foreign matters being filtered off, a clear and colourless filtrate was left, having a slight smell, more perceptible on warming, and distinctly alkaline to litmus paper. Neither tin nor lead was found in this solution. The relative density of the water at 14° was 1.0029. On analysis the following numbers were obtained:—

Nitrogen from nitrates and nitrites .. .. .	4.496 grs. per gallon.
Total solids .. .. .	219.5 " "
Chlorine .. .. .	69.3 " "
Free and saline NH <sub>3</sub> .. .. .	71.4 parts per million.
Albumenoid NH <sub>3</sub> .. .. .	2.2 " "
Hardness in terms of MgCO <sub>3</sub> .. .. .	23.3

The hardness in degrees of CaCO<sub>3</sub> = 43.05, but as the

water was found to contain very little calcium and large quantities of magnesium, the hardness is given in terms of the latter, although probably it is mainly due to chlorides and sulphates.

The oxidised nitrogen present, determined by Lunge's nitrometer, was 4.496 grains per gallon = 19.91 grains NO<sub>3</sub>.

On igniting the residue, white fumes from ammonium salts were given off, while the residue browned considerably and lost in weight an amount corresponding to 35.5 grains per gallon.

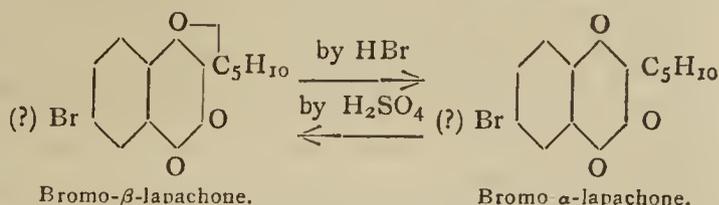
The following are the quantities of some of the constituents of the water actually determined and calculated on 219.5 grains of total solids to the gallon.

SiO <sub>2</sub> .. .. .	3.0
Al .. .. .	0.8
Ca .. .. .	0.5
Mg .. .. .	6.6
K .. .. .	24.3
Na .. .. .	38.3
NH <sub>4</sub> .. .. .	5.3
Cl .. .. .	69.3
SO <sub>4</sub> .. .. .	30.7
NO <sub>3</sub> .. .. .	19.9

Professor Crookshank was kind enough to make an exhaustive bacteriological examination of some of the water, but was unable to discover any trace of living organisms. The water was sterile, as might well be expected, after its having been hermetically sealed and in total darkness during forty years.

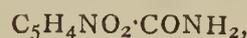
87. "The Preparation and Properties of Bromolapachol." By SAMUEL C. HOOKER.

The author shows that although bromolapachol cannot be prepared by the direct action of bromine on lapachol, it is readily obtained by reducing dibromolapachone, the preparation of which he has previously described (*Trans.*, 1893, 424). Bromolapachol crystallises in golden scales melting at 170–171°; it yields bromo-β-lapachone when dissolved in concentrated sulphuric acid. Bromo-β-lapachone closely resembles lapachone in its behaviour, being converted into bromo-α-lapachone by the action of bromhydric acid; the latter compound being re-converted into the former by dissolving it in concentrated sulphuric acid. Bromo-α-lapachone is a pale yellow substance melting at 178°; the isomeric β-compound is orange-red, and melts at about 205°.



88. "Studies on Citrazinic Acid." Part II. By T. H. EASTERFIELD and W. J. SELL.

The authors find that when diammonic citrate is heated during several hours at 130° in an open vessel, about 6 per cent of citrazinic acid is produced. The ethylic salt of citrazinic acid yields the ammonium salt of citrazinamide when heated in a sealed tube with strong ammonia. Sodium amalgam reduces citrazinamide,—



to citrazinyl alcohol, C<sub>5</sub>H<sub>4</sub>NO<sub>2</sub>·CH<sub>2</sub>OH, a small quantity of the corresponding hydrobenzoin being simultaneously produced; this behaviour is analogous to that of the amides of aromatic acids. The alcohol crystallises from water in monohydrated colourless prisms, melting at 158°; its solution is very acid to litmus.

89. "The Oxides of the Elements and the Periodic Law." By R. M. DEELEY.

The author discusses the properties of the oxides of

the elements in connection with the modified periodic arrangement of the elements described in his previous communication (*Trans.*, June, 1893).

In the diagram which accompanied that paper, the "volume heats" and "volume atoms" of the elements were plotted as ordinates, the abscissæ being the atomic weights. Similarly a diagram has now been prepared, in which the ordinates are numbers obtained by dividing the relative densities of the oxides by the atomic weights of the corresponding elements. The results obtained are, in general, confirmatory of those deduced from the previous diagram, and lead to a somewhat similar periodic table, although the arrangement differs in several important respects from that proposed by Mendeleeff.

90. "The Freezing-points of Alloys in which the Solvent is Thallium." By C. T. HEYCOCK and F. H. NEVILLE.

The addition of lead to thallium raises the freezing-point. The atomic falls caused by gold, silver, and platinum in thallium are closely accordant, the mean value being 6.31° as that due to 1 atomic proportion dissolving in 100 atomic proportions of thallium; with the aid of this value, the latent heat of fusion of 1 grm. of thallium is calculated to be 5.12 calories. Bismuth exhibits the phenomena of a triple alloy, probably owing to the presence of impurity in the thallium.

#### PHYSICAL SOCIETY.

Ordinary Meeting, December 8th, 1893.

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

MESSRS. J. H. GILLET and F. HOVENDEN were elected Members of the Society.

A paper by Mr. JAMES SWINBURNE on "A Potentiometer for Alternating Currents" was read by Mr. BLAKESLEY.

After referring to the many advantages of the "potentiometer method" of measurement, the author describes an arrangement by which alternating pressures can be measured. A quadrant electrometer with a double fish-tail-shaped needle suspended by a torsionless fibre is employed. The electrostatic attraction exerted by an alternating pressure between the needle and one pair of quadrants is balanced by the force due to a steady pressure between the needle and the other pair of quadrants. The magnitude of the steady pressure is determined by a potentiometer and standard cell, and the effective value of the alternating pressure thus deduced. For measuring alternating currents a differential electro-dynamometer having two fixed coils and one moving coil and no controlling spring is used. A direct current, measured by the fall of potential over a small resistance, is passed through one of the fixed coils, the alternating current through the other fixed coil, and the moving coil is included in both alternating and direct current circuits. When the two forces balance, the currents are taken as equal. Several small inaccuracies to which the method is subject are mentioned in the paper.

Prof. S. P. THOMPSON enquired if the fishtail-shaped needle of the electrometer was novel.

Mr. BLAKESLEY said the author had mentioned the needle previously. He (Mr. Blakesley) thought the name "potentiometer" was not very suitable. In effect the so-called measurement of pressures was a comparison of two powers.

The PRESIDENT announced that Mr. Preece's note on the "Specific Resistance of Sea-water" had been temporarily withdrawn.

Prof. G. M. MINCHIN, M.A., made a communication on the "Calculation of the Coefficient of Self-induction of a Circular Current of given Aperture and Cross-section."

Instead of assuming the cross-section of the wire small

and the current density constant over the section, as is usually done, the author takes into account the dimensions of the section and the non-uniform distribution of the current. Making use of the expressions for the vector potential (G) of the current given in his previous papers (*Phil. Mag.*, April and August, 1893), the author calculates the total normal flux of force through a surface intersected once in the positive direction by every tube of force emanating from the given current. This flux, divided by the current, gives the coefficient of self-induction. The surface chosen is the circular aperture of the current and half of the anchor ring formed by the wire. When the current density is inversely proportional to the distance from the axis of the circular current, the value for the coefficient of self-induction is found to be—

$$\pi \left\{ 4a(L-2) + 2c \left( L - \frac{5}{4} \right) - \frac{c^2}{16a} (2L+19) \right\},$$

where  $a$  is the radius of the central filament of the current,  $c$  the radius of the cross section of the wire, and—

$$\lambda/e \left[ \log_e \frac{\delta a}{c} \right].$$

Clerk-Maxwell's approximate expression agrees with this in the principal term. As an example of the closeness of the approximation, the case of a current in a wire 2 m.m. diameter bent to a circle of 2 c.m. mean diameter had been taken, the approximate and corrected coefficients being 58.866 and 59.207 absolute units respectively. When the current in the wire is superficial, as in case of alternating currents of high frequency, the coefficient is somewhat greater, being given by the expression—

$$\pi \left\{ 4a(L-2) + 2c \left( L + \frac{3}{2} \right) + \frac{c^2}{16a} (4L+11) \right\}.$$

Incidentally it was pointed out that the function  $G_x$ , where  $G$  is the vector potential at a point distance  $x$  from the axis of a circular current, was the same as Stoke's current function in hydrodynamics.

Another paper on the "Magnetic Field of a Current Running in a Cylindrical Coil" was read by Professor MINCHIN.

The cylindrical coil is regarded as a series of equal circles lying close together and forming a cylindrical surface. Replacing each circular current by its equivalent magnetic shell, the problem of finding the magnetic potential at a point resolves itself into calculating the gravitational potential due to two circular plates of attracting matter, one positive and the other negative, situated respectively at opposite ends of the cylinder. The magnetic potential due to one plate is then deduced in terms of elliptic integrals of the first, second, and third kinds. The President had pointed out that the expressions given in the printed proof of the paper only applied when the perpendicular from the point to the plate fell within the circle; the author had therefore modified the formula so as to be true generally. From this formula the equipotential curves can be constructed. The same system of curves serve for the plate at the other end of the cylinder by changing the signs of the numerals representing the potentials, and giving the curves a motion of translation equal to the length of the cylinder in the direction of its axis. The equipotential curves for the coil can then be deduced by drawing through the points of intersection of the two sets of curves whose numerical values have a constant sum. In determining the curves the author had to calculate tables of elliptic integrals of the third kind, and these he hoped to complete before the paper was published.

In reply to a question on the first paper which had been brought before him by Prof. Perry, the author said that as the diameter of the wire diminished indefinitely, both the self-induction and resistance became infinite, but the ratio  $L/R$  became zero. It was interesting to

examine what relation between the aperture and cross section gave minimum impedance. If the ordinary expression for  $L$  be taken, the problem was impossible, but the corrected form admitted of a solution.

Prof. PERRY hoped the work Prof. Minchin had done so well for circles and cylinders would be extended to cylindrical coils of rectangular cross-section. It was most important to be able to find the shape of the field produced by such coils.

Prof. S. P. THOMPSON enquired if there was any way of deducing the expression for the magnetic force at a point other than that given in the paper on the "Magnetic Field of a Circular Current" (*Phil. Mag.*, April, 1893).

In reply, Prof. MINCHIN explained how the formula followed at once from the fundamental theorem that magnetic force is the curl of the vector potential. This was based on Laplace's expression for the force between a magnetic pole and an element of current, which had been proved experimentally.

#### ROYAL INSTITUTION OF GREAT BRITAIN.

*Special General Meeting, Friday, December 15, 1893.*

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.,  
Treasurer and Vice-President, in the Chair.

THE following Resolution, in reference to the decease of Dr. John Tyndall, Honorary Professor of Natural Philosophy of the Institution, was read and unanimously adopted:—

Resolved, That the Members of the Royal Institution of Great Britain, in Special General Meeting assembled, hereby record their deep regret at the death of Dr. John Tyndall, D.C.L., LL.D., F.R.S., who was for forty years connected with the Institution, as Lecturer, Professor, and Honorary Professor of Natural Philosophy, and who, by his brilliant abilities and laborious researches, has nobly promoted the objects of the Institution, and conspicuously enhanced its reputation, while at the same time he extended scientific truth and rendered many new additions to natural knowledge practically available for the service of mankind; and that the Members of the Royal Institution further desire to convey to Mrs. Tyndall an expression of their sincere sympathy and condolence with her in the bereavement she has sustained in the loss of her gifted and distinguished husband.

Letters of regret for non-attendance were read from His Grace the Duke of Northumberland, K.G. (the President), H.R.H. the Count of Paris, the Right Hon. Lord Kelvin, the Right Hon. Lord Rayleigh, Lady Amherst, of Hackney, Lady A. F. Elphinstone, Sir James N. Douglass, Sir William O. Priestley, the Rev. Canon Jenkins, Mr. Joseph Brown, Mr. A. B. Bassett, Professor T. E. Thorpe, Mr. John Bell Sedgwick, and many others.

### CORRESPONDENCE.

#### EASY RULES FOR CONVERTING THERMOMETRICAL DEGREES.

*To the Editor of the Chemical News.*

SIR,—I think Mr. Hersey, whose letter appears in CHEM. NEWS, vol. lxxviii., p. 293, underestimates his own mental powers. The point is simply, *e.g.*, whether it is easier to multiply a number by 5 and divide by 9, or to double it and subtract all but the last figure. None but Mr. Hersey of those to whom I showed it had any doubt about the superiority of the doubling method. The whole matter is perhaps too simple to be worth a discussion, but I think

it desirable to employ arithmetical shorthand wherever possible. My method also avoids more than one "remainder" or fraction: the old method, as per Mr. Hersey, would give remainders that would double the time needed, and lead to possible mental errors.—I am, &c.,

G. WATMOUGH WEBSTER.

### NOTICES OF BOOKS.

*Laboratory Teaching, or Progressive Exercises in Practical Chemistry.* By CHARLES LOUDON BLOXAM. Edited by A. G. BLOXAM, Head of the Chemistry Department, The Goldsmith Institute, New Cross, London. Sixth Edition. London: J. and A. Churchill. 1893. Small 8vo., pp. 324.

BLOXAM's "Laboratory Teaching" has been long a favourite both with teachers and students, and we are bound to say with the fullest right. Whilst in the present edition the general character of the book has been preserved, certain additions and modifications have been adopted which will increase its value. Among these improvements may be mentioned schemes and explanatory instructions for the analysis of complex substances. The section on blowpipe analysis has been remodelled and arranged for the same purpose. The detection of organic substances, especially in mixtures, has been facilitated by the introduction of group-tests and instructions for the elimination of substances which, if present, may occasionally mask the reactions of those sought for. For this purpose the scheme given on p. 282, with the succeeding directions, will be found very useful.

Among poisons we note that chromium has been overlooked (p. 391); yet it is decidedly more formidable than copper, and the numerous uses of its compounds in the arts render its accidental presence in articles of food far from improbable. Uranium is so rarely present, except in insoluble colours, that its omission is perfectly justifiable.

We cannot doubt but that the present edition will be no less favourably received than its predecessors.

### 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. cxvii., No. 23, December 4, 1893.

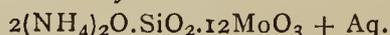
**Assay of the Manganese Oxides by Oxygenated Water.**—Harry C. Jones.—A paper bearing this title has been recently communicated to the Academy by M. Ad. Carnot (*Comptes Rendus*, cxvi., 1295). I request permission of the Academy to point out that the analytical method indicated by M. Carnot is the application of a more general method elaborated by myself about four years ago and published three and a-half years ago or thereabouts. It has long been known that on the contact of the metallic peroxides with hydrogen peroxide there ensues an evolution of oxygen. G. Lunge has shown that in presence of an acid this reaction is effected quantitatively. He has determined manganese peroxide by means of oxygenated water in presence of sulphuric acid. M. Carnot mentions merely the method of A. Riche, who determines oxygenated water by means of manganese peroxide in sulphuric acid. In the method which he proposes the determination of manganese peroxide is effected by means of oxygenated water in presence of nitric acid. Under these

conditions the oxygen evolved is derived half from the manganese peroxide and half from the oxygenated water, according to the equation—



If we know the quantity of the substance employed and measure the oxygen evolved a very simple calculation shows the quantity of manganese peroxide. M. Adolphe Carnot shows also that the same method may serve to determine the oxides  $\text{Mn}_3\text{O}_4$  or  $\text{Mn}_6\text{O}_{11}$ , and gives us finally to understand that the method may be utilised for the analysis of the ores of manganese. On consulting the *American Chemical Journal* (xii., 279, 1890) it will be seen that this is precisely the method which I have discovered and developed. The same method has been inserted in the *Analyst* (xvi., 215), and an abstract is to be found in the *Centralblatt*, Ser. 2, p. 1027, 1890. On the same occasion I showed that minium and lead peroxide may be determined by means of lead peroxide in presence of nitric acid. Half of the oxygen evolved is obtained from the lead oxide and the other half from the oxygenated water. As I mentioned above Prof. Lunge has shown that manganese peroxide may be determined by means of oxygenated water in presence of sulphuric acid. I have pointed out that nitric acid may be used with advantage, as it peroxidises any ferrous oxide found in the ores of manganese and thus prevents any loss of oxygen. I have further shown that we may determine oxygenated water by means of an excess of minium or lead peroxide in presence of nitric acid as well as by Lunge's method, which involves the use of chloride of lime.

**The Complex Acids Formed by Molybdic Acid with Titanic Acid and Zirconia.**—E. Péchard.—If we add hydrofluosilicic acid to a hot solution of ordinary ammonium molybdate the mixture turns yellow, and on cooling deposits a crystalline precipitate if the liquid is sufficiently concentrated. If the liquid is dilute the addition of hydrochloric acid at once causes the formation of the same yellow crystalline precipitate, which is the ammonium silico-molybdate—



This method of preparing the silico-molybdates has enabled the author to obtain salts containing molybdic acid with titanic acid or zirconia. He describes the ammonium and potassium titanio-molybdates, titanio-molybdic acid, and the zincono-molybdates. The process enables us to foresee the existence of analogous compounds of molybdic acid with stannic acid and boric acid.

**Researches on the Constitution of the Albumenoids Extracted from the Vegetable Organism.**—E. Fleurent.—It is now established that the animal albumenoids have a different composition from the albumenoids of the vegetable organism. Thus, caseine contains—C, 48.55; H, 8.20; whilst gluten contains—C, 49.70; H, 8.20.

**Stability and Conservation of Dilute Solutions of Mercuric Chloride.**—L. Vignon.—The antiseptic value of the solutions of sublimate is evidently connected with the preservation of their initial state, which varies rapidly with time.

**Detection of Abrastol in Wines.**—M. Sanglé Ferrière.—Abrastol is the sulphuric ether of  $\beta$ -naphthol combined with calcium,  $[\text{C}_{10}\text{H}_7\text{O}(\text{SO}_3)_2\text{Ca}]$ . To detect this compound in wine we take 200 c.c. of wine and add 8 c.c. of hydrochloric acid, and heat for an hour with an ascending condenser. The liquid when cold is exhausted with 50 c.c. of benzene, which is washed and exposed to slow evaporation without any rise of temperature. The residue is then taken up in 10 c.c. of chloroform, which is put in a test-tube into which is dropped a fragment of caustic potash and heated for one or two minutes to the temperature of the ebullition of chloroform, when there appears a fine blue colour, which changes quickly to green and then to yellow. This reaction is sensitive to 1-80,000th, and enables us to detect 0.10 grm. abrastol per litre.

## MEETINGS FOR THE WEEK.

WEDNESDAY, 27th.—British Astronomical, 5.  
THURSDAY, 28th.—Royal Institution, 3. "Air, Gaseous and Liquid,"  
by Prof. Dewar, M.A., LL.D., F.R.S.  
SATURDAY, 30th.—Royal Institution, 3. "Air, Gaseous and Liquid,"  
by Prof. Dewar, M.A., LL.D., F.R.S.

## FLETCHER'S THERMO-HYDROMETER.



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THE CHEMICAL NEWS.

VOL. LXVIII., No. 1779.

NOTE ON  
NATIVE COPPER FROM YUNNAN (CHINA).

By W. GOWLAND, Assoc. R.S.M.,  
Late of the Imperial Japanese Mint.

THE specimen of native copper—the subject of this note—was sent from the province of Yunnan, in China, to the Imperial Mint, Osaka, Japan, to be examined and reported on.

The mineral was obtained from an outcrop, in which it was said to occur in great abundance, and which it was proposed to exploit by western methods. As the occurrence of native copper in this locality has not hitherto been reported, and as the specimen is of great purity, the following brief account of it may be of interest to mineralogists and metallurgists:—

The specimen consisted of a flat nodular nucleus of metallic copper without crystalline structure, which was

The percentage of copper was not directly determined in it, as, after several volumetric determinations, it was found to be of greater purity than the specimens of electrolytic copper which had been supplied to the Mint as especially pure from two different sources.

In the principal works on mineralogy it is generally stated that native copper is usually pure or nearly pure. Dana, in his "System of Mineralogy," qualifies this, saying that "it often contains silver, bismuth, mercury, &c." I have, however, failed to find that these statements of the text-books are based on many exhaustive analyses, and hence append the accompanying Table containing all the analyses of native copper of which I can find any record, including, for the sake of comparison, this specimen from Yunnan.

From these it will be seen that the native copper from Chili and Lake Superior alone—and the latter not always—are of great purity, that this from Yunnan very closely approaches them in purity, and that the other localities given yield an impure mineral containing considerable proportions of one or more metals.

December 19, 1893.

NOTE.—Since the Table below was in type I have met with another analysis of a specimen, which I append:—

Analyses of Native Copper.

Locality	Chili.	Lake Superior.	Yunnan.	Lake Superior.	Lake Superior.	Brazil.	Ural, Siberia.	Bolivia.	Bolivia.	Bolivia.	Lake Superior.
Analyst	Abel.*	Abel.*	Gowland.	Rammelsberg.†	Abel.*	Marchand and Scheerer.‡	Abel.*	Von Bibra.§	Von Bibra.	Von Bibra.§	Haute-feuille.†
Copper..	—	—	99.946	—	—	99.56	—	97.39	97.50	97.48	—
Silver ..	min. trace	0.002	0.026	nil	0.56	0.30	0.034	—	—	—	7.30
Gold ..	nil	nil	nil	—	nil	0.08	—	—	—	—	—
Iron ..	min. trace	„	0.028	0.31	„	0.10	—	1.80	2.02	2.24	—
Bismuth ..	nil	„	nil	—	„	—	0.011	—	—	—	—
Arsenic ..	„	„	„	—	„	—	1.28	—	—	—	—
Antimony ..	„	„	„	—	„	—	—	trace	trace	trace	—
Tin ..	„	„	„	—	„	—	—	—	—	—	—
Lead ..	„	trace	„	—	„	—	min. trace	—	—	—	—
Mercury ..	—	—	—	—	—	—	—	—	—	—	0.03
Nickel and cobalt	—	—	nil	—	—	—	—	—	—	—	—
Gangue ..	—	—	„	—	—	—	—	0.44	0.21	—	—
			100.000			100.04		99.63	99.73	99.72	

\* *Journal Chemical Society* (2), i., p. 89.

† Kammelsberg, "Handbuch der Mineral Chemie," Art. "Kupfer."

‡ Percy, "Metallurgy," i., 286.

§ *Journal fur Prakt. Chemie*, xcvi., 205.

incrusted with layers of cuprite and green carbonates of copper. Unfortunately no traces of gangue were attached to it, and no specimens of the other materials of the rim or of the "country" rock were received, hence the mineralogical and geological conditions of its occurrence could not be determined.

The weight of the metallic portion was 208.6 grms., and of the incrusting material 89.5 grms.

The metal was of extraordinary toughness and could be bent over completely, even when first deeply cut with a chisel, without showing the slightest trace of fracture. A careful analysis was made of the metal after it had been perfectly freed from the incrusting matter. The following results were obtained:—

Copper (by diff.)	99.946
Iron ..	0.028
Silver ..	0.026
Gold ..	nil
Lead ..	„
Arsenic ..	„
Antimony ..	„
Bismuth ..	„
Nickel and cobalt ..	„

A special search for these metals was made, but no trace of any were found.

100.000

Locality	Bolivia.
Analyst	Kroeber.¶
Copper..	98.605
Silver ..	trace
Gold ..	—
Iron ..	1.376 (as loss)
Bismuth ..	—
Arsenic ..	—
Antimony ..	—
Tin ..	—
Lead ..	—
Mercury ..	—
Nickel and cobalt ..	—
Insoluble ..	0.004
Silica ..	0.015

100.000

¶ Bristow, "Glossary of Mineralogy," p. 252.

Medal.—The Bronze Medal of the National Gardeners' Association was unanimously awarded on December 5th to Dr. A. B. Griffiths "for his books on Manures, and for distinguished services rendered to horticultural science."

## PREPARATION OF CUPROUS OXIDE.

By EDWARD J. RUSSELL.

IN preparing cuprous oxide by the ordinary method, viz., by reducing  $\text{CuSO}_4$  with cream of tartar and glucose in presence of excess of alkali, there is sometimes a difficulty in decanting or filtering, especially if we follow the directions given in Watts's "Dictionary," and attempt to "boil until the supernatant liquid is colourless."

The method I have found most convenient is the following modification of a well-known method:—A mixture of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with excess of  $\text{NaCl}$  is dissolved in water and a fairly concentrated solution is obtained.  $\text{SO}_2$  is now passed through to saturation; the  $\text{CuCl}_2$  formed, however, instead of being precipitated, remains dissolved in the excess of  $\text{NaCl}$ . On now heating to expel  $\text{SO}_2$ , we obtain a solution which is either colourless or slightly tinged with green. Solid  $\text{Na}_2\text{CO}_3$  is then added while hot and a beautiful bright red precipitate of  $\text{Cu}_2\text{O}$  obtained. This very speedily settles, and can readily be washed by decantation.

If there is any doubt as to whether the reduction has been completed, a little  $\text{Na}_2\text{CO}_3$  can be added to the solution, and the precipitate thus obtained filtered off; the filtrate will be found to be quite colourless, and can be treated as above described with more  $\text{Na}_2\text{CO}_3$ . A quantity of a very pure product can thus be very speedily and easily prepared.

University College of Wales, Aberstwyth.

ON ENDOTHERMIC DECOMPOSITIONS  
OBTAINED BY PRESSURE.\*PART II.—TRANSFORMATIONS OF ENERGY BY SHEARING  
STRESS.

By M. CAREY LEA.

OF the relations which exist between two forms of energy, mechanical and chemical, very little, if anything, is known. In the second volume of his "Lehrbuch," Ostwald remarks that as to these relations "almost nothing" is known.†

There are certain familiar cases in which mechanical energy may seem at first sight to be converted into chemical energy. The fulminates, iodimide, and other substances explode by shock. But it is hardly necessary to remark that all such reactions are exothermic, and need an external impulse only, to start them—if this impulse were not needed such compounds could not exist at all. Were such reactions taken as true transformations of energy, an absence of due relation between cause and effect would be involved. For the shock that suffices to explode a grain of fulminate will equally explode a ton. The faint spark that will explode a grain of gunpowder will also explode a magazine.

Present opinion holds undoubtedly that no true transformation of mechanical into chemical energy is known. Most text-books do not consider the question at all. But Dr. Horstmann in the volume of theoretical chemistry which forms part of the last German edition of Graham Otto's "Chemistry," discusses the matter. His views are so much to the point that I shall translate a few sentences, putting in italics the statements to which I would specially refer:—

"We must consequently admit that through a rough mechanical attack the molecular structure of certain

chemical compounds can be disrupted and destroyed. This will certainly be possible only for compounds in whose molecules the arrangement of the atoms does not correspond to a stable equilibrium and in which therefore the chemical energies themselves are already striving to form simpler and more stable compounds out of the constituents of the existing substance. *For it cannot be admitted that actual chemical changes can be brought about by a mechanical impulse.*" (L. c., p. 350).

In another chapter he says with equal distinctness:—

"*By mechanical means alone no reaction against the force of chemical energy can be brought about.* By a shock or blow the molecular structure of chemical compounds can indeed be so far loosened that free play is given to chemical forces; *but against these forces we cannot by mechanical means separate the atoms nor combine them in a definite way.*" (P. 594).

These expressions of a distinguished chemist will sufficiently indicate what has been up to the present time the opinion of chemists as to the possibility of transforming mechanical energy into chemical.

In the first part of this paper I believe I have been able to show in a qualitative way the production of true endothermic reactions by mechanical force. In the present part I hope to show an increased number of such reactions, and in one case to exhibit actual quantitative results, at least so far as to obtain the product of the transformation in weighable quantities.

In the first part decompositions were described that were brought about by *simple pressure*. Compounds formed by exothermic reactions, and therefore requiring expenditure of energy to break them up, were decomposed. The investigation might probably have been made to include a still larger range of substances. But it was found that the efficiency of pressure was so enormously increased by the addition of shearing motion, that decompositions requiring a force of hundreds of thousands of pounds with pressure alone, could be effected by the mere strength of the hand when shearing stress was used. More than this, decompositions which enormous pressures failed to effect, readily took place under the action of shearing stress.

(It would not have been difficult to obtain much greater pressures than those described in the first part of this paper. This could be effected by means of the differential screw. I had planned for a screw with threads of 40 turns in 10 inches and  $39\frac{1}{2}$  turns in 10 inches respectively. The mechanical efficiency of such a screw is that of one having 320 turns to the inch, if such a thing were practicable; at the same time a thoroughly strong construction can be obtained. The massive steel nut to advance  $\frac{1}{8}$  of an inch would require 40 full turns of this screw. This arrangement compares as follows with that previously employed. In it to cause the vice jaws to approach by 1 inch required that the point of the lever at which the force was applied should pass through a space of 113·1 feet: this relation, 1 inch to 113·1 feet, or 1 : 1357·2, gives the measure of the efficiency of the instrument. With the double screw, on the other hand, to cause the nut to advance  $\frac{1}{8}$  of an inch the end of the lever (two feet long) must pass through a space of 500 feet, or in the proportion of 1 inch to over three-quarters of a mile. The circumference described by the lever being approximately  $12\frac{1}{2}$  feet, and the screw requiring 40 turns to advance the nut  $\frac{1}{8}$  of an inch, we get the proportion of 1 inch to 4000 feet, or 1 to 48,000, which is the measure of the efficiency of such an instrument. Therefore, supposing two men to pull on the end of the lever, each with a pull of 100 lbs., the pressure exerted on the nut (disregarding loss by friction) would be 9,600,000 lbs., which could be doubled by using a 4-foot lever. Such a combination is quite practicable, the only real difficulty being to obtain sufficient solidity of construction to resist the strain. I had made drawings for this instrument, but gave it up in consequence of observing the enormously greater efficiency of shearing

\* From the *American Journal of Science*, xvi., December, 1893.

† "Andererseits ist von der Verhältnis zwischen mechanischer und chemischer Energie, fast nichts bekannt." A few lines below, this remark is repeated with emphasis. "Lehrbuch," 2nd German ed., vol. ii., p. 12.

stress as a means of transforming mechanical into chemical energy).

(I.)

It was mentioned in a previous paper on the decomposition of the silver haloids by mechanical force that when silver chloride was sharply ground for some time in a mortar, both the pestle and mortar became covered with a deep purple varnish of silver photochloride, thus indicating a partial reduction to subchloride. It has since proved that there is no more effectual method than this of applying shearing stress, and that in this way a number of quite stable chemical compounds formed by exothermic reactions can be broken up. The mortar and pestle should be very solid and of unglazed porcelain. With metal, there would be danger of action between the metal and the substance, and with agate mortars sufficient force cannot well be applied. In many cases success depends on the exertion of great pressure on the pestle. It is also absolutely essential that the quantity of material acted upon should be small. When a larger quantity is employed the particles slip or roll over each other, and thus escape the action of the stress. It is no doubt for this reason that the very remarkable results which can be obtained in this way have hitherto escaped attention.

A small quantity, a few decigrams., of the substance having been placed in the mortar, the first thing is to spread it in a thin uniform coat over the bottom and part of the sides. The pestle is then to be rotated with the utmost force that can be exerted.

*Sodium Chloraurate.*—The salts of gold are particularly well adapted to this examination, as the reduction is complete and the gold appears in the metallic state, so that it can be weighed and the exact amount of reduction can be fixed. It will be seen by (3) below that it may amount to as much as over 4 per cent of the gold present.

(1) Two or three decigrams. of chloraurate with a moderate trituration left 1.8 m.grms. of metallic gold. Under the action of the pestle the yellow colour of the salt gradually deepened to an olive shade. When water was poured on, the undecomposed salt dissolved, leaving the gold as a delicate purple powder. The colour of the gold being purple, instead of the more usual brown shade, explains the olive colour just mentioned, yellow and purple combining to form olive.

(2) Half a gram. of the salt was taken. This specimen was more neutral than the preceding, and was therefore more easily reduced. Half an hour's trituration had for effect the reduction of 9.2 m.grms. of gold.

(3) A similar treatment of the same quantity of chloraurate resulted in the separation of 10.5 m.grms. of gold.

These may seem at first somewhat small proportions. But it is to be recollected that the force is necessarily applied at a disadvantage and that the equivalent in work of chemical affinity is always very large. In the present case the figures are as follows:—Thomsen found as the heat equivalent for the combination of gold with chlorine to form auric chloride 28.8 great calories. Taking the atomic weight of gold as 197, we find that one gram. of gold in forming auric chloride disengages 115.7 small calories or water-gram-degrees, whose equivalent, taking Rowland's determination, is 49,288.2 gram-meters, corresponding to  $4.83 \times 10^9$  ergs or 483 joules.

The small quantity of gold reduced in (3), 10½ milli-grms., would by conversion to auric chloride generate 1.215 water-gram-degrees of heat whose equivalent in work is 518 gram-meters. As heat is a degraded form of energy such an actual transformation without loss to a higher form would be impossible. It is more correct to say, therefore, that the amount of energy which would raise 518 grms. to the height of one metre can be transformed into the same amount of heat, 1.215 water-gram-degrees, as is evolved by 10.5 m.gs. of gold by conversion into auric chloride. Consequently this work, 518 gram-meters represents the amount of mechanical energy transformed into chemical energy in operation (3).\*

It does not appear that in effecting these reactions and the others which remain to be described, mechanical energy undergoes an intermediate conversion into heat. Rapid movements are not needed, what is required is strong pressure with movement, but this need not be rapid. Nor does the mortar or the pestle become sensibly warm. The operation does not need to be continuous, but may be broken up with any number of intervals. But a decisive conclusion can be drawn from those cases in which decompositions are effected in this way that *cannot be produced by heat*. For example, in the next instance to be mentioned there is a partial reduction of corrosive sublimate to calomel. By heat, corrosive sublimate sublimes unaltered and the same is true of mercurous chloride. The three silver haloids fuse unchanged at a red heat. The same conclusion can be drawn from other reactions.

These results were obtained in an atmosphere absolutely free from dust, so that the reducing action of this substance was completely excluded.

*Mercuric Chloride.*—A specimen which after lightly powdering did not darken in the least with ammonia was trituated in the manner just described with several intervals, in all for 15 minutes. It then became grey in a very striking way when moistened with ammonia.

This is a very interesting reaction. In the first part of this paper it was mentioned that mercuric chloride could be subjected to a pressure of about 70,000 atmospheres absolutely without change. It appears, however, that a pressure amounting to less than a hundred pounds causes decomposition when combined with movement, showing the enormously greater efficiency of shearing stress as compared with simple pressure. Not only this, but, as just mentioned, shearing stress produces decompositions which heat is not competent to effect.

*Mercurous Chloride.*—When calomel was sharply trituated in a mortar it first became yellow and then blackened without difficulty.

*Turbeth Mineral*,  $3\text{HgO} \cdot \text{SO}_3$ .—Reduces rather slowly.

*Mercuric Oxichloride*,  $2\text{HgO} \cdot \text{HgCl}_2$ , obtained by precipitating corrosive sublimate by potash acid carbonate, exhibited the following reaction. Its brownish purple colour by light grinding became lighter, and then when strong force was used it blackened with remarkable ease.

*Mercuric Iodide* shows a trace of blackening.

*Mercuric Oxide.*—This substance yields much more readily to trituration than to simple pressure. Especially on the sides of the mortar it was quite blackened. The layer of material must be quite thin, otherwise little effect is produced.

*Platinic Chloride.*—Gradually darkened in a very marked way, finally becoming blackish.

*Ammonium Platinichloride* gave same result.

*Silver Tartrate.*—When spread in a very thin skin over the mortar each sharp stroke of the pestle left a black line behind it. This is a strong contrast with the complete resistance of this substance to simple pressure.

*Silver Carbonate.*—Action similar.

*Silver Citrate.*—Blackens very easily.

*Silver Oxalate.*—At least as easily.

*Silver Arsenate.*—Nearly as easily.

*Silver Sulphite.*—Effect visible in five minutes and gradually increasing. Very well marked.

*Silver Salicylate.*—No silver salt appears to be so easily reducible as this. Every sharp stroke of the pestle leaves a brown mark behind it.

*Silver Orthophosphate.*—Affected easily. After the phosphate has been a good deal reduced the unchanged part may be dissolved out with ammonia. The black residue after washing readily dissolves in dilute nitric acid and the solution gives a white cloud with hydrochloric acid.

as the thermochemical equivalent of formation of sodium chloraurate would slightly exceed that of auric chloride. For the chloraurate I do not find a determination, but preferred to use this salt in the operation as being both more stable and more neutral than auric chloride.

\* The amount of energy required would in fact slightly exceed this,

*Potassium Ferridcyanide.*—A crystal of the pure salt sharply ground in a mortar becomes in portions brown and in others blue. The quantity used must, as indeed in all of the above cases, be small—one or two decigrams. If a little distilled water be added an insoluble blue powder is left behind and the solution formed strikes a blue colour when added to one of ferric alum. This indicates that the decomposition is twofold. The experiment is quite a striking one and the result is easily obtained.

## (II.)

This form of mechanical force, shearing stress, may be applied to effect endothermic change in other ways. A very simple, and at the same time very efficient, method is that of pressure with a glass rod. Pure strong paper is to be imbued with a solution of the substance, if it is soluble, or if not it is to be made into a paste with water and then applied with a brush. The paper is to be then very thoroughly dried and is to be laid upon a piece of plate glass. Characters are to be marked on it with the end of a glass rod that has been rounded by heat, using as much pressure as is possible without tearing the paper.

More than twenty years ago I was able to show that marks made in this way on sensitive photographic films could be developed, as an invisible image had been impressed. That, however, is a somewhat different matter from actual and visible decomposition following each stroke of the rod, a result which may be obtained with various salts of gold, mercury, silver, and other metals.

*Potassium Ferridcyanide.*—Pure paper was imbued with a dilute solution of this salt. After thorough drying it was laid on a glass plate and marks were made with a glass rod in the manner just described. These marks were immediately visible and when the paper was plunged into dilute solution of ferric ammonia alum or of ferric chloride they became dark blue. It is probable that the decomposition here effected was two-fold (see above).—The *nitroprussides* appear to be much more stable than the ferridcyanides. When sodium nitro-prusside paper was treated with pressure, followed by appropriate reagents, no indications of decomposition were obtained.

*Auric Chloride.*—Paper imbued with a solution of auric chloride and marked in the manner described was thoroughly soaked in water to remove, as far as possible, the rest of the gold salt. The marks were very distinct and gradually gained with time. Colour dark purplish grey.

*Platinic Chloride.*—After drying and marking, the paper was thoroughly soaked in water and dried. The marks were very distinct, of a yellow colour.

*Ammonium Platinichloride.*—Marks very visible. Continued to slowly deepen, and in a few weeks were almost black.

*Silver Carbonate.*—The traces of the rod were brown. When the paper was placed in ammonia the carbonate dissolved, but the marks resisted the action of the ammonia and remained.

*Silver Phosphate.*—Action very similar to the preceding.

*Silver Arsenate.*—Similar action.

*Silver Tartrate and Oxalate.*—These salts gave analogous results to the preceding, but not so well marked. The carbonate phosphate and arsenate show this reaction best and about equally well. What is rather curious is that silver chloride does not exhibit a visible action.

*Mercuric Oxide.*—Paper imbued with a saturated solution of mercuric nitrate and then treated with solution of potash and dried shows this reaction very distinctly. Mercuric oxide appears to be quite sensitive to light.

*Turpeth Mineral.*—Mercuric sulphate was dissolved in water with the aid of sulphuric acid. Paper was soaked in the solution, allowed to become nearly dry and then washed. This paper showed the reaction very moderately, but the marks were brought out more strongly by immersion in ammonia.

*Ferric Alum (Ammonia).*—Paper imbued with solution

of this salt dried and marked was immersed in solution of potassium ferridcyanide. The marks came out blue, showing that the ferric salt had undergone partial reduction.

It is easily conceivable that the action of shearing stress should be enormously greater than that of simple pressure. For it seems probable that pressure can only cause decomposition when the resulting product is more dense, has a greater specific mass, than the original substance. With shearing stress the case is altogether different. All matter is in a state of vibration, and it is easily conceivable that the forcible friction of a hard substance may increase vibration in somewhat the same way as does a bow drawn over a stretched cord. Both the elasticity and the tension of the atoms themselves are vastly greater than those of any stretched cord, so that the increased vibration may easily be sufficient to shatter the molecule.

The transformation of light, heat, and electricity into mechanical energy as well as the converse transformations are extremely familiar. That mechanical energy may be transformed into chemical energy is proved by the results in these papers described. The converse transformation, that of chemism into work, is in an industrial point of view by far the greatest chemical problem now waiting for solution. But it is by no means certain that such a transformation is practically possible. At least it seems probable that the improvement in our method of obtaining work from the chemism of carbon may be in the direction of substituting electricity for heat as the intermediary.

## LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1893.

By WILLIAM CROOKES, F.R.S.,

and

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,  
Professor of Chemistry at the University of Oxford.

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

London, December 12th, 1893.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the 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 November 1st to November 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 182 samples examined two were recorded as "clear, but dull," the remainder being clear, bright, and well filtered.

Comparing the average composition of the five Thames-supplied waters during the month of November with that of the corresponding month last year, we see considerable differences. In November, 1893, the common salt, nitric acid, and hardness are practically the same as they were last year, but in the other constituents—those which may be termed the contaminating factors—the month just ended shows a diminution of more than 50 per cent, whilst the brown colour, a good rough criterion of the

organic matter present, has sunk from 24.5 to 15.5. This improvement is well seen by reference to the following Table:—

Comparison of the Averages of the Five Thames Supplies for the Months of November, 1892 and 1893.

	Common salt per gallon.	Nitric acid per gallon.	Hardness, de- grees.	Oxygen re- quired per gallon.	Organic car- bon per gal- lon.	Organic car- bon per gal- lon.	Colour.	
							Means.	Maxima.
1892	2.238	0.839	16.29	0.076	0.142	0.199	24.5	20
1893	2.248	0.766	15.33	0.033	0.068	0.096	15.5	20

As compared with the composition of the October waters, that of November shows scarcely an appreciable difference, and for all practical purposes they may be looked upon as of the same excellent quality that has characterised the waters for several months past.

Again we have to record a deficient rainfall. Whilst the mean rainfall for twenty-five years at Oxford has been 2.31 inches for the month of November, there has actually fallen 1.68 inches during the month, giving a deficiency of 0.63 inch.

We are, Sir,  
Your obedient Servants,  
WILLIAM CROOKES.  
WILLIAM ODLING.

### ON ALGINE.

By A. M. VILLON.

ALGINE is a mucilaginous matter resembling gum arabic, obtained by Mr. Stanford from the red algæ or laminariæ (*L. stenophylla* and *L. digitata*).

It is manufactured in the following manner:—The seaweeds are treated with a boiling solution of sodium carbonate, which dissolves the alginic acid in the form of sodium alginate, and leaves as a residue the cellular tissue of the plant, consisting of a special cellulose named algulose. The alkaline solution is filtered and treated with hydrochloric acid, which precipitates the alginic acid in a gelatinous state, of an amber colour. The precipitate is separated by means of the filter-press, re-dissolved in a solution of sodium carbonate, evaporated to a thick consistence, and finally dried by being spread in flat vessels of porcelain or glass placed in a stove moderately heated, as is done with albumen.

*Soluble algine*, which is an alkaline alginate, appears in the form of flexible transparent laminæ of the following composition:—

	Per cent.
Water .. .. .	18.22
Organic matter .. .. .	59.05
Sodium carbonate . . . .	18.05
Neutral salts . . . . .	2.87
Insoluble substances .. ..	1.81

Algine is very similar to gelatin, but it differs by not coagulating to a jelly, and by not being precipitated by tannin. It differs from albumen by not being coagulated by heat. It differs from gum arabic because it is precipitated from its solutions in an insoluble state by the mineral acids and by the oxalic, tartaric, citric, lactic, and picric acids.

Algine forms soluble salts with the alkalis. By double decomposition with the metallic salts it yields alginates which are insoluble, except those of magnesium and manganese.

The solutions of algine are very viscid. It has fourteen times the viscosity of starch, and thirty-seven times that

of arabic. This property enables it to be used in tissue-printing as a thickener, in place of gum or dextrin.

It gives cloths a thick, soft, elastic handle, and furnishes a transparent dressing, which may be made insoluble and impermeable by taking the cloth through a dilute solution of algine and then through very dilute hydrochloric acid, which fixes the alginic acid on the fibres in an insoluble state.

The alkaline alginates may be used as salts for "dyeing," for fixing iron and aluminium mordants upon cotton tissues.

Aluminium alginate, dissolved in ammoniacal water, serves to render cloth waterproof. It is merely necessary to steep the cloth, and to aerate it so as to expel the ammonia, when the aluminium alginate is left in the pores of the cloth in an insoluble state. In this manner we have rendered leather impermeable.

Aluminium alginate is used as a mordant.

Copper alginate dissolved in ammonia-water has been proposed for impregnating substances to preserve them from decomposition or from the attacks of insects. We have employed it successfully against the cryptogamic diseases of the visa. The double iron and ammonium alginate is employed in medicine as a styptic.

A mixture of sodium dichromate and alginate is sensitive to light.

Algine has been proposed as an anti-incrustation agent in steam-boilers, as it precipitates calcareous salts.

Lastly, it is employed for emulsifying oils and clarifying wines and spirits.

Insoluble algine is alginic acid.—*Société Chimique de Paris.*

### ON METALLIC SEPARATIONS IN ALKALINE SOLUTION OF HYDROGEN PEROXIDE.

By PAUL JANNASCH.

*Behaviour of Copper Solutions.*—If to the neutral solution of a copper salt there is added dilute ammonia, drop by drop, until the precipitate first formed is just re-dissolved, and if we then add a 3 per cent solution of hydrogen peroxide, the liquid froths up briskly, and we obtain a bulky flocculent precipitate of black olive-greenish per-cupric hydroxide. Unfortunately I have not yet succeeded in effecting this precipitation quantitatively, for in numerous trials with about 0.5 gm. of copper sulphate, in different concentrations and at different temperatures, appreciable quantities of copper (averaging 1.5 to 2 per cent copper oxide) remained in solution. For these approximately quantitative precipitations large quantities of hydrogen peroxide were required (150 to 250 c.c.). Further, on weighing the results were invariably too high, in consequence of the presence of considerable admixtures of silica, which showed that hydrated copper peroxide in an alkaline liquid somewhat attacks the porcelain vessels.

On studying the influence the presence of organic substances, such as tartaric acid, exerts upon the precipitation of copper by hydrogen peroxide, I had the opportunity of observing a remarkable chemical action, by means of which we can, on the one hand, demonstrate the simultaneously oxidising and reducing properties of a compound which easily gives off oxygen, and, on the other hand, the formation of all three stages of oxidation of copper in one and the same reaction. For this purpose we precipitate a solution of copper sulphate in a roomy test-tube with an excess of soda-lye (copper hydroxide); add then so much tartaric acid as to produce a clear solution of hydrogen peroxide until there appears an abundant precipitate (hydrated copper peroxide). If this precipitate is then rapidly heated over a high flame the precipitate entirely disappears with brisk effervescence, whilst the liquid takes transitively a splendid dark velvety

green colour, and, when it has again become blue, there is lastly formed an abundant yellowish-red deposit of cuprous oxide. The separation of cuprous oxide generally ensues suddenly, when the liquid is removed from the flame and allowed to remain for a short time undisturbed. Thus the entire process is a so-called "time-reaction." The author used—

1. A mixture of 2 c.c. solution of copper, 3 c.c. tartaric acid, 4 c.c. soda-lye, and 15 c.c. hydrogen peroxide at 2 per cent gives, after a momentary effervescence, on cooling, an abundant deposit of bright red granular cuprous oxide.

2. Two c.c. copper sulphate, 1 c.c. tartaric acid, 1 c.c. soda-lye, and 10 c.c. hydrogen peroxide give, after boiling until the restoration of the blue colour, a reddish-brown flocculent deposit, whilst the liquid is decolourised.

3. Two c.c. copper sulphate, 1 c.c. tartaric acid, 0.5 c.c. soda-lye, and 5 to 10 c.c. hydrogen peroxide yield a flocculent pale green deposit, which on prolonged standing becomes a heavy yellow sediment, with fine light blue supernatant flakes.

4. Two c.c. copper sulphate, 1 c.c. tartaric acid, 0.5 c.c. soda-lye, and 15 c.c. hydrogen peroxide give a light blue precipitate unchanged on boiling.—*Ber. der Deutsch. Chem. Gesell.*

### ON LIFE AT LOW TEMPERATURES.

By RAOUL PICTET.

IN the 76th meeting of the Swiss Society of Naturalists, held at Lausanne, from the 5th to the 8th of September, the author described the struggle of Nature against external attacks. If a dog is placed in a copper receiver, cooled down to  $-60^{\circ}$  to  $-90^{\circ}$ , its temperature rises by half a degree in the first ten minutes. On prolonging the experiment the extremities become cold, but the body resists for some time. After 90 minutes the temperature falls by  $1^{\circ}$ . Then follows a point where the struggle is given up, the temperature falls rapidly, and the animal dies suddenly. Pictet has made similar experiments on himself and others, exposing his arm to such low temperatures. Pain occurs within the arm on the periosteum, whilst the epidermis experiences no pain.

All insects resist a cold of  $-28^{\circ}$ , but not of  $-35^{\circ}$ . Myriapods resist down to  $-50^{\circ}$ , and snails to  $-120^{\circ}$ . The eggs of birds lose their vitality at  $-2^{\circ}$  or  $3^{\circ}$ , the eggs of ants at  $0^{\circ}$ . Frog-spawn bears  $-60^{\circ}$ , and silkworms' eggs  $-40^{\circ}$ . Infusoria died at  $-90^{\circ}$ , and bacteria retained their virulence at  $-213^{\circ}$ . This cold was produced by frozen atmospheric air.—*Chemiker Zeitung.*

### ANALYSIS OF THE BUTTERS OF COMMERCE.

By C. VIOLETTE.

THE method which I employ comprises two series of operations; in the former the butters are classified according to their specific gravities taken at  $100^{\circ}$ , in three groups—the margarined butters, the doubtful butters, and the pure butters and those which may be considered as such.

*Classification of Butters.*—When operating by the bottle method upon pure butters, margarines, and mixtures, and taking account of all the necessary corrections, I have found—1, that the weight in a vacuum of 1 c.c. of butter, at  $100^{\circ}$  varies in general from 0.86320 gm. to 0.86425 gm.; 2, that for margarines this same quantity varies from 0.85766 gm. to 0.85865 gm.; 3, that the density of a mixture of butter and margarine is exactly the mean of the density of the constituents; 4, that

beasts principally fed on hay yield butters the densities of which are close upon 0.86320, whilst cattle chiefly fed on grass, pulps, cakes, and farina yield butters of higher densities, close upon 0.86425; 5, that in more than 150 samples examined I have found only two obtained from cattle of Le Nord, and well nourished with oil-cakes, &c., which had densities reaching to 0.86530 and 0.6540; and a single one, from a cow fed on straw and dry hay, had a density of 0.86277. These three exceptions, from a general point of view, have little importance.

The exact determination of the densities of a certain number of samples of butter, of margarine, and of mixture, have furnished me with bases for the graduation of a densimeter which shows at  $100^{\circ}$  all the densities comprised between those of margarine and of butter. This instrument is extremely sensitive, for the units of the fourth decimal place occupy on the scale a length of 1.4 millimetre. A simple reading on the stem of the instrument plunged into butter heated to  $100^{\circ}$  enables us to establish the classification of a butter in one of the three categories above mentioned.

The apparatus which enables me to heat fatty bodies conveniently and rapidly to  $100^{\circ}$  is composed of a water-boiler formed of two cylindrical parts connected by a small bent-piece. The steam-chamber of the boiler communicates with a worm cooled by a stream of water. On the platform, situate below the first joint, is soldered a test jar of tinned copper, fitted at its lower part with a tube having a cock opening outwards, and permitting the fatty substance to be withdrawn after each operation. The boiler is set vertically upon a covering support, and heated by means of a strong gas-burner. A quarter of an hour is sufficient to raise the fatty substance to  $100^{\circ}$ , indicated by a thermometer. The melted butter is stirred repeatedly, raising and lowering the densimeter, and the degree is noted after allowing it to rest for a few moments.

This arrangement, necessary for my researches, which extended at once to butters, margarines, and their mixtures, has the inconvenience of requiring a considerable quantity of the sample, about 480 grms. of melted butter. To obviate this inconvenience I have subdivided the densimeter into a series of smaller floaters, graduated by comparison with the type instrument. Their volume is 36 c.c., and they require only 50 grms. of butter for each observation.

A simple floater, No. 1, enables us at once to classify the butters. The stem has merely three marks; that in the middle corresponds to the density 0.86266; the lower one, 0.86320, for very numerous pure butters; and the upper mark corresponds to the density 0.86215, which indicates a proportion of 25 per cent of margarine in a medium butter. If the level of immersion is between the middle and the lower lines, it may happen that the butter is pure, but it is very probably mixed with margarine. This is why I regard such butters as doubtful, and put them aside for a more complete examination by chemical methods. If the floating-level is at the lower mark and below, it will be well to make use of the floaters No. 2 and No. 3, the marks on which, corresponding to higher densities, permit us to ascertain the nature of the butter. In case the floating-level is above the higher mark, we have recourse to another series of floaters comprising the densities of 0.86266 to 0.857, and indicating the approximate proportions of margarine.

This classification cannot be absolute, since butters of high density may be brought to a marginal density by the addition of margarine. Thus the expert should be careful to work, from time to time, upon the mean butters of the region, so as to know their normal density. In general this density varies little for butters obtained from cattle fed on the same diet. Thus butters obtained from cattle feeding in Calvados, Côtes-du-Nord, Tarn, Ardennes, and Loire (May, 1891), had densities between 0.86415 and 0.86465, the range being 0.0005. A butter from the dairy of Braine-le-Comte (Belgium, Nov., 1892),

derived from the milk of thirty-three farms, had the density 0.86425. The butter of a single cow of this dairy had the density 0.86385: difference, 0.0004 gm.

The application of this method does not require special chemical knowledge. It is rapid in execution, permitting an operator with an assistant to classify easily a hundred samples per day. The doubtful butters are reserved for a chemical examination the particulars of which I will shortly describe.—*Comptes Rendus*, cxvii., p. 856.

## RESEARCHES ON SAMARIUM.

By LECOQ DE BOISBAUDRAN.

I HAVE elsewhere said that the reversal bands of Sm change their relative lustre with the experimental conditions. Thus  $Z\zeta$  614.4 gains a little as regards the orange when the spark is very short, when the solutions are concentrated, when there is a great excess of HCl, a case in which  $Z\zeta$  even slightly passes the orange (with the spark in the middle of the liquid), &c. These observations have led me to suppose that the increase of  $Z\zeta$  at the head of the fractionation by  $NH_3$  was perhaps due to changes in the experimental conditions. I have therefore anew compared the head and the middle of this fractionation, endeavouring to equalise the conditions.

The increase of all the fluorescence and the relative increase of  $Z\zeta$  seemed then decidedly less pronounced, though they were still observed in passing from the middle to the head of the fractionation by  $NH_3$ . The electric rays,  $Z\epsilon$ , were also found a little more marked at the head than at the middle, the difference, however, being less than that previously observed.

I have fractionated very carefully, by  $NH_3$ , the head of my previous fractionation by oxalic acid, which had itself been effected on the head of the first fractionation by  $NH_3$ . The very small mass of matter left in the oxalic tailings contained all the  $Z\beta$ . If the relative strengthening of the  $Z\zeta$  observed at the head of the first fractionation by  $NH_3$  was due to the concentration of any particular element, we might expect that this intensification would be much heightened at the head of the second fractionation by  $NH_3$ , which is, moreover, the last practicable, on account of the extreme scantiness of the matter.

In the head of the last fractionation by  $NH_3$ ,  $Z\zeta$  has not a relative lustre greater than in the tailings, where the other bands are slightly brighter than at the head, and where we do not see a trace of  $Z\beta$ , no more than at the head. But both at the head and at the tailings of the last fractionation  $Z\zeta$  is relatively and absolutely slightly superior to what it is at the middle of the first fractionation by  $NH_3$ .

Besides the reversal bands of samarium already described—red, orange-red, orange (double), and green—there exists another green band, much weaker, which I have observed long ago, and which is not without interest. Its maximum of luminosity (measured on the prismatic scale) is  $\lambda=535.4$  (a mean of the best measurements). The band is very cloudy, especially to the left, and it is distinctly narrower than the first green (maximum of the first green  $\lambda=560.6$ ). The brightness, always very moderate, varies with the experimental conditions, the nature of the acid, and also slightly with the portion of the fractionation.

The band 535.4 seems to gain a little when the spark strikes at the margin of the liquid instead of being drawn near the centre, and when the spark is very short. It is seen better in a very acid hydrochloric liquid than in a solution which is nearly neutral. It is a little stronger in  $NHO_3$  than in HCl. It is also produced in an acetic solution, although rather more feeble than in HCl. The band 535.4 is slightly stronger at the head than at the middle of the fractionation by  $NH_3$ .

Comparison of  $Z\zeta$  and of 535.4.—Nitric acid strengthens these two bands with respect to the orange, but the in-

crease of  $Z\zeta$  is by far the greater. The two bands are so much better developed in the hydrochloric solution the more acid it is (always provided that the quantity of HCl is not such as to precipitate  $Sm_2Cl_6$ ). The two bands were slightly more marked at the head than at the middle of the first fractionation by  $NH_3$ . They gain a little with the shortness of the spark. The band 535.4 is only slightly enfeebled by acetic acid, whilst  $Z\zeta$  is extinguished or reduced to a trace.  $Z\zeta$  gains very distinctly if the spark strikes at the middle of the liquid, but 535.4 seems rather to be enfeebled.

I have already mentioned the extinction of  $Z\zeta$  by acetic acid (said to be pure). I believe, however, that I have seen  $Z\zeta$  faintly with a concentrated acetic solution. The red and green bands (643.4 and 560.6) seemed a little more developed (with reference to the orange) than in solution in HCl. The addition of a volume of acetic acid (at 8°) weakened 535.4 slightly and rendered  $Z\zeta$  very feeble or null, but rather strengthened the other bands.

With  $NHO_3$  the red and green bands (643.4 and 560.6) are distinctly stronger with reference to the orange than with HCl, but this increase is less than that of  $Z\zeta$ .

I had previously measured the ray rather cloudy but narrow which forms the right margin of  $Z\zeta$ , and found  $\lambda=611.2$ . Having repeated this measurement, I again found  $\lambda=611.2$ .—*Comptes Rendus*, cxvii., p. 199.

## ON THE PREPARATION OF METALLIC LITHIUM.

By M. GUNTZ.

THE preparation of metallic lithium might seem at first sight an easy operation, but on repeating the experiments of Bunsen, Hillier, and Troost we quickly perceive, on making quantitative determinations, that the yield, though very variable in different operations, is in general extremely low with reference to the intensity of the current employed.

On studying the best conditions for the preparation of lithium, we have found that the yield of metal is so much the higher as the temperature of the electrolysis is lower. An impure salt, containing potassium and sodium chlorides, gives, when electrolysed at its melting-point, much better results than pure lithium chloride. This result led us to lower the melting-point of the lithium chloride by the addition of potassium chloride. I have found that LiCl melting about 600°, the mixture of LiCl and KCl at equal weights melts about 450°. A mixture of equal mols. of the two chlorides melts about 380°; a mixture of 2 mols. KCl with 1 mol. of LiCl melts at 550°; and pure potassium chloride melts at 740°. The most favourable mixture for electrolysis contains equal weights of the two chlorides. This mixture can be easily kept in fusion below 450°; and, moreover, during the electrolysis the mixture loses lithium chloride and its fusibility becomes greater. This is not the case with the mixture formed of equal mols. of LiCl and KCl, the fusibility of which diminishes rapidly under the same conditions.

To obtain large quantities of lithium we heat from 200 to 300 grms. of the mixture of the two chlorides in equal weights in a porcelain capsule over a simple Bunsen burner. The mixture melts very readily, and the two electrodes are then introduced. The positive electrode is a rod of carbon of about 8 m.m. in diameter; the negative electrode is a rod of iron from 3 to 4 m.m. in diameter, which is placed in the axis of a glass tube of 20 m.m. in diameter. The current is passed in, and the experiment goes on very rapidly by using, e.g., an electromotive force of 20 volts and a current of 10 ampères. At the end of an hour the lithium exceeds the level of the liquid in the glass tube by more than a centimetre. To extract the metal the tube is raised after interrupting the current; the lithium floats on the surface of the melted chloride.

without igniting. It is taken up in an iron spoon and poured into a dry ingot mould.

The metal thus obtained is free from iron and silicon, but contains 1 per cent of potassium by weight, which corresponds to 1 atom Ko to 273 atoms Li. For most uses the metal is sufficiently pure.

When the electrolysis is effected at a red heat, about 700°, with pure lithium chloride, the metal arriving at the negative pole combines with the chloride to yield a lithium sub-chloride,  $\text{Li}_2\text{Cl}$ , which remains at the negative pole. This compound, less conductive than the original chloride, diminishes the intensity of the current as it is observed at the ammeter. This sub-chloride, being diffused in the melted liquid, arrives at the positive pole, where it recombines with the chlorine with emission of light; this compound producing oscillations of the needle of the ammeter. When the temperature of electrolysis reaches 500° or even falls lower, the lithium does not combine with lithium chloride, and is found altogether at the negative pole, and may be collected. This is the reason of the high yield obtained in this case.

This phenomenon of the formation of metallic sub-chlorides by electrolysis seems general for the alkaline metals. I have not yet been able to obtain by this method compounds in a state of satisfactory purity.—*Comptes Rendus*.

#### THE STABILITY OF STANDARD SOLUTIONS OF TARTAR EMETIC.\*

By HIPPOLYTE GRUENER.

DURING the progress of some investigations on antimony, I found it desirable to know to what extent a solution of tartar emetic could be relied on to retain its strength when kept for a length of time. Accordingly I made up a number of solutions of tartar emetic, whose strength was determined by titration in presence of an alkaline tartrate and bicarbonate with decinormal iodine, standardised against arsenious oxide. These solutions were put aside in stoppered bottles for a number of months, when they were again determined with iodine standardised against the same arsenious oxide.

Solution A was simply tartar emetic in distilled water, 16 grms. to the litre. At the end of five months this was found to have lost strength to a considerable extent, while a deposit, seemingly a mixture of antimonious oxide and of fungus growth, had settled at the bottom of the bottle. At the end of fourteen months a still greater loss of strength was observed, corresponding in all to about 3.5 per cent. of the tartar emetic, of which 4 grms. were present. The sediment was drained, dissolved in tartaric acid, and titrated with iodine. It was found to correspond to 0.13 gm. of tartar emetic or approximately the amount lost. This shows clearly that under the conditions no great loss is caused by the formation of the pentoxide, in closed bottles at least.

Solution B was slightly alkaline with sodium bicarbonate in presence of sodium tartrate. On this solution after five months there was developed in addition to a fungus growth a deposit, probably antimonious oxide; there was here a slight loss in the strength of the solution, amounting to 1 per cent.

Solution C was acid with tartaric acid only. After ten months the solution was found of the same strength and clearness as it was originally; but four months later there was a slight deposit accompanied by a loss of 1.2 per cent.

Parallel experiments to A gave like results. Two repetitions of C with varying amounts of tartaric acid present showed in each case a decided fungus growth with no loss of strength at the end of five months, whereas at the end of nine months the loss amounted to

1 per cent. for the larger amount of tartaric acid and 0.3 per cent for the smaller amount.

It seems then that there is little danger of any oxidation of the antimonious oxide occurring, and provided enough tartaric acid is present to keep all the antimonious oxide in solution, the solution should maintain its strength for at least five or six months. The fungus growth has not been found to interfere in practical work with the solutions, yet it seemed advisable to prevent its formation if it could be done simply. To test the possibility of this, a number of solutions were prepared containing varying amounts of hydrochloric acid, which should act as a steriliser; enough tartaric acid was added to counteract any tendency towards precipitation. In one series of experiments the solutions were sterilised at the beginning by boiling; in the other series distilled water which had been exposed more or less to the air for a number of days was directly used. Where the solutions had been thus sterilised no sign of fungus growth had appeared at the end of five months, and in the case of the unsterilised solutions there was never more than a trace. Where the hydrochloric acid present was not more than 10 c.m.<sup>3</sup> to 500 c.m.<sup>3</sup> of water, there was at the end of three months only the faintest trace of a deposit and no material loss of strength. Where the hydrochloric acid was present to the extent of 25 c.m.<sup>3</sup> in 500 c.m.<sup>3</sup> of water a decided granular precipitate was observed, accompanied by a loss of strength of about 10 per cent. The granular precipitate dissolved in tartaric acid and titrated accounted almost exactly for this loss.

A number of solutions were prepared under varying conditions and left open to the air for three months, at the end of which time no loss from oxidation was found.

It may be seen that tartar emetic in a solution of 16 grms. to the litre is not oxidised either in closed or open bottles. If it is desired to keep this solution as a standard for a moderate length of time it can be done in presence of enough tartaric acid (20 to 30 grms. to the litre) to prevent precipitation. The addition of 1 c.m. hydrochloric acid to one litre of solution is enough to prevent any decided formation of fungus growth, at the same time not enough to cause a deposit, as happens when large amounts of hydrochloric acid are used.

In the titration of tartar emetic in presence of starch the permanent blue colour was taken in every case as the indication of the end reaction, as all other shades of colour were found unsatisfactory. It is a well known fact that in the titration of antimony salts the colour of the starch iodide is not developed until there is a considerable excess of iodine present, so that as compared with arsenious oxide, iodine gives high results with antimony. Thus, for example, the mean of six series of determinations made at various times and aggregating twenty-nine determinations showed the presence of 43.95 per cent of antimonious oxide in tartar emetic. ( $\text{Sb} = 120$  and tartar emetic  $\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O} = 332$ , requiring 43.37 per cent).

The facts above shown, that tartar emetic may be kept in stable solution by means of tartaric acid and hydrochloric acid in the proportions given, make it possible to use and keep such solutions for standardising iodine for the determination of antimony, and thus to eliminate the error due to the tardy development of the starch iodide blue in presence of antimony salts, observed when compared arsenious oxide is used as a standard.

On the Acyclic Isomers of Borneol.—Ph. Barbier. —These compounds are coriandrol and licareol. Licareol possesses a double isomerism, optical and geometrical, and exists in four distinct modifications: 1. Instable sinistro-licareol from the essence of licari, the stable isomer of which is dextro-licarhodol. 2. Instable dextro-licareol from essence of coriander, the stable isomer of which is sinistro-licarhodol.—*Bull. de la Soc. Chim. de Paris*, ix. and x., No. 23.

\* From the *American Journal of Science*, vol. xlvi., Sept., 1893.

NOTICES OF BOOKS.

*Animal and Vegetable Fixed Oils, Fats, Butters, and Waxes: Their Proportions and Properties, and the Manufacture therefrom of Candles, Soap, and other Products.* By C. R. ALDER WRIGHT, D.Sc. (Lond.), B.Sc. (Vict.), F.R.S. With 144 Illustrations. London: C. Griffin and Co., Limited. 1894. 8vo., pp. 570.

IT must be admitted that, of all the groups of natural organic substances, the fatty oils admit of the most numerous and varied uses, and that, at the same time, they are open not merely to natural fluctuation in their qualities, but to elaborate sophistications. Hitherto we have had, in the English language on these subjects, papers read before our learned Societies and inserted in the scientific and technical press, but no complete monograph treating of the oils and fats more comprehensively and in fuller detail than it is possible to do in general works. Dr. C. R. Alder Wright has supplied this deficiency in a manner which we may safely pronounce admirable. He has not merely "read up" the mass of information to be found in existing authorities, English and foreign; he has verified and digested their statements. He does not enter upon an examination of the mineral and volatile oils. From considerations of space he disclaims the attempt at a minute discussion of the analytical methods required in each possible case of sophistication.

Assuming general chemical principles as known to the reader, he commences with a general view of the composition of the oils, fats, &c., and their sources. He then enters upon saponification in the widest sense of the term, and of its products, alcoholiform and acid.

The section on physical properties of oils brings us to their characters as assisting in the recognition of their nature. We have here reference to the cohesion figures of Tomlinson, to the taste, odour, and colour of oils; their behaviour with polarised light, their solubility in various solvents, their fusing and solidifying points, specific gravity, their relative densities as affected by temperature, and on viscosimetry.

The next section enters upon the chemical properties of the oils, the separation of their constituents, the determination of the free-acid number, of unsaponifiable constituents, of water, and of suspended matters—too commonly present in lard and tallow.

A succeeding chapter treats of flashing points—important, of course, chiefly in mixtures containing mineral oils,—of the elaidin reaction, the nitric acid test, and the zinc test.

Among the quantitative reactions figure the Kœttstorfer test, the saponification equivalents, Hehner's test, Reichert's test, the bromine process, the iodine process, Hübl's test, and the tests of Benedikt and Ulzer, and of Zeisel.

The fourth section describes the processes used for extracting, rendering, refining, and bleaching oils, and the recovery of fatty matters from soap-suds.

In Section V. we find the classification of oils into the olive, the rape, the castor, the lard oils, the cotton-seed, the linseed and the train classes, the vegetable butters and waxes, the animal butters, the sperm oils, the non-glyceric waxes, and the bees'-wax class. Hereupon follow the principal uses of oils and fats,—*e.g.*, margarine, lamp oils, oils for paint and varnish, lubricants, Turkey red or alizarin oils, and lanoline.

The detection of adulterations is particularly given for the cases of olive oil, rape and colza, linseed, sperm, tallow, bees'-wax, and spermaceti.

The question whether the wax of bees, &c., is a secretion due to their own vital action, or is a substance pre-contained in the pollen and nectar of the flowers, is not absolutely decided, though the author gives reasons for accepting the former view. It is stated, in a note, that wax from the Bordeaux district is the most difficult to bleach.

The remainder of the book is devoted to the great industries of candles, soap, and glycerin. Notwithstanding the rise and progress of gas and of paraffin oils, the candle manufacture is far from declining. Simplicity and portability give the candle an advantage which in many cases outweighs its higher cost. As regards toilet soap, the author has in his "Cantor" lectures proposed their classification into three grades, according to the amount of free alkali present. This objectionable constituent may range from 0.2 to 7.5 per cent. He points out that sugar, very generally present in transparent soaps, is as irritating to the skin as free alkali, and that some of the essential oils used as scents are open to a similar objection.

We do not find any mention of the "soap-powders" and "extracts of soap" so extensively advertised, and employed by manufacturers and laundresses.

The only flaw we can find in this excellent work is that the author terms cocoa-nut oil "coker-nut" oil. This is, we believe, the first time that this vulgarity has found its way into scientific literature. To prevent the confusion between the cocoa-nut, the chocolate-nut, and the cuca, it would be surely better to call the first-mentioned product cocos-nut.

As a whole, Dr. Alder Wright's work merits to be accepted by all dealers in and manufacturers of the oily and fatty products as *the* standard authority.

*Intensity Coils; How Made and How Used.* By "DYER." With a Description of the Electric Light, Electric Bells, Electric Motors, the Telephone, the Microphone, and the Phonograph. Eighteenth Edition. London: Perkin, Son, and Rayment. 8vo., pp. 79.

WE have had the pleasure of noticing a former edition of this little work, and we feel by no means inclined to retract what we then said.

Several additions have been made, which will distinctly increase the value of the present book. The most interesting is entitled "Seeing by Electricity," and refers to an invention which if realised must throw all the "phones" completely into the shade. Imagine switching on a wire and being able to see in a camera lucida what is going on in a different room.

*Catalogue of Chemical Apparatus, Balances, Drying Ovens, Furnaces, Laboratory Stands, &c.* Part III. London: Gallenkamp and Co.

THIS part contains chiefly appliances of metal, wood, &c. Balances figure here very largely, of the makes of Sartorius, Becker and Sons, Roberzahl, and Rueprecht. All the sets of weights—metric of course—are made on the principle, objectionable as it seems to us, of the rejection of all weights which are not sub-multiples of 10. We will venture to say that the metric system would be more frequently adopted in England but for its nomenclature and its arrangement of 5, 2, 1, 1.

In appliances for the production and application of heat, whether by means of oil, gas, coke, charcoal, &c., the Catalogue is very rich. The furnaces of Fletcher, Luhme, Sefström, Hempel, Griffin, L. Meyer, Erlenmeyer, &c., are figured and described.

Incubators, sterilisers, and thermostats are shown of different makes, together with the additional apparatus used in bacteriological research.

In a letter Messrs. Gallenkamp tell us that the lower scale of prices is for the convenience of consumers who order their requisites direct from the manufacturers in Germany. The higher figures charged at their London establishment are to cover the risk of transit.

The firm also state that the reason why the earlier parts of the Catalogue were printed in Antwerp is cheapness. They tell us that the lowest estimate they could obtain

in England was £100 for 2000 copies, whilst the Antwerp printers offer 3000 copies for £50. This is certainly a substantial difference, but we hope that Messrs. Gallenkamp will not come in collision with Trades-Unionism, which is now the ruling power in England.

*Micro-Organisms and Fermentation.* By ALFRED JÖRGENSEN, Director of the Laboratory for the Physiology and Technology of Fermentation at Copenhagen. New Edition. Translated from the re-written and much-enlarged Third Edition in German, by ALEX. K. MILLER, Ph.D., F.I.C., and E. A. LENNHOLM, and revised by the Author. With 56 Illustrations. London: F. W. Lyon. 1893.

THIS work, says the author, appeals to chemists, botanists, and biologists,\* likewise to those technologists who are engaged in the branches of industry named.

Herr Jörgensen's work is specially devoted to a study of the microbia of alcoholic fermentation, and takes merely an incidental notice of the septic and pathogenic organisms. Hence it is to be hoped that the watchful dragons of bestiarism will not roar for its "withdrawal."

The first chapter of this work treats of staining, sterilisation, disinfection, nutritive media, the preparation of pure cultures, and the enumeration of yeast-cells. Under "Disinfection" we find the interesting remark that disinfectants, when very much diluted, may act upon the yeasts as *stimulants*. Alcoholic fermentation is promoted by the addition of mercuric chloride in a dilution of 1:300,000, by solution of salicylic acid at 1:6000, or boracic acid of 1:8000. This is very suggestive.

Pure cultures for morphological research seem to have been first employed in 1821 by Ehrenberg. Of the production of pure cultures for physiological inquiries, the first method, that of dilution, seems to have been originated by Lister in 1878, and was further developed by Hansen in 1881. Schröter, in 1872, first employed solid nutrient media, *e. g.*, slices of potato. The improved method of plate culture was due to Koch, in 1883. For yeasts Hansen's modification is a further advance, though for bacteria the plate-method is still the best at our disposal.

The second chapter takes up the examination of air and water. We learn that the atmospheric microbia are very apt to occur in groups or clouds, whilst the intervening spaces are either germ-free or contain merely isolated micro-organisms.

Chapter III., which treats of bacteria, opens with the unquestionable statement that the more our knowledge of these micro-organisms becomes enlarged the more difficult it becomes to give a general definition of them. It is found that one and the same species of bacterium can occur in very different forms. Hence our names for these organisms often express merely growth-forms of the same species, and not distinct species. We have then to encounter the question—"Under what conditions does a species occur in this or that particular form?"

In this connection we find mention of Pasteur's important discovery of the two classes of microbia, the anaërobic and the aërobic, between which Duclaux recognises intermediate forms.

Among the forms which chiefly concern the fermentation industries we find mention of the butyric bacteria, the spores of which can resist the temperature of ebullition for three to twenty minutes; but they are killed on exposure to 90° for six hours in a solution of glucose, and in glycerin for six to eleven hours.

\* The term biology and its paronyms are used on the Continent in a manner quite different from their English acceptation. With us biology is the total including morphology, physiology, embryology, and taxonomy. In France and Germany biology has a very indefinite meaning; bordering upon physiology.

The growth of moulds is considered a sign that other growths of a more injurious character are also present.

Our present knowledge of the alcoholic ferments, an ill-defined class, is mainly owing to the researches of Hansen. The researches of this *savant* are fully recognised both by practical brewers and by scientific men. The opinion is expressed that, thanks to Hansen's method, the pure yeast question has been solved both for top fermentation and bottom-fermentation.

The work concludes with an elaborate bibliography of the literature of fermentation. To all persons engaged in the manufacture and commerce of alcoholic liquids this work must prove a treasure.

*Agricultural Journal*: Published by the Department of Agriculture of the Cape Colony. Vol. vi., No. 22.

*Maize and Wheat Exhibits at Chicago.*—In a paper by Edmund Mitchell bearing this title we find the strange statement that, "except in Southern Europe, maize cannot be matured in the Old World." We think some of the readers of the *Agricultural Journal* will be startled at learning that "mealies" will not grow in Africa!

*Boring for Water.*—Artesian wells seem to have been successfully carried out at Albert and Colesberg. At Hanover, Hope Town, and Jansenville, flowing water was less generally obtained, though enormous supplies rose to within a short distance of the surface. It is pointed out as a delusion to expect that an abundant flow may always be found on going deep enough.

There is good prospect of a great improvement in the quality of Cape wines by the introduction of pure selected ferments.

The avidity of the potato for potash is distinctly pointed out. On the other hand, soda is a poison to the plant. Are there no potash deposits or potassiferous waters in South Africa?

*Practical Agricultural Chemistry for Elementary Students.*

By J. B. COLEMAN, A.R.C.Sc., F.I.C., and F. T. ADDYMAN, B.Sc., F.I.C. London and New York: Longmans. 1893. Small 8vo., pp. 88.

THE work before us is a treatise on qualitative analysis, arranged with especial reference to the wants of agricultural students. The first section treats of chemical apparatus and manipulations.

A second section is devoted to the constituents of air and water. In the third section we have experiments on soils, manures, feeding materials, and dairy produce. Section four embraces instructions for the recognition of the metals and the acid radicles, with tables for qualitative analysis. The fifth and concluding section includes instructions concerning apparatus, chemicals, and reagents with various useful tables.

The instructions given are sound and accurate, and are clearly described. Another good feature of the book is that it contains no reference to any "syllabus" or examination. The experiments described can be performed at a very small outlay for apparatus and reagents. Hence the work is well suited for schools in which economy is a necessary consideration.

*Select Tables from the U.S. Pharmacopœia* (1890). Reprinted for ready reference in daily practice. Published by the Committee of Revision, 1893. Philadelphia: J. B. Lippincott Company.

THESE tables comprise an alphabetical list of volumetric assays, *i. e.*, of standard solutions for volumetric analyses, with the accompanying indicators, also E. R. Squibb's alcoholometric table, the saturation tables of the U.S.

Pharmacopœia, the equivalents of customary and metric weights and measures, and a table of thermometric equivalents, all from the same source.

It will be seen that in America, as in Germany, the nomenclature of chemical compounds for medical and pharmaceutical purposes differs greatly from that of commerce and of chemical science. Still the United States terminology is less perplexing than that recognised in the German empire. The American gallon is decidedly different from that used in Britain, being much smaller, equal in fact to the old English wine gallon. In weights, as used in the United States and in Britain, we can find no difference.

There are no comparative tables of the different hydro-metric scales.

## CORRESPONDENCE.

### INSTRUCTION IN BACTERIOLOGY.

To the Editor of the Chemical News.

SIR,—I beg to call your attention to the evening classes in bacteriology held here. Two courses are given; the one (Course A) deals for the most part with the disease germs, the other (Course B) with the organisms of fermentation; and both courses form a good introduction to microscopy and bacteriology.

Bacteriology is daily becoming more important in its relation to chemical science, and many chemists might like to know of our courses.—I am, &c.,

R. T. HEWLETT.

Bacteriological Laboratory,  
King's College, W.C.

### INTERNATIONAL INDEX TO CHEMICAL LITERATURE.

To the Editor of the Chemical News.

SIR,—The publication in the CHEMICAL NEWS of October 20 of my Address to the Congress of Chemists at Chicago, on an "International Index to Chemical Literature," has brought me a letter from Dr. Bechhold, of Frankfurt-am-Main, in which he announces the speedy issue of a monthly index.

The material will be classified under sixteen principal headings and a number of minor ones, to wit:—

- I. Apparatus.
- II. Theoretical Chemistry:—(a) Gases. (b) Liquids. (c) Solids. (d) Solutions. (e) Atomic and Molecular Properties. (f) Affinities. (g) Thermo chemistry, (h) Electro-chemistry. (i) Photo chemistry and Spectroscopy. (k) Crystallography.
- III. Inorganic Chemistry (arranged on the Periodic System).
- IV. Organic Chemistry (arranged practically as in Beilstein's work).
- V. Analytical Chemistry:—(a) General Methods. (b) Inorganic Substances. (c) Organic Substances. (d) Special Methods of Analysis; Sanitary, Physiological, and Legal Chemistry.
- VI. Technical Chemistry (in forty sub-divisions).
- VII. Physiological Chemistry (in twenty-three sub-divisions).
- VIII. Pharmaceutical Chemistry:—(a) New Remedies. (b) Valuations. (c) Galenical Preparations.
- IX. Foods and Food Chemistry (in eighteen sub-divisions).

X. Agricultural Chemistry:—(a) Soils. (b) Plant-culture. (c) Animal-feeding.

XI. Mineralogy.

XII. Bacteriology and Hygiene.

XIII. Official Reports and Laws.

XIV. Personal Notices and Biography.

XV. Statistics and Commercial Items.

XVI. Books.

This monthly index is intended to include all languages, and at the end of one year a year-index and at the end of ten years a general-index are planned. The work will be edited by Dr. Ephraim, and published by Bechhold, of Frankfurt-am-Main. The first number will be awaited with great interest, and chemists can but hope that the undertaking will completely fill the gap so long open, and so greatly needing to be closed.—I am, &c.,

H. CARRINGTON BOLTON.

University Club, New York City,  
December 12, 1893.

Institute of Chemistry Examinations.—Of the candidates examined in the new Laboratories of the Institute at 30, Bloomsbury Square, the following have passed (11):—E. A. Andrews, Mason College, Birmingham; G. E. Brown, Mason College; R. M. Caven, University College, Nottingham; R. P. Charles, King's College, London; P. H. Kirkaldy, King's; C. A. Mitchell, King's; H. B. Stocks, University College, Liverpool; H. Tate, Royal University, Ireland; W. H. Willcox, University College, Notts.; S. B. Wright, student under E. G. Clayton, F.I.C., and at King's College; and H. S. Young, King's. Of candidates examined in Dublin the following five were successful, viz.:—W. S. Barratt, T. Byrne, P. M. Davies, H. E. Ivatts, and C. McMullen, all trained at the Royal College of Science, Dublin. Of candidates examined in Glasgow the following six were successful:—T. Chambers, Yorkshire College, Leeds, and Glasgow and West of Scotland Technical College; H. Findlay, R. Fulton, jun., W. Hannah, F. W. McKillop, each of Glasgow and West of Scotland Technical College, and N. McCulloch, Glasgow.

The Analysis of Silicon Carbide.—Dr. Otto Muhlhauser.—Carborundum is a grinding agent which is in part superseding bort and corundum. The difficulty in its analysis is its extreme hardness. Carborundum can only be brought into a state susceptible of being opened up by prolonged grinding in the agate mortar followed by elutriation with distilled water. The powder is shaken up with distilled water, allowed to subside for a given time, and the matter remaining in suspension after five minutes is submitted to analysis. The combustion of the carbide is effected in contact with lead chromate *alone*. For estimating the silicon the material is fused with a mixture of soda and potash.—*Zeitschrift f. Anal. Chem.*, xxxii., Part 5.

On Borax as a Basis for Alkalimetry.—Th. Salzer.—From the author's experiments it appears that accurate titration may be effected with a decinormal solution of borax, using litmus as indicator. The acid to be determined must be decinormal. It is coloured a faint onion-red with a *few* drops of sensitive tincture of litmus, and the solution of borax is added until the colour changes to a bluish-red and does not revert to onion-red. If the solution of borax is added until a pure blue colour is produced the value obtained is too high by about 10 per cent. Methyl-orange is preferable as an indicator only in the case of concentrated inorganic acid. For dilute acids it is less suitable, and for organic acids it is quite useless. Citric acid is preferably determined with potassa, using phenol-phthaleine as indicator.—*Zeitschrift f. Anal. Chem.*, xxxii., Part 5.

## 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. cxvii., No. 24, December 11, 1893.

**The Sublimation of the Yellow and Red Mercury Iodides.**—M. Berthelot.—Mercuric iodide appears in two distinct isomeric conditions—as red iodide, stable at ordinary temperatures, and as yellow iodide, produced by the action of heat upon the former and stable at a high temperature. Both are crystalline. The yellow iodide can be easily converted into the red form at common temperatures, especially on contact with the least trace of crystals of the red iodide. This transformation, produced without the concurrence of any external energy, is intelligible because it is accompanied by a liberation of heat equal to + 3.0 cal. for  $\text{HgI}_2 = 354$  grms. It is known that each of the iodides may be separated as such by the action of certain solvents at the ordinary temperature; the red iodide being in general obtained by precipitation (?), and the yellow form separating on cooling or by the addition of water to its alcoholic solution. Frankenstein considered that these two iodides might both exist in the state of isomeric vapours, on the faith of the following experiment. If we carefully heat a mixture of the two iodides upon a plate of glass, holding a second glass plate at a very small distance, and operating at a very low temperature so that the red crystals may not be transformed, there condenses upon the upper plate a sublimate containing at once yellow and red crystals. The experiment may be easily repeated, but it does not prove the existence of the two isomers in the state of vapour. Without doubt the condensation of the vapour of the mercuric iodide gives direct rise to the yellow iodide, but the contact of the least trace of crystals of the red iodide is sufficient to change the yellow iodide to the red form. But if we examine the conditions of the above experiment it is easy to recognise the impossibility of avoiding the projection of fine dust of the red iodide, placed upon the lower plate, which deprives the conclusion of all validity.

**Transformation Produced in Iron by a Permanent Deformation in the Cold.**—Georges Charpy.—It appears that a permanent deformation in the cold produced in irons and steels of different kinds a modification which may be regarded, at least provisionally, as an allotropic transformation of iron, the two states produced being called by Osmond iron  $\alpha$  and iron  $\beta$ .

**Rates of Etherification of Hydrofluoric Acid.**—Maurice Meslans.—The rate of etherification decreases rapidly when the proportion of water accompanying the hydrofluoric acid increases, but etherification takes place even with the acid mixed with 2 vols. of water, but at the temperature of 220°, at which this hydrate must be strongly dissociated.

**Analysis of the Butters of Commerce.**—C. Violette.—(See p. 312).

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. viii., No. 93.

**On Alloys.**—Prof. W. C. Roberts-Austen.—This paper is the translation of the Second Report given in by the author to the Alloys Research Committee of the Institute of Mechanical Engineers.

**Liquid Chlorine.**—M. Fribourg.—From the *Bull. de la Soc. Chim. de Paris*.

## MEETINGS FOR THE WEEK.

TUESDAY, Jan. 2nd.—Royal Institution, 3. "Air, Gaseous and Liquid," by Prof. Dewar, M.A., LL.D., F.R.S. Pathological, 8.30.  
THURSDAY, 4th.—Royal Institution, 3. "Air, Gaseous and Liquid," by Prof. Dewar, M.A., LL.D., F.R.S.  
FRIDAY, 5th.—Quekett Club, 8. Geologists' Association, 8.  
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